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THE ADSORPTION OF PHENOLIC AND ORGANOTIN COMPOUNDS BY
CLAYS AND CATION EXCHANGED CLAYS

MONIQUE ANN MARIE LAWRENCE

A Thesis Submitted for the Degree of Doctor of Philosophy

The University of Aston in Birmingham

January 1996

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Quaternary ammonium exchanged laponites (Quat-laponites) show selectivity in the adsorption of phenols and chlorinated phenols. Strong adsorbate-adsorbent interactions are indicated by adsorption isotherms.

Adsorption of phenols and chlorinated phenols by Quat-smectites is greater than that by the Bi Quat-smectites prepared in this study. It is thought that the quaternary ammonium exchanged smectite components of the Bi Quat-smectites interact with each other (adsorbent-adsorbent interactions) reducing the number of sites available for adsorbate-adsorbent interactions.

Solidification/stabilisation studies of 2-chlorophenol show that a blend of ground granulated blast furnace slag and ordinary Portland cement attenuates 2-chlorophenol more effectively than ordinary Portland cement alone.

Tetramethyl ammonium- (TMA-) and tetramethyl phosphonium- (TMP-) montmorillonites were exposed to solutions of phenol or chlorinated phenols. TMP-montmorillonite was the better adsorbent and preferentially adsorbed 4-chlorophenol over phenol. Hydration of the interlayer cations occurs to a greater extent in the TMA-montmorillonite than the TMP-montmorillonite restricting interlayer adsorption.

Contrary to that observed for phenols and chlorinated phenols, the Quat-smectites were ineffective as adsorbents for triphenyltin hydroxide and bis(tributyltin) oxide at room temperature. Under microwave conditions, only bis(tributyltin) oxide was adsorbed by the quaternary ammonium exchanged smectites. Bis(tributyltin) oxide was adsorbed from ethanol on the surface of the smectite clays at room temperature and under microwave conditions. The adsorbate-adsorbent interactions were weak. Adsorption is accompanied by conversion of bis(tributyltin) oxide to a different tin(IV) species and the release of sodium cations from the montmorillonite interlayer region.

Attempts to introduce conditions suitable for charge transfer interactions between synthesised quaternary ammonium compounds and 2,4,6-trichlorophenol are documented.

Transition metal complex exchanged clays adsorb 2,4,6-trichlorophenol and phenol. Strong adsorbate-adsorbent interactions (Type I isotherms) occur when the adsorbate is 2,4,6-trichlorophenol and when the adsorbent is $[\text{Fe}(\text{bipy})_3]^{2+}$ exchanged montmorillonite or $[\text{Co}(\text{bipy})_3]^{3+}$ exchanged montmorillonite. The 2,2'-bipyridyl ligands of the adsorbents are electron rich and the 2,4,6-trichlorophenol is electron deficient. This may have enhanced adsorbate-adsorbent interactions.

Key words:

quaternary ammonium exchanged smectites, bi quaternary ammonium exchanged smectites, transition metal complex exchanged clays, chlorinated phenols, bis(tributyltin) oxide

*To My Family and David,
and in loving memory of Kevin*

If I knew back then what I know now,
If I understood the what, when, the why and how,
Well it's clear to me, what I should of done,
In hindsight it's twenty-twenty vision.

George Benson

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CONTENTS

Title Page.....	1
Thesis Summary	2
Dedication.....	3
Acknowledgements	4
List of Contents	5
List of Tables	13
List of Figures.....	16
Chapter 1.....	21
Introduction.....	21
1.1 Introduction	21
1.2 The structure of clay minerals.....	22
1.2.1 The Kandite group.....	24
1.2.2 The Illite group.....	25
1.2.2.1 The Micas.....	25
1.2.2.2 Pyrophyllite and Talc.....	25
1.2.2.3 The Illites	25
1.2.3 The Smectite group	26
1.2.4 The vermiculite group	27
1.2.5 The chlorite group.....	27
1.2.6 Mixed layer minerals.....	28
1.3 Properties of the smectite clays	28
1.3.1 Crystal size and surface area.....	28
1.3.2 Exchangeable ions and ion exchange	29
1.3.3 Hydration	29
1.3.4 Clay-organic/inorganic interactions	30
1.3.4.1 Cation Exchange.....	30
1.3.4.2 Intercalation	34
1.3.4.3 Pillaring.....	34
1.4 Clay-organic/inorganic interactions.....	37
1.4.1 Quaternary ammonium cation exchanged smectites.....	38
1.4.1.1 Mechanism for the exchange reaction	38
1.4.1.2 Arrangement of exchanged cations in the interlayer region.....	40
1.4.1.3 Properties of quaternary ammonium cation exchanged montmorillonites	41
1.4.1.3.1 Stability of the quaternary ammonium cation exchanged montmorillonites	41

1.4.1.3.2	Water adsorption	41
1.4.1.3.3	Adsorption of organic compounds from vapour and gaseous phases	42
1.4.2	Transition metal complex exchanged smectites	44
1.4.2.1	Mechanism of exchange	44
1.4.2.2	Arrangement in the interlayer region	45
1.4.2.3	Properties of transition metal complex exchanged smectites.....	45
1.5	Adsorption by montmorillonite and modified montmorillonites	46
1.5.1	Mechanisms and Classification of adsorption	46
1.5.1.1	Definitions.....	46
1.5.1.2	Classification of adsorption isotherms	47
1.5.1.2.1	Gases	47
1.5.1.2.2	Solutes.....	49
1.5.2	Adsorption of organic compounds by amine and ammonium modified clays from aqueous solution.....	50
1.5.2.1	Early studies.....	50
1.5.2.1.1	The nature of the adsorbent - comparison of amine and ammonium derivatives.....	50
1.5.2.1.2	Ammonium compound type and the adsorption of phenols	52
1.5.2.1.3	Adsorbate functional group and its effect on adsorption ..	53
1.5.2.1.4	The thermodynamics of adsorption	54
1.5.2.2	Modern concerns regarding water quality and the adsorption of organic compounds by ammonium modified clays from aqueous solution.....	55
1.5.2.2.1	Selectivity	55
1.5.2.2.2	Comparison with granular activated carbon.....	57
1.5.2.2.3	Hydrophobicity.....	57
1.5.2.2.4	The effect of clay layer charge and aqueous media on adsorption.....	58
1.5.3	Adsorption of inorganic compounds from aqueous solution ..	61
1.6	Industrial applications of clays.....	61
1.6.1	The industrial use of clay minerals.....	61
1.6.2	Uses of smectite clays	62
1.6.3	Uses of organophilic clays.....	63
1.7	Water pollution and current methods of treatment	64
1.7.1	Water Pollution.....	64
1.7.1.1	Groundwater pollution.....	65

1.7.1.2	Hazardous wastes	67
1.7.2	Current methods of treatment and/or disposal	68
1.7.2.1	Methods for disposal.....	68
1.7.2.2	Landfill and leachates	69
1.7.2.2.1	Environmental impact of landfill	69
1.7.2.3	Methods for pre-treatment	72
1.7.2.3.1	Recover/recycle/reuse.....	72
1.7.2.3.2	Thermal treatment	73
1.7.2.3.3	Chemical/physical treatment	73
1.7.2.3.4	Biological treatments.....	73
1.7.2.3.5	Solidification/Stabilisation	74
1.7.2.4	Cements and the properties that influence solidification / stabilisation	75
1.7.2.4.1	Background.....	75
1.7.2.4.2	Portland Cement.....	75
1.7.2.4.3	Hydration of Portland cement	77
1.7.2.4.4	Composite cements	81
1.7.2.4.5	Properties of hardened cements	82
1.8	Objectives.....	83
1.8.1	Hazardous Wastes	83
1.8.2	Clays selected for investigation as adsorbents.....	85
1.8.3	Project Objectives	86
Chapter 2	88
Standard methods for preparation and analytical techniques	88
2.1	Chemicals and materials used	88
2.1.1	Chemicals and solvents.....	88
2.1.2	Clay minerals	88
2.1.3	Cementitious materials.....	88
2.2	Preparation of Wyoming Bentonite for use in exchange reactions.....	88
2.2.1	For exchange via shaker method	88
2.2.2	For exchange via the microwave oven.....	89
2.3	Analytical Techniques.....	89
2.3.1	Atomic Absorption spectrophotometry (AA)	89
2.3.2	Elemental Analysis.....	89
2.3.3	Fourier Transform Infra-red spectroscopy (FTIR).....	89
2.3.4	High Performance Liquid Chromatography	89
2.3.5	Melting Points	89

2.3.6 Methylene Blue dye titration for the determination of cation exchange capacity	90
2.3.7 Mössbauer spectroscopy	90
2.3.8 Nuclear Magnetic Resonance Spectroscopy (NMR)	90
2.3.9 Secondary Ion Mass Spectrometry (SIMS)	90
2.3.10 Ultraviolet/Visible spectrophotometry (UV)	91
2.3.11 X-Ray Diffraction Spectroscopy (XRD)	91
2.3.12 X-Ray Photoelectron spectroscopy (XPS)	91
Chapter 3	92
The adsorption of phenolic compounds by quaternary ammonium exchanged smectite clays and the study of solidification/stabilisation as a pre treatment to the landfilling of chlorinated phenols.	92
3.1 Introduction	92
3.1.1 Adsorption of phenolic compounds	92
3.1.2 Objectives	93
3.2 Preparation of exchanged Quat-montmorillonites	95
3.2.1 Exchanged montmorillonites: Preliminary studies	95
3.2.2 Preparation of fully exchanged montmorillonites	99
3.2.3 Characterisation of the fully exchanged montmorillonite clays	99
3.2.4 Exchanged montmorillonites - Conclusions	111
3.3 Preparation of exchanged Quat-laponites by the Wet method	111
3.3.1 Exchanged laponites: Preliminary studies	112
3.3.2 Preparation of fully exchanged laponites	116
3.3.3 Characterisation of fully exchanged laponites	117
3.3.4 Exchanged Laponites - Conclusions	121
3.4 Adsorption Isotherms	122
3.4.1 The nature of adsorption	125
3.4.2 Adsorption isotherms - Conclusions	132
3.5 Adsorption of 2-chlorophenol by HDTMA-montmorillonite	134
3.5.1 Preparation of 2-chlorophenol-HDTMA-montmorillonite	134
3.5.2 Characterisation of the 2-chlorophenol-HDTMA-montmorillonite material	135
3.5.3 2-chlorophenol-HDTMA-montmorillonite - Conclusions	141
3.6 Bi Quat-smectites	142
3.6.1 Preparation of Bi Quat-smectites	143
3.6.1.1 Preparation of a mixture of Quat-smectites	143
3.6.1.2 Preparation of Double-Quat-smectites	143

3.6.2	Characterisation of double-Quat-montmorillonites and laponites.....	144
3.6.3	Adsorption of phenols by Bi Quat-smectites.....	147
3.6.4	Bi Quat-smectites - Conclusions	158
3.7	The use of commercial Quats for adsorption	159
3.7.1	Preparation of ARQUAD 218,178G-montmorillonite.....	159
3.7.2	Adsorption of phenols by ARQUAD 218,178G-montmorillonite.....	160
3.7.3	ARQUAD 218,178G-montmorillonite - Conclusions	160
3.8	The Langmuir model - an alternative measure of adsorbate-adsorbent interactions.....	160
3.8.1	Background.....	160
3.8.2	Data Analysis	162
3.8.3	The Langmuir model - Conclusions	164
3.9	Solidification/stabilisation as a method of landfill pre treatment	164
3.9.1	Preparation of 2-chlorophenol-HDTMA-montmorillonite stabilised materials	165
3.9.2	Preparation of solidified/stabilised 2-chlorophenol materials.....	165
3.9.3	Leach testing.....	166
3.9.3.1	Diffusion of 2-chlorophenol from the solidification/ stabilisation material	166
3.9.3.2	Leaching as observed by water percolation tests.....	168
3.9.4	Solidification/stabilisation - Conclusions.....	172
3.10	Further work.....	172
Chapter 4.....		174
	Adsorption of phenol and mono-chlorinated phenols from aqueous solutions by tetramethylammonium-, tetramethylphosphonium- and tetraphenylphosphonium-exchanged montmorillonites	174
4.1	Introduction	174
4.2	Preparation of exchanged montmorillonites	176
4.2.1	Preparation of sodium saturated montmorillonite	176
4.2.2	Preparation of exchanged clay.....	176
4.3	Characterisation of exchanged clays.....	177
4.4	Adsorption studies.....	178
4.4.1	Adsorption isotherms.....	178
4.4.2	Competitive adsorption studies.....	183
4.5	Conclusions and Further work.....	186

Chapter 5.....	188
Adsorption of organo-tin compounds by exchanged and non-exchanged smectites.....	188
5.1 Introduction	188
5.2 Adsorption of organo-tin compounds by quaternary ammonium exchanged smectites	191
5.2.1 Quaternary ammonium exchanged smectite preparation.....	191
5.2.2 Adsorption Isotherms.....	191
5.3 Adsorption of organo-tin compounds by smectite clays at ambient temperatures	193
5.3.1 Clay preparation.....	193
5.3.2 Adsorption isotherms and the nature of the adsorption process	194
5.3.3 Characterisation of the tin-smectite materials	196
5.4 The effect of microwave radiation on organo-tin clay interactions.....	202
5.4.1 Adsorption of bis(tributyltin) oxide and triphenyltin hydroxide by various clay materials under microwave conditions	204
5.4.2 Adsorption of bis(tributyltin) oxide by non-exchanged clays	204
5.4.3 Characterisation of the tin-smectite products.....	205
5.4.4 Adsorption of bis(tributyltin) oxide by quaternary ammonium exchanged clays under microwave conditions.....	209
5.4.5 Characterisation of tin-Quat-smectite materials	210
5.5 The de-alkylation of organo-tin compounds.....	212
5.5.1 Introduction.....	212
5.5.2 Adsorption of bis(tributyltin) oxide by smectite clays under microwave conditions: the effect of time.	213
5.5.3 Characterisation of the tin-smectite materials	215
5.6 Conclusions and Further Work	221
Chapter 6.....	225
Adsorption Characteristics of Transition Metal Complex Exchanged Smectites.....	225
6.1 Introduction	225
6.2 Synthesis of 2,2'-bipyridyl and tri-(2-pyridyl)amine transition metal complexes.....	225
6.2.1 Ligand synthesis	225
6.2.2 Complex preparation	226
6.2.2.1 Tris 2,2'-bipyridyl iron(II) perchlorate	226
6.2.2.2 Tris 2,2'-bipyridyl copper(II) perchlorate	226
6.2.2.3 Tris 2,2'-bipyridyl cobalt(II) perchlorate trihydrate.....	227

6.2.2.4	Tris 2,2'-bipyridyl cobalt(III) perchlorate	227
6.2.2.5	Bis tri-(2-bipyridyl)amine iron(II) perchlorate	227
6.2.2.6	Bis tri-(2-bipyridyl)amine cobalt(II) perchlorate	228
6.3	Characterisation of transition metal complexes	228
6.4	Preparation of transition metal complex exchanged smectites.....	229
6.5	Characterisation of transition metal complex exchanged smectites	229
6.5	The reaction of 2,2'-bipyridyl with montmorillonite	240
6.6	Adsorption by transition metal complex exchanged smectites	240
6.6.1	Equilibration time and methods of phenol and 2,4,6-trichlorophenol analysis	240
6.6.2	Adsorption isotherms.....	241
6.6.2.1	Adsorption by exchanged montmorillonites	241
6.6.2.2	Adsorption by 2,2'-bipyridyl transition metal exchanged laponites.....	249
6.7	Conclusions and Further work.....	249
Chapter 7.....		251
Electron Donor-Acceptor (charge transfer) complexes for the enhancement of adsorbate-adsorbent interactions		251
7.1	Introduction	251
7.1.1	Electron Donor-Acceptor (Charge-Transfer) complexes	251
7.1.2	Application of electron donor-acceptor (charge-transfer) interactions to adsorption of 2,4,6-trichlorophenol	252
7.2	Synthesis	253
7.2.1	The synthesis of quaternary ammonium compounds	253
7.2.2	Synthesis of triethyl-2,4,6-trimethylbenzylammonium chloride.....	254
7.2.3	Synthesis of triethyl-2,4,6-trimethylbenzylammonium iodide	256
7.2.4	Synthesis of triethyl-4-methoxybenzylammonium chloride	257
7.2.5	Attempted synthesis of triethyl-2,4,6-trimethoxybenzylammonium-smectites.....	258
7.3	Electron Donor-Acceptor complexes between 2,4,6-trichlorophenol and triethyl-2,4,6-trimethylbenzylammonium chloride.....	262
7.3.1	Ultraviolet/Visible solution spectrophotometric investigations	262
7.3.2	¹ H NMR spectroscopic investigations	263
7.4	Exchange of triethyl-2,4,6-trimethylbenzylammonium chloride onto montmorillonite.....	264

7.5 Adsorption of 2,4,6-trichlorophenol and phenol by triethyl-2,4,6-trimethylbenzylammonium-montmorillonite	265
7.6 Conclusions and Further work	268
References	271

LIST OF TABLES

Table 1.1 Primary sources of hazardous waste.....	68
Table 1.2 Tertiary treatments used in Waste management.....	72
Table 1.3 The composition of Portland cement.....	76
Table 1.4 The percentage composition of the main constituents of slag	81
Table 1.5 The phenol group and the metal group of priority pollutants.....	84
Table 3.1 The quaternary ammonium compounds used in the studies of Mortland.....	93
Table 3.2 The relationship between fraction of HDTMA ⁺ Br ⁻ added for the exchange reaction and the sodium released	97
Table 3.3 The effect of washing on sodium release for HDTMA- montmorillonite.....	97
Table 3.4 Results from the exchange reaction between HDTMA ⁺ Br ⁻ and montmorillonite beyond the c.e.c and the accompanying release of Na ⁺ cations.....	98
Table 3.5 Quat-montmorillonites washed with 1 dm ³ water - percentage exchange and basal spacing results	100
Table 3.6 Characteristic FTIR absorptions and assignments for montmorillonite....	104
Table 3.7 Characteristic FTNIR absorptions and assignments for montmorillonite in the 5000 - 4000 cm ⁻¹ region	105
Table 3.8 Summary of the ²⁹ Si MASNMR analysis of HDTMA-montmorillonite...	107
Table 3.9 XPS Br(3d) data for exchanged montmorillonites	108
Table 3.10 XPS N(1s) data for exchanged montmorillonites.....	110
Table 3.11 Percentage exchange observed for washed HDTMA-laponite products prepared in ethanolic solution.....	112
Table 3.12 Summary of ²⁹ Si MASNMR results of laponite materials.....	113
Table 3.13 Summary of ²⁹ Si MASNMR results of exchanged laponite products....	113
Table 3.14 HDTMA-laponite exchanged in aqueous solution	116
Table 3.15 Percentage exchange and basal spacing results from the synthesis of Quat-laponites washed with 1 dm ³ distilled water	118
Table 3.16 XPS analysis of bromine in HDTMA-laponite.....	119
Table 3.17 XPS analysis of nitrogen in HDTMA-laponite.....	119
Table 3.18 Summary of adsorption of phenol and chlorinated phenols by Quat- montmorillonites	122
Table 3.19 Adsorption of phenol and chlorinated phenols by Quat- montmorillonites - results obtained in this study	124
Table 3.20 Adsorption of phenol and chlorinated phenols by Quat-laponites.....	125
Table 3.21 Basal spacings of 2-chlorophenol-HDTMA-montmorillonite adsorption product.....	135

Table 3.22 XPS results of 2-chlorophenol-HDTMA-montmorillonite adsorption products	136
Table 3.23 Percentage exchange for the double-Quat-smectites	144
Table 3.24 Summary of ²⁹ Si MASNMR analysis double-Quat-laponite	145
Table 3.25 Summary of adsorption of phenols by single and bi Quat-montmorillonite adsorbents	149
Table 3.26 Summary of adsorption of phenols by single and bi Quat-laponite adsorbents.....	149
Table 3.27 Adsorption isotherms and Langmuir model data for adsorbate-adsorbent interactions.....	162
Table 3.28 Experimental mix details for attenuation studies	166
Table 4.1 Properties of Parent reference smectite and Quat-smectite.....	177
Table 4.2 Water solubilities and Ultraviolet absorption bands of phenols investigated	178
Table 5.1 Summary of adsorption of organo-tin compounds by Quat-clays and percentage adsorption, after Meer	190
Table 5.2 Basal spacing, d(001), results of smectite clays and the organo-tin smectite materials.....	196
Table 5.3 XPS results of tin compounds used as standards	199
Table 5.4 XPS results of the bis(tributyltin) oxide smectite reaction products.....	200
Table 5.5 Percentage uptake of bis(tributyltin) oxide by smectite clays	205
Table 5.6 The displacement of sodium cations during the adsorption reaction and the accompanying change in basal spacing.....	206
Table 5.7 XPS results of the tin-clay products formed during reaction under microwave conditions	208
Table 5.8 Uptake of bis(tributyltin) oxide by adsorbents and the accompanying change in basal spacings	210
Table 5.9 Binding energies (Sn 3d5) and percentage of tin compounds present after reaction of bis(tributyltin) oxide with various Quat-clays	211
Table 5.10 Results of the effect of time on adsorption of bis(tributyltin) oxide from ethanol onto smectite clays under microwave conditions	215
Table 5.11 Sn(3d5) XPS analysis of the presence of tin in the products of the timed reactions and the binding energy at which they were detected.....	216
Table 5.12 Basal spacings of the products of the reactions between bis(tributyltin) oxide and smectite clays under microwave conditions.....	221

Table 6.1 Colours of synthesised complexes	228
Table 6.2 Percentage exchange observed for selected transition metal complex exchanged smectites	230
Table 6.3 The colours of the transition metal complexes and their respective exchanged smectites	232
Table 6.4 FTNIR peaks of the transition metal exchanged montmorillonites, 5000-4000 cm ⁻¹ region only	234
Table 6.5 Summary of adsorption of phenol and 2,4,6-trichlorophenol by transition metal complex exchanged montmorillonites.....	242
Table 7.1 Experiments for the UV study of EDA complexes formed between 2,4,6-trichlorophenol and triethyl-2,4,6-trimethylbenzylammonium chloride.....	262
Table 7.2 Experiments for the preliminary ¹ H NMR study of EDA complexes formed between 2,4,6-trichlorophenol and triethyl-2,4,6- trimethylbenzylammonium chloride.....	263

LIST OF FIGURES

Figure 1.1 Diagrammatic representations of the tetrahedral sheet in layered silicates.....	22
Figure 1.2 Schematic representation of clay mineral groups.....	23
Figure 1.3 The arrangement of the silicate layers in smectite clays.....	27
Figure 1.4 The structure of manganese porphyrins used as cations in cation exchange reactions.....	33
Figure 1.5 A schematic representation of the properties of the montmorillonite clay precursor and the product IOC.....	36
Figure 1.6 Scheme for the thermal recycling of a surfactant modified pillared clay adsorbent.....	37
Figure 1.7 A schematic representation of the keying which may occur when quaternary ammonium cations exchange into clay materials.....	39
Figure 1.8 The variation in basal spacing with the number of carbon atoms in the alkyl chain with percentage of internal basal plane area occupied by the cation, in complexes of montmorillonite with primary n-alkylammonium ions.....	40
Figure 1.9 The two step process as proposed by Lagaly for the adsorption of molecules possessing polar and non-polar sections onto clay materials.....	43
Figure 1.10 Types of adsorption isotherm.....	48
Figure 1.11 Cresols used in the Cowan and White study.....	52
Figure 1.12 Dihydroxybenzenes used in the Cowan and White study.....	52
Figure 1.12 TMPA cations arranged in the interlayer region of clays with different layer charge.....	59
Figure 1.13 The interactions between interlayer organic cations and the size of adsorption sites.....	60
Figure 1.14 The water cycle - a detailed diagram of the paths of water in the ground.....	66
Figure 1.15 The fate of contaminants on exposure to land.....	67
Figure 1.16 Etched Portland cement clinker.....	76
Figure 1.17 Electron microscope photographs showing the hydration of Portland cement over 28 days.....	79
Figure 3.1 Arrangement of Quats in the interlayer region of smectite clays.....	100
Figure 3.2a FTIR spectrum of montmorillonite.....	102
Figure 3.2b FTIR spectrum of HDTMA-montmorillonite.....	103
Figure 3.3 Diffuse reflectance FTNIR spectrum of montmorillonite.....	106
Figure 3.4 ²⁹ Si MASNMR spectrum of bentonite clay.....	109
Figure 3.5a ²⁹ Si MASNMR spectrum of laponite.....	114
Figure 3.5b ²⁹ Si MASNMR spectrum of HDTMA-laponite.....	115
Figure 3.6a Br(3d) XPS spectrum of NaBr.....	120

Figure 3.6b Br(3d) XPS spectrum of HDTMA ⁺ Br ⁻	120
Figure 3.6c Br(3d) XPS spectrum of HDTMA-laponite	121
Figure 3.7a Adsorption of phenols from water on HDTMA-montmorillonite	126
Figure 3.7b Adsorption of phenols from water on HDTMA-laponite	127
Figure 3.8a Adsorption of phenols from water on HDPY-montmorillonite.....	128
Figure 3.8b Adsorption of phenols from water on HDPY-laponite.....	129
Figure 3.9a Adsorption of phenols from water by TMPA-montmorillonite.....	131
Figure 3.9b Adsorption of phenols from water by TMPA-laponite.....	132
Figure 3.10a XPS wide scan of 2-chlorophenol-HDTMA-montmorillonite	137
Figure 3.10b XPS scan in the 55-80 eV binding energy region, of 2- chlorophenol-HDTMA-montmorillonite.....	137
Figure 3.10c XPS N(1s) analysis of 2-chlorophenol-HDTMA-montmorillonite.....	138
Figure 3.11a SIMS spectrum of 2-chlorophenol-HDTMA-montmorillonite.....	140
Figure 3.11b SIMS spectrum of 2-chlorophenol-HDTMA-montmorillonite.....	140
Figure 3.11c SIMS spectrum of 2-chlorophenol-HDTMA-montmorillonite.....	141
Figure 3.12a ²⁹ Si MASNMR spectrum of laponite	146
Figure 3.12b ²⁹ Si MASNMR spectrum of HDTMA-TMPA-laponite	147
Figure 3.13(a) Adsorption of 2,4,6-trichlorophenol by the single Quat- montmorillonite, the mixture of Quat-montmorillonites, and the double-Quat- montmorillonite.....	150
Figure 3.13(b) Adsorption of 2,4,6-trichlorophenol by the single Quat-laponite, the mixture of Quat-laponites, and the double-Quat-laponite	151
Figure 3.14(a) Adsorption of 2-chlorophenol by the single Quat-montmorillonite, the mixture of Quat-montmorillonites, and the double-Quat-montmorillonite.	152
Figure 3.14(b) Adsorption of 2-chlorophenol by the single Quat-laponite, the mixture of Quat-laponites, and the double-Quat-laponite.....	153
Figure 3.15(a) Adsorption of phenol by the single Quat-montmorillonite, the mixture of Quat-montmorillonites, and the double-Quat-montmorillonite.....	154
Figure 3.15(b) Adsorption of phenol by the single Quat-laponite, the mixture of Quat-laponites, and the double-Quat-laponite.....	155
Figure 3.16 Schematic diagram of adsorbent-adsorbent interactions in the Bi Quat-smectites.....	156
Figure 3.17 The leaching of 2-chlorophenol from solidification/stabilisation treated materials	168
Figure 3.18 The percolation column	169
Figure 3.19 (a) The leaching of 2-chlorophenol from solidification/stabilisation treated materials.	170
Figure 3.19 (b) The leaching of 2-chlorophenol from stabilisation only treated materials.....	170

Figure 4.1 Adsorption of phenols from water by TMP-montmorillonite.....	179
Figure 4.2 Adsorption of phenols from water by TPP-montmorillonite.....	180
Figure 4.3 Schematic representation of hydration of the TMA and TMP cations in the montmorillonite interlayer region.	182
Figure 4.4 Adsorption of 4-chlorophenol from water by TMP-montmorillonite in the presence of phenol.....	185
Figure 4.5 Adsorption of phenol from water by TMP-montmorillonite in the presence of 4-chlorophenol.....	186
Figure 5.1 Adsorption of organo-tin compounds from ethanol by HDTMA-montmorillonite.....	189
Figure 5.2 Adsorption of organo-tin compounds from ethanol by TMPA-montmorillonite.....	190
Figure 5.3(a) Adsorption of organo-tin compounds from ethanol by montmorillonite.....	195
Figure 5.3(b) Adsorption of organo-tin compounds from ethanol by laponite	195
Figure 5.4 Schematic representation of bis(tributyltin) oxide adsorption into the montmorillonite interlayer.....	197
Figure 5.5a FTNIR spectrum of laponite.....	198
Figure 5.6a Sn(3d5) XPS spectrum of SnO ₂	201
Figure 5.6b Sn(3d5) XPS spectrum of bis(tributyltin) oxide.....	201
Figure 5.6c Sn(3d5) XPS spectrum of bis(tributyltin) oxide-montmorillonite material	202
Figure 5.7 Diagram of Teflon container used in microwave reactions.....	203
Figure 5.8 Proposed mechanism for the de-alkylation of organo-tin compounds....	214
Figure 5.9 FTNIR of bis(tributyltin)oxide montmorillonite material after 1 minute of reaction.....	217
Figure 5.10 FTNIR of bis(tributyltin)oxide montmorillonite material after 5 minute of reaction	218
Figure 5.11 FTNIR of material resulting from the ethanol - montmorillonite reaction	219
Figure 6.1 The structure of (a) 2,2'-bipyridyl and (b) tri-(2-pyridyl)amine.....	226
Figure 6.2 A schematic representation of the reaction between smectite clays and transition metal complexes	231
Figure 6.3a The FTNIR spectrum of montmorillonite.....	236
Figure 6.3b The FTNIR spectrum of [Fe(bipy) ₃] ²⁺ - montmorillonite.....	237
Figure 6.3c The FTNIR spectrum of [Co(bipy) ₃] ²⁺ - montmorillonite	238
Figure 6.3d The FTNIR spectrum of the tri-(2-pyridyl)amine complex of cobalt(II) exchanged with montmorillonite.....	239

Figure 6.4a Adsorption of phenols by tris 2,2'-bipyridyl iron(II) perchlorate exchanged montmorillonite	243
Figure 6.4b Adsorption of phenols by bis 2,2'-bipyridyl copper(II) perchlorate exchanged montmorillonite	244
Figure 6.4c Adsorption of phenols by tris 2,2'-bipyridyl cobalt(II) perchlorate exchanged montmorillonite	245
Figure 6.4d Adsorption of phenols by tris 2,2'-bipyridyl cobalt(III) perchlorate exchanged montmorillonite	246
Figure 6.4e Adsorption of phenols by bis tri-(2-pyridyl)amine iron(II) perchlorate exchanged montmorillonite.....	247
Figure 6.4 f Adsorption of phenols by tri-(2-pyridyl)amine complex of cobalt(II) exchanged montmorillonite	248
Figure 6.5 A schematic representation of interactions between 2,4,6- trichlorophenol and the 2,2'-bipyridyl iron(II) complex	248
Figure 7.1 Electron Donor-Acceptor interactions between 2,4,6-trichlorophenol and substituted benzenes	253
Figure 7.2 ¹ H and ¹³ C assignments for triethyl-2,4,6-trimethylbenzylammonium chloride.....	257
Figure 7.3 The synthesis of phenol-formaldehyde resin	261
Figure 7.4 Possible mechanisms in the synthesis of 1,3,5-trimethoxybenzene oligomer formed on reaction with chloromethyl methyl ether.	261
Figure 7.5 XRD spectrum of triethyl-2,4,6-trimethylbenzylammonium exchanged montmorillonite	266
Figure 7.6 Adsorption of 2,4,6-trichlorophenol by triethyl-2,4,6- trimethylbenzylammonium-montmorillonite	267
Figure 7.7 Diagram representing structures of compounds that may further facilitate 2,4,6-trichlorophenol adsorption	270

Chapter 1

Introduction

1.1 Introduction

In the wake of increasing public concern and increased legislation surrounding environmental issues, it is surprising that methods used for the disposal of waste materials have remained unchanged for the last two decades. Currently the majority of waste from the chemical industry is disposed of in landfills, with little or no pre-treatment. However the increase in legislation and public awareness has resulted in new laws that will change our current methods of disposal. One current form of pre-treatment is that of adsorption. This involves the use of granular activated carbon (GAC), which has a high surface area and high porosity, to adsorb contaminants from a waste stream.

Adsorption by activated carbon is a non-selective process¹; this may result in adsorption of less hazardous contaminants over the hazardous contaminants. Thus, adsorption capacity may be significantly reduced due to competitive reactions taking place.

Research carried out over the last forty years has established that clays modified by organic compounds can also be effective as adsorbents for some hazardous compounds and selectivity can be bestowed upon the adsorbent so that particular compounds are adsorbed preferentially².

There are at least three ways in which a clay may be defined:

- (i) any fine-grained, natural, earthy material³,
- (ii) as a rock term describing a large group of crystallite minerals known as clay minerals,
- (iii) in terms of particle size, where the particle size is no more than 2 μm .

The definition chosen depends on the discipline within which the area of clays is being studied. Mackenzie⁴ defines crystalline clay minerals as "hydrous silicates with layers or chain lattices consisting of sheets of silica tetrahedra arranged in hexagonal form, condensed with octahedral sheets; they are usually of small particle size." This is the definition generally used by chemists and it will be used as a basis for the work described in this thesis.

1.2 The structure of clay minerals

Clay minerals are hydrous silicates, layered in structure. These layer silicates are constructed from two units: a sheet of corner linked tetrahedra and a sheet of edge linked octahedra. The condensation of the tetrahedral SiO_4 unit gives a network with composition Si_2O_5 . This network extends in two dimensions as a tetrahedral sheet. The dominant cation in the tetrahedral sheet is the Si^{4+} ion but substitution by Al^{3+} and Fe^{3+} occurs. The tetrahedral sheet can be envisaged as each tetrahedron resting on its triangular face, sharing the oxygens at all three corners with three other tetrahedra thus extending infinitely in two dimensions. The fourth, apical, oxygen points upwards, perpendicular to the base of the tetrahedra (See Figure 1.1).

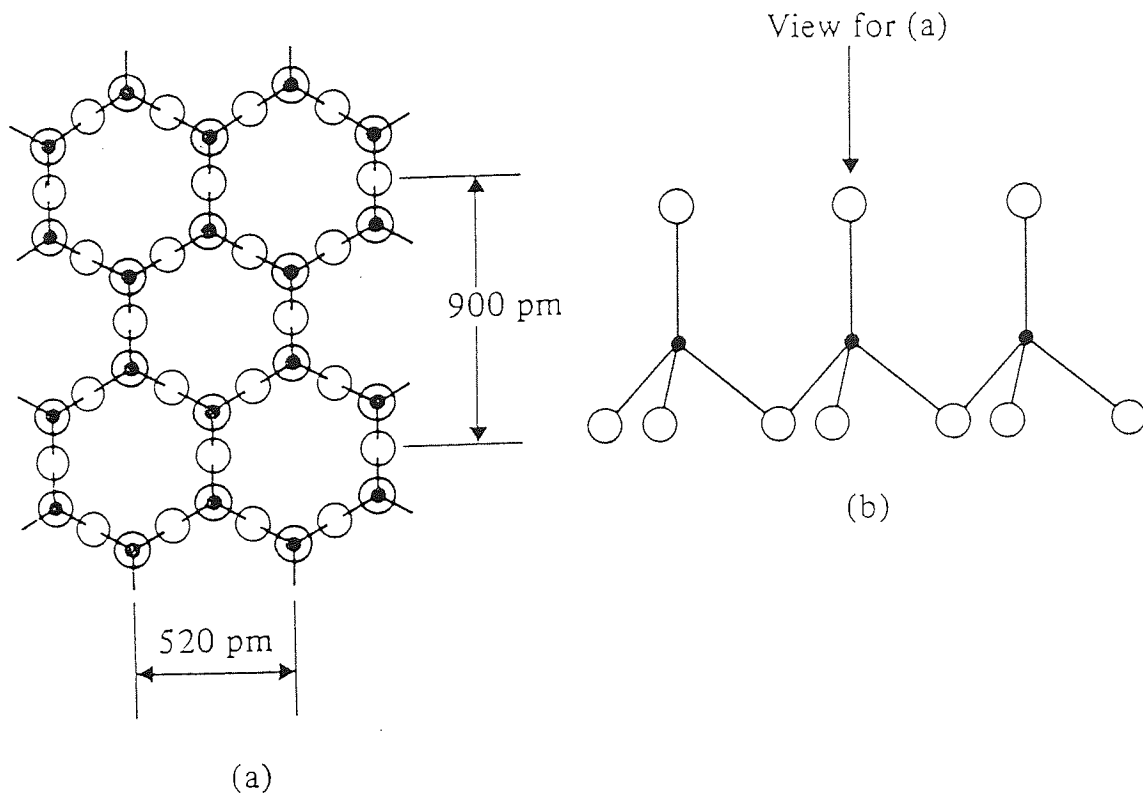


Figure 1.1 Diagrammatic representations of the tetrahedral sheet in layered silicates.

(a) plan as seen looking down the O-Si direction and (b) side elevation.

The octahedral sheet consists of $\text{M}_{2/3}(\text{OH})_6$ octahedra, where $\text{M} = \text{Al}^{3+}$, Mg^{2+} , Fe^{2+} or Fe^{3+} cations. The octahedral holes in the sheet can be filled in two ways. If all the octahedral holes are filled then the sheet is trioctahedral, for example, brucite, $\text{Mg}_3(\text{OH})_6$. Where two-thirds of the octahedral holes are filled, for example, gibbsite, $\text{Al}_2(\text{OH})_6$, the mineral is termed dioctahedral.

The tetrahedral and octahedral sheets are joined by the apical oxygens of the tetrahedra replacing two out of three of the hydroxyl ions in the lower plane of the octahedral sheet. The joining of the sheets in a one to one ratio results in a *1:1 layer silicate structure* (see kaolinite in Figure 1.2). A *2:1 layer silicate* structure is achieved by inverting a tetrahedral sheet and bringing it down on top of the 1:1 silicate, approaching the octahedral sheet, and again replacing two thirds of the hydroxyls with apical oxygens (e.g. see mica in Figure 1.2).

A structure is classed as electronically neutral when no substitution occurs in the octahedral or tetrahedral sheets. In the octahedral layer three Mg^{2+} ions may be replaced by two Al^{3+} ions and electronic neutrality will be maintained. This is due to the fact that Al^{3+} initially fills only two thirds of the octahedral holes present, substitution for Mg^{2+} resulting in all the octahedral holes being filled. However, substitution in the tetrahedral sheet, for example, Si^{4+} for Al^{3+} , or in the octahedral sheet Fe^{3+} for Fe^{2+} may occur. Substitution normally occurs for cations of similar size and lower valency. Such substitution can result in the layer silicates being negatively charged. This negative charge is neutralised by various interlayer cations and hydrated cations which may or may not be exchangeable.

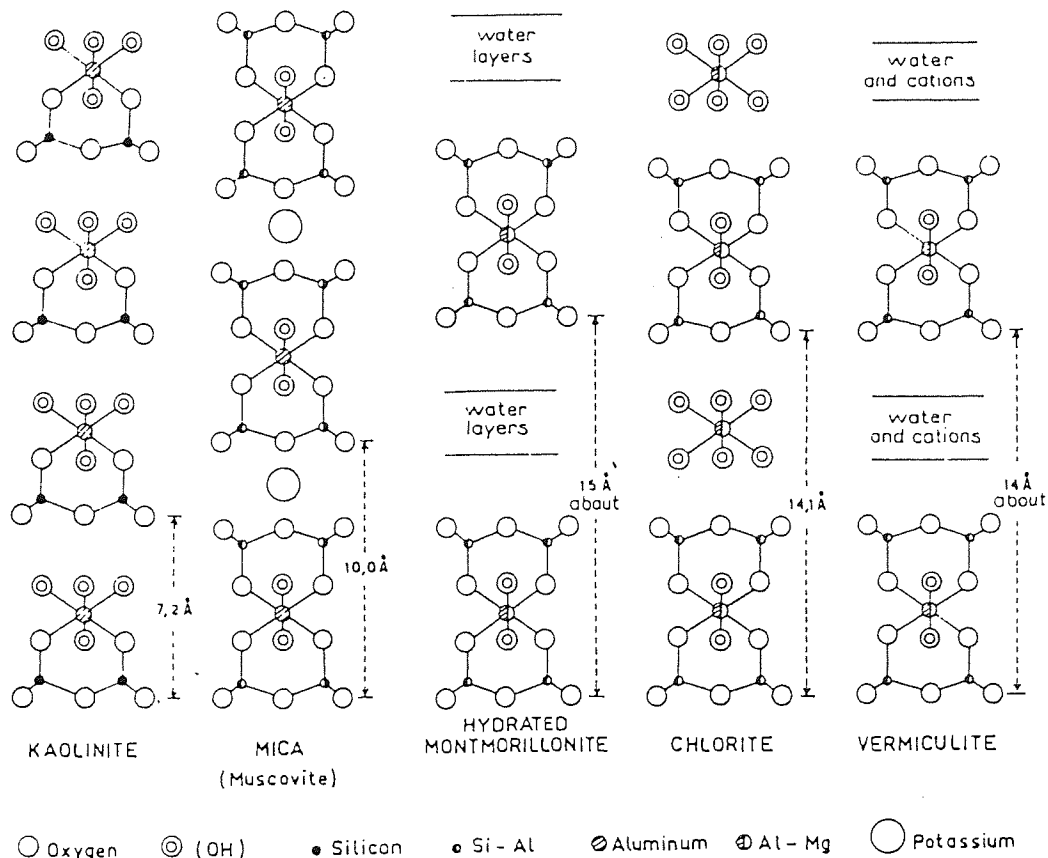


Figure 1.2 Schematic representation of clay mineral groups

The presence of interlayer cations gives clay minerals the property of cation exchange capacity (c.e.c.). This is a measure of the ability to displace these interlayer cations by exchange reactions. The cation exchange capacity is normally expressed as milliequivalents per 100 g of clay (meq/100 g). A low meq/100 g is that between 0 and 10; a clay with such a c.e.c exhibits low cation exchange properties. A clay which readily undergoes cation exchange, at a high level typically has c.e.c values of above 100 meq/100 g. The c.e.c. is not directly related to the extent of substitution or magnitude of layer charge, as not all interlayer cations are exchangeable.

Clays are capable of extending infinitely in two directions. These directions are the a and b crystallographic axes. The c axes denotes the repeat distance between sheets and is the d(001) reflection obtained from X-Ray Diffraction measurements. The property is referred to as basal spacing and is denoted by the dashed lined in Figure 1.2. In the clays this is a variable parameter, since swelling may occur through intercalation of solvents, and shrinkage from drying.

The most important layered clay mineral groups are: Kandites (Kaolinite group); Illites (Mica group); Smectites (Montmorillonite group); Chlorites and Vermiculites. The groups are differentiated principally by

- (i) 1:1 or 2:1 layer silicate structure
- (ii) dioctahedral or trioctahedral sheets
- (iii) layer charge/substitution/presence of interlayer cations
- (iv) swelling properties.

These properties will be considered as the clay groupings are discussed below. Detailed studies of clay mineralogy can be found in texts such as Grim³ and Brindley and Brown⁵.

1.2.1 The Kandite group

The clay minerals in this group are characterised by their 1:1 layer structure. The most industrially useful is Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. As the chemical formula suggests, it is a dioctahedral clay. The extent of substitution is negligible and this is reflected in the low c.e.c.s observed for this group of clay minerals (typically 3-15 meq/100 g clay)³. Thus kaolinite has low shrinkage and swelling properties, its basal spacing being 7 Å. When the kaolinite layers are separated from each other by sheets of water the mineral is termed halloysite, and the basal spacing increases to approximately 10 Å.

1.2.2 The Illite group

2:1 layer structures are typical of this group of clay minerals. The layers are charged, and neutrality is achieved by cations that are strongly bonded between the layers. The interlayer cation is not exchangeable. The strong bonding differentiates this group from the smectite group where the interlayer cation is relatively weakly held. The basal spacing is 10 Å. The illites can be divided into three separate groups: Micas; Pyrophyllite and Talc; and Illites.

1.2.2.1 The Micas

The micas may be either dioctahedral, (typical cations being Al^{3+} , Fe^{3+}) for example muscovite, $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$; or trioctahedral, (where Mg^{2+} , Fe^{2+} are the common cations), for example biotite, $(\text{Mg}^{2+}, \text{Fe}^{2+})_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$. In the tetrahedral sheet Si^{4+} is commonly replaced with Al^{3+} , this results in charge deficiency. Generally potassium ions are employed to achieve neutrality.

1.2.2.2 Pyrophyllite and Talc

Pyrophyllite, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$, and talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, do not undergo substitution in either the tetrahedral or octahedral sheets, thus the layer charge is neutral and interlayer cations are not required. The c.e.c. of both minerals is zero and they do not swell in water. Due to the absence of interlayer cations, the layers are only held together by van der Waals forces, allowing the talc layers to slip past each other.

1.2.2.3 The Illites

The illites are the most common clay minerals in nature. In the octahedral layer, substitution of Al^{3+} for Mg^{2+} , Fe^{2+} or Fe^{3+} frequently occurs. Substitution in the tetrahedral layer is not as extensive as that found to occur in micas, that is, less than one in four Si^{4+} ions for Al^{3+} ions. Such substitution results in a reduction of interlayer cations compared to mica and the structural formula is as follows:



The interlayer cation can be potassium (most commonly), sodium, calcium, or the hydroxonium ion, H_3O^+ . The presence of the hydroxonium ion in the interlayer region of the clay results in the layers being less strongly bound and expansion may occur. The c.e.c. of the illites lies between 10-40 meq/100 g clay.

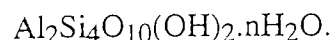
1.2.3 The Smectite group

Clay minerals in this group have a 2:1 layer structure, closely resembling the mica group structure, but with weaker bonds between the unit layers. As for the micas, the smectites can be dioctahedral or trioctahedral. The chemical formulae for the smectites are similar to either pyrophyllite or talc; substitutions in either sheet are accompanied by the addition of interlayer cations so that charge balance is achieved. The interlayer cations are generally exchangeable.

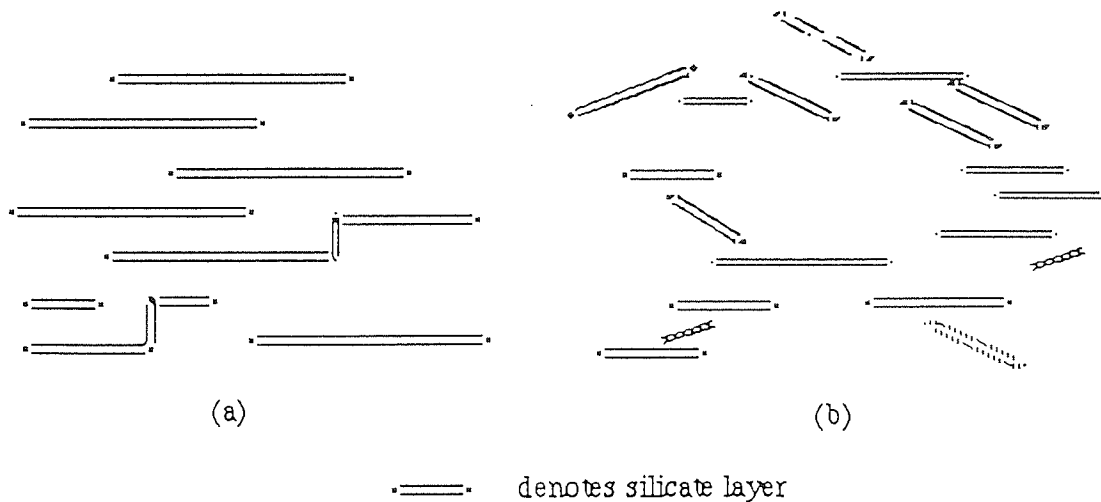
In most smectites, substitution occurs in the octahedral layer, and the resultant charge is distributed through the unit layer. This charge distribution can be compared with micas where tetrahedral substitution results in the charge being localised at the point of substitution. The distribution of charge throughout the octahedral layer in the smectites means that the interlayer cations are held less strongly than in the micas. Therefore the bonds between adjacent clay layers are weak - dipolar or van der Waals interactions - enabling varying degrees of water to be incorporated into the interlayer region, giving the clays their characteristic swelling properties. Only in the smectite clays are the interlayer cations exchangeable and the interlayer surface susceptible to hydration. The presence of exchangeable cations results in the smectites having a relatively high c.e.c. of some 80 - 150 meq/100 g clay.

The basal spacing of these clay minerals is found to be between 10 Å, corresponding to the fully dehydrated state and 20 Å, when the clay is fully hydrated. Frequently a value of 14 Å is found. The arrangement of the layers in smectites tends to be turbostratic, that is, the layers are randomly stacked with respect to the 'a' and 'b' axes of the adjoining layers (see Figure 1.3). Complete dispersion of the crystallites can occur at high relative humidities.

Sodium is the most common interlayer cation for the smectite group, but other cations found are calcium, magnesium, and potassium. The general formula for this clay group is:



Montmorillonite $\text{Na}_{0.33}(\text{Al}_{1.67}\text{Mg}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2$ is an example of a dioctahedral smectite and hectorite $\text{Na}_{0.33}(\text{Mg}_{2.67}\text{Li}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2$ is a trioctahedral smectite. The two smectites can be seen to be based on the formulas and structures of pyrophyllite and talc respectively.



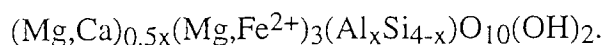
(a) Aggregated but deflocculated clay particles (normal arrangement)

(b) Edge-to-face flocculated and aggregated (fully hydrated clay)

Figure 1.3 The arrangement of the silicate layers in smectite clays

1.2.4 The vermiculite group

Clay minerals of the vermiculite group have a 2:1 layer structure. Vermiculites are similar to the trioctahedral members of the smectite group. Substitution of aluminium for silicon in the tetrahedral layer occurs and the interlayer cation incorporated into the structure is usually magnesium or calcium. These cations tend to be hydrated. The c.e.c. of these clays is 100 - 150 meq/100 g clay. Any expansion is limited to approximately 5 Å. The basal spacing is variable but tends to be around 14 Å. Thus this group is separated from the smectites due to the difference in swelling/expansion properties. The structural formula may be expressed as:



1.2.5 The chlorite group

The structure of chlorite consists of a 2:1 layer structure interleaved with an additional octahedral layer in the interlayer region. Its layer structure is therefore designated 2:1:1. True chlorites are trioctahedral in both the octahedral layers, the 2:1 layer being mica like in structure, bonded by brucite, $\text{Mg}_3(\text{OH})_6$, sheets. Both fully dioctahedral chlorites (chlorites dioctahedral in both the 2:1 and the interleaved layer), and di-trioctahedral chlorites (dioctahedral in the 2:1 layer and trioctahedral in the interleaved layer but not the reverse) are known. Substitutions are varied, but the chlorites tend to have a small unit layer charge and consequently a small c.e.c. of 10 - 40 meq/100 g

clay. The hydroxy-interlayers are sites for anion retention and reduce fixation of cations. The basal spacing is 14 Å, but in contrast to the smectites and vermiculites, is not variable. The high ferrous iron content renders many chlorite samples green, hence the name of the group.

1.2.6 Mixed layer minerals

Clay minerals also appear in nature as mixed-layer clays consisting of interstratified layers of different minerals. The interstratified clays cannot be separated by physical means. There are three types of mixed-layer structure:

- (i) irregular layers, randomly interstratified
- (ii) regular layers of different minerals e.g. ABABAB
- (iii) layers segregated within one crystallite into zones of regular and irregular interstratification.

The majority of mixed layer clays consist of combinations of illite, montmorillonite, vermiculite and chlorite. The most common is illite-montmorillonite mixed layering.

1.3 Properties of the smectite clays

1.3.1 Crystal size and surface area

The size of smectite crystals ranges from 0.2 µm to 2 µm, the average size being about 0.5 µm⁶. The morphologies are also variable: rhombic, hexagonal, lamellar, lathe and fibre shapes are found. Aggregate types have been determined by the habit or shape of individual crystallites and by their arrangement in the aggregate⁶. Crystal size, crystal shape and aggregate characteristics can have an important influence on physical and rheological properties of the clay. The effective particle size of smectite clays is often larger than the actual particle size; and the effective surface area of smectite clays is often considerably less than the actual surface area because of aggregation. The aggregation process results in crystals becoming interlocked and difficult to separate, except by a strong shearing force. Sodium smectites yield the smallest effective crystal size and the largest surface area in clay water systems because their natural clay size tends to be small and swelling pressure tends to disrupt interlocked crystals.

1.3.2 Exchangeable ions and ion exchange

The presence of exchangeable cations in the interlayer region of the smectite clays is a property unique to this group of clay minerals. The exchangeable cations associated with smectite clays are easily and reversibly replaceable. Exchangeable cations play a dominant role in the commercial use of smectite clays. Where sodium is the predominant exchangeable cation, smectite clays may have a swelling capacity. The presence of sodium tends to promote the development of many oriented water layers on interlayer surfaces. The hydration associated with the sodium ion may produce swelling to the extent of complete dissociation of the individual smectite crystals, the result being a high degree of dispersion and maximum development of colloidal-like properties, that is, high natural viscosity. The presence of calcium and magnesium ions in the interlayer region, even when fully hydrated, shows only a small degree of swelling.

1.3.3 Hydration

The weakness of forces between smectite clay layers allows hydration and dehydration to occur in the interlayer region⁵. Hydration is governed by the electrostatic attraction between the polar water molecule and the charge density of the interlayer cation. The extent of hydration is dependent on:

- (i) the type of exchangeable cation
- (ii) the size and charge density of the cation
- (iii) the magnitude and location of the negative layer charge of the adjacent silicate sheets⁷.

The type of exchangeable cations influences the order or disorder of the water molecules and the number of water layers incorporated into the interlayer region. It has been suggested that multivalent ions promote the formation of rigid structures in the first few adsorbed layers, but as additional water layers are adsorbed these ions promote disorder (or act to make the water more fluid). Monovalent ions appear to reinforce the rigid structure of the water layers because they dissociate from the layer surface and so are, in effect, dissolved in the water structure.

The origin of the negative charge on the clay layers effects the point localisation (tetrahedral substitution) or delocalisation (octahedral substitution) of charge. This in turn will affect the positioning of the interlayer cations. Tetrahedral substitution tends to result in an ordering of the interlayer cations. Such ordering does not occur where substitution occurs in the octahedral sheet since the negative charge is delocalised

throughout the sheet and therefore the clay layer. When only one or two layers of water molecules are adsorbed, the molecules are arranged in a highly ordered manner, regardless of the degree of point localisation of the interlayer cations. Additional water layers, however, may be disrupted if the cation is held strongly to the silicate surface.

The hydration of the interlamellar region occurs in a stepwise manner. At high humidity levels, between one and four layers of water molecules may be formed, depending on the exchangeable cation present. Hydration to the four layer phase results in basal spacing of 20 Å. At this stage the basic smectite clay structure remains intact. Hydration beyond this point results in electrostatic and van der Waals forces becoming balanced by osmotic pressure of the interlayer cations, the basal spacing jumps to 40 Å. Eventually, as the water content is increased, the individual layers dissociate completely, the clay is now said to be delaminated. However, only lithium and sodium smectites display this further swelling, because multivalent cations form a stronger interaction with the facing silicate surfaces, so inhibiting unlimited swelling. The delamination of the clay may also lead to gelation, which can occur at concentrations of as low as 2% by weight of the clay in water. The cause of gelation is thought to be the result of layer edge-to-face interactions which generate a "house of cards" structure as shown in Figure 1.3⁸.

1.3.4 Clay-organic/inorganic interactions

The amount of literature available in the field of clay-organic interactions surpasses that available in the field of clay-inorganic interactions. This however is set to change as clays are considered as viable materials for use as adsorbents for inorganic compounds and for use as catalysts. Three interactions will be discussed here: cation exchange, intercalation, and pillaring.

1.3.4.1 Cation Exchange

It was in 1850 that Thompson published results which showed that, when soils were mixed with ammonia and then leached with water, the greater part of the ammonia was held back⁹. Such exchange was then termed base exchange, even after it was established that the hydrogen ion may take part in the exchange reaction. Way¹⁰ showed that cation exchange in soils was restricted to the clay fraction, and Forschamer¹¹ showed that calcium and magnesium are released from soil by leaching with sea water.

Smectite clays have the ability to sorb certain cations (and anions). They are able to do this by exchange reactions involving the interlayer cations and cations in aqueous solution. The exchange reaction is stoichiometric, causing each clay mineral to have a particular cation exchange capacity (c.e.c.). This is measured in milliequivalents (meq) per 100 g of clay, and at pH 7.

Factors affecting cation exchange capacity are

- (i) broken bonds around the edges of the clay layers,
- (ii) substitutions within the clay lattice, and
- (iii) the hydrogen of exposed hydroxyls.

Broken bonds leave the clay layer with unsatisfied charges, which would be balanced by adsorbed cations. The number of broken bonds and hence the exchange capacity would increase as the particle size decreased. In montmorillonites, broken bonds are responsible for approximately 20% of c.e.c., the other 80% being due to substitutions from within the lattice.

The exchangeable cations, resulting from the balance of negative charges as a consequence of isomorphous substitution in the clay layers, are found in the interlayer regions or basal cleavage surfaces of the layer clay minerals. Interlayer cations resulting from substitutions principally in the tetrahedral sheet, are bonded more strongly than those resulting from substitutions in the octahedral sheet due to the distance through which the charges have to act. Substitutions in the octahedral layer generally have most effect on the c.e.c.

The hydrogen of exposed hydroxyls may be replaced by a cation which would be exchangeable. The presence of hydroxyls both at the broken edges and in the interlayer region would allow for such a process. Though exchange at hydroxyl sites would be important for clay minerals of the kaolinite group because of the presence of the sheet of hydroxyls on one side of the basal cleavage plane, the structure of montmorillonite as defined to date would not facilitate this mode of exchange.

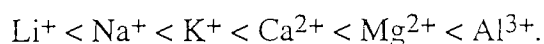
From consideration of the three factors affecting c.e.c., it is clear why it is not possible to give a single c.e.c. value for a specific group due to variation in substitution processes and in the proportion of edge sites within a specific group.

In clay minerals where cation exchange results from broken bonds, the exchangeable cations are held around the edge sites. Where exchange is due to lattice substitutions, the cations are mostly in the interlayer regions.

The rate of cation exchange varies with the clay mineral, the concentration of the cations and the nature and the concentration of the anions. The reaction for kaolinite is the most rapid due to exchange on the edge particles being able to take place quickly. It is slower for the montmorillonites as entrance to the interlayer region requires more time.

Grinding of the clay mineral causes an increase in the number of broken bonds and will therefore also increase the c.e.c. of a clay mineral, having more effect on a clay where the c.e.c. is predominantly dependant on edge sites for cation exchange.

Exchangeable cations are not equally replaceable nor do they have the same replacing power. For the montmorillonites the series of increasing replacing power is such that



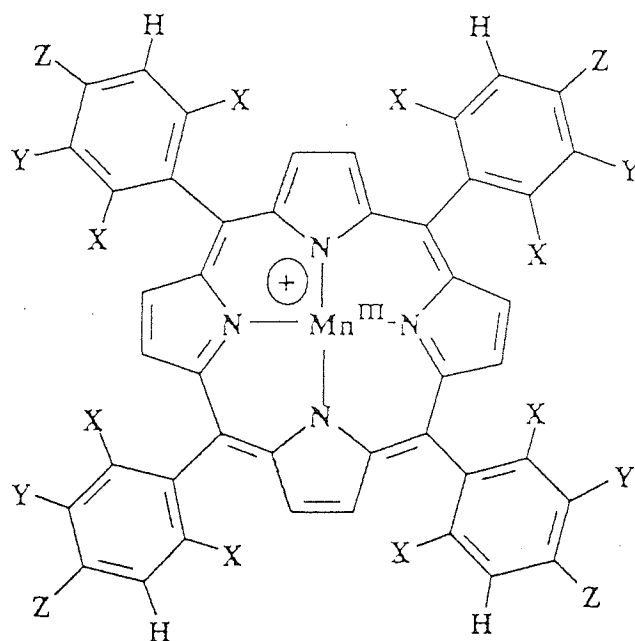
Trivalent ions will readily replace divalent ions, which will readily replace monovalent ions, but the reactions are not readily reversible. Where the ions are the same valency, the effect of size will determine the ease of replacement.

Concentration effects may also be considered. The concentration of the respective cations is a factor in any replacement reaction. A dilute solution of the replacing ion will lead to less exchange than if a more concentrated solution is used.

As well as alkali metal cations, other main group metals have been successfully exchanged into smectite clays; such metals include aluminium¹² and bismuth¹³. Transition metal cations in the form of complexes may be exchanged into clays; examples are tris-bipyridyl metal complexes, $[\text{M}(\text{bipy})_3]^{2+}$, where $\text{M} = \text{Fe}^{2+}, \text{Cu}^{2+}$ ¹⁴, exchanged into hectorite, as well nickel¹⁵, and chromium¹⁶ complexes. Cluster compounds such as molybdenum containing the $\text{Mo}_6\text{Cl}_{12}^{n+}$ core¹⁷ and niobium and tantalum compounds in the form $\text{M}_6\text{Cl}_{12}^{n+}$ (where $n = 2,3$)¹⁸ can be exchanged into smectite clays. Manganese porphyrins have been found to cation exchange with the inorganic cations present in the natural clay¹⁹, Figure 1.4. Results suggest that smectites could be used as inorganic supports for bivalent metalloporphyrins, which are known to be catalysts for oxidative dehydrogenation, and to act as reversible oxygen carriers.

Positively charged organic species will also undergo exchange reactions with clays. As early as 1934, Smith²⁰ demonstrated that it was possible to exchange various amine

hydrochlorides onto montmorillonite clay. Since this date much work has carried out on the interaction of alkylammonium cations with clays. A more detailed account of these systems can be found later in Section 1.4.



$X = Y = Z = H$		$Mn^{III}(TPP)$
$X = Cl$	$Y = Z = H$	$Mn^{III}(TDCPP)$
$X = Y = H$	$Z = COO^-$	$Mn^{III}(TCPP)$
$X = Y = H$	$Z = SO_3^-$	$Mn^{III}(TSPP)$
$X = Cl$	$Y = SO_3^- \quad Z = H$	$Mn^{III}(TDCSPP)$

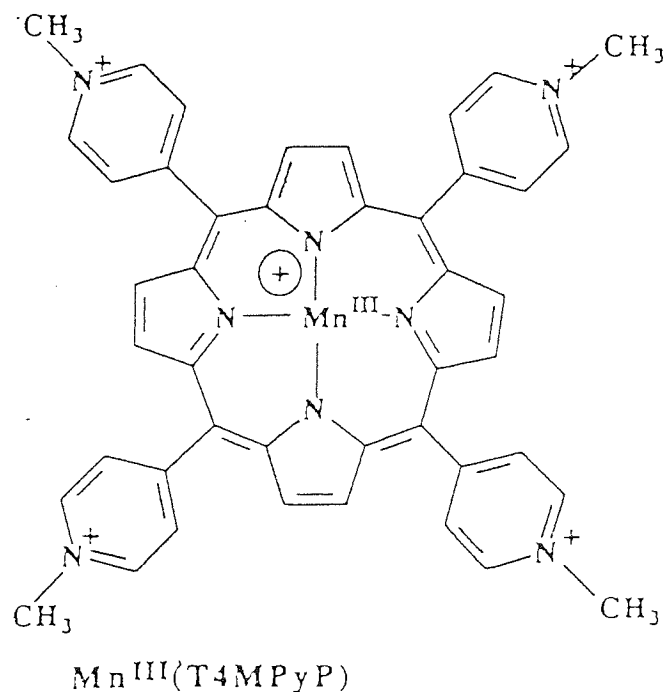


Figure 1.4 The structure of manganese porphyrins used as cations in cation exchange reactions, after Barloy et al.¹⁹

1.3.4.2 Intercalation

Intercalation is the reversible insertion of atoms, ions, or neutral molecules into a solid host lattice with the host lattice retaining its major structural features. The host and guest may experience changes in their geometrical, optical, electrical and chemical properties. Clays as host molecules are able to incorporate interlamellar water⁸, and inorganic/organic species¹²⁻¹⁸ into the interlayer region. Intercalation can result in a great number of modified clay products. It may result in loss of interlayer water, or the loss of interlayer cations, indeed cation exchange reactions are a type of intercalation reaction. For the purpose of this study however, intercalation reactions and cation exchange reactions shall be considered separately.

In the intercalation of organic compounds, competition will arise between the organic compound and water for the same ligand positions around the exchangeable cation for intercalation to occur. Aliphatic compounds with chain length greater than five units and aromatic compounds are able to compete effectively and intercalate. The clay surface contributes to the intercalation process via hydrogen bonding between its oxygens or hydroxyl groups and the functional group of the organic molecule. It may also contribute via protonation of an organic compound. The intercalation of metal ion complexes has yielded systems that have been shown to be efficient catalysts²¹.

Intersalation, the intercalation of inorganic salts, is used to denote the presence of cation-anion pairs in the interlayer region.

1.3.4.3 Pillaring

Previously, in the study of chemically modified clays for use as catalysts, it was found that at elevated temperatures (200 - 300 °C) the clay would dehydrate and collapse. The insertion of thermally robust molecules, enables the silicate layers to be propped open and remain open at high temperatures, yielding a new group of materials applicable for use in the field of heterogeneous catalysis.

The first pillared clays were produced using tetraalkyl ammonium ions in montmorillonite²². These were not thermally stable, decomposing between 250 °C and 500 °C.

Pillared clays based on polynuclear hydroxymetal cations, that are stable above 500 °C, have been prepared. They result from the calcination of smectites intercalated with oligomeric or polymeric cationic complexes of metals. Metals used include aluminium,

titanium, nickel, zirconium, vanadium, silicon, magnesium, tin, iron, niobium. The synthesis of pillared clays is in two steps:

- 1 cationic exchange of the natural clay by the cationic metal complex,
- 2 calcination which is able to transform the cationic metal complex into metal oxide pillars attached to the clay sheets²³.

An example is aluminium pillared clay derived from the $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ cation complex²⁴. The high thermal stability of the pillared clays is accounted for by the dehydroxylation of the oligomer to Al_2O_3 pillars at elevated temperatures. The metal oxide pillars produced keep the silicate layers apart; thus an open, cavity-like structure is formed, similar to that of zeolite. It is interesting to note that the pore sizes produced are significantly larger than those found in zeolite, 2 - 25 Å compared to 2 - 8 Å. Pillared layer clays have an advantage over zeolite in that size, separation and composition of pillars can be adapted for a specific application. This porous structure allows reactions such as molecular sorption, chemical synthesis and catalysis to take place.

In the case of molecular sorption, pillared clays are being considered as adsorbents for toxic organic compounds. Recent work by Srinivasan and Fogler²⁵ has investigated the combination of organic cations with hydroxyaluminium clays, for example, cetylpyridinium hydroxyaluminium montmorillonite. These clays are claimed to be better adsorbents for mixtures of wastes than organo-clays alone, and as good as granular activated carbon, the standard for waste water treatment. The inorganic-organo-clays (IOCs) are also stable with respect to desorption. They are claimed to be better than organo-clays because some flocculation of organo-clays occurs resulting in internal hydrocarbon cores which effectively reduce the concentration of organo-clay actively available for adsorption. However, for the IOCs, the charged hydrophilic head group of the adsorbent pointing away from the surface may provide an effective electrostatic shield against flocculation. Furthermore, the externally oriented, charged head groups may have lowered the contact angle between the surface and the solution. These two surface properties of the inorgano-organo-clays are probably responsible for the stronger affinity between toxic organics and the IOCs. The orientation of the hydrocarbon part of the adsorbent appears to be as important as the amount of organic carbon itself. Figure 1.5 shows a schematic representation of the IOCs, the relative flocculation and stabilisation of the precursors and the resulting IOC.

Michot and Pinnavaia²⁶, in similar studies have also enrolled the use of Al-pillared clays, but in this case in combination with Tergitol, an alkyl polyethylene oxide, which

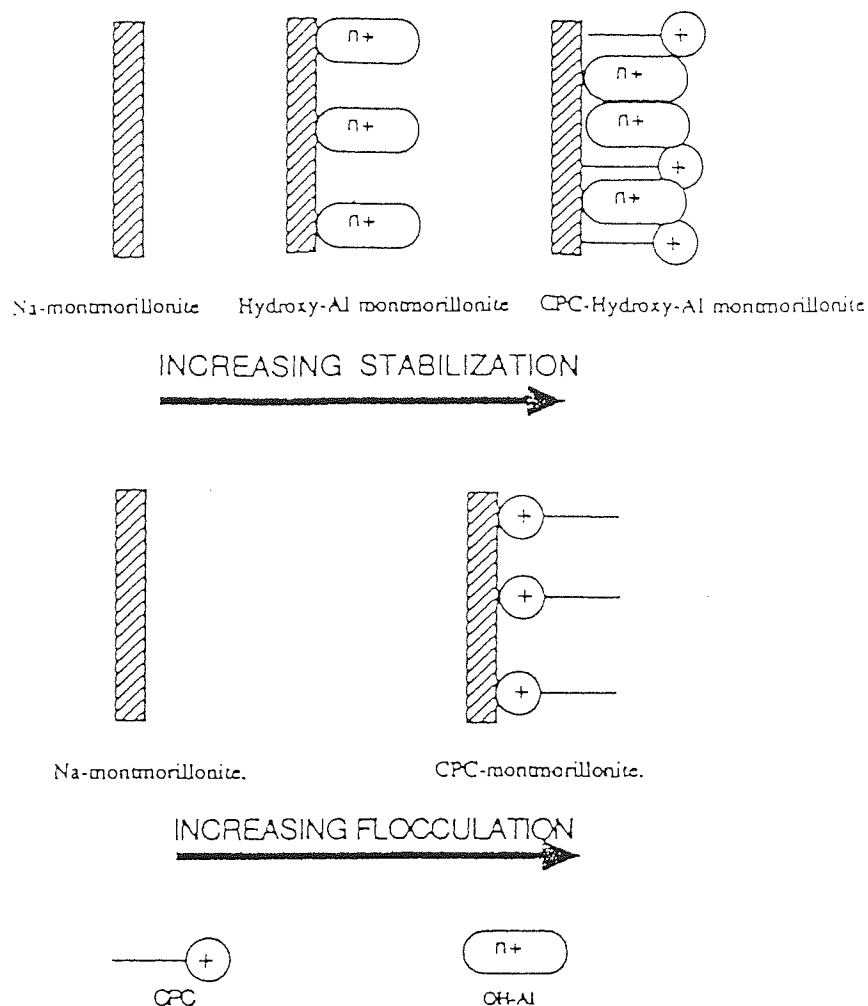


Figure 1.5 A schematic representation of the properties of the montmorillonite clay precursor and the product IOC²⁵

is a non-ionic surfactant, see Figure 1.6. They concluded that this adsorbent increases the affinity of the microporous interlayer adsorption sites and that the surfactant molecules create new adsorption sites on the external surfaces of the clays.

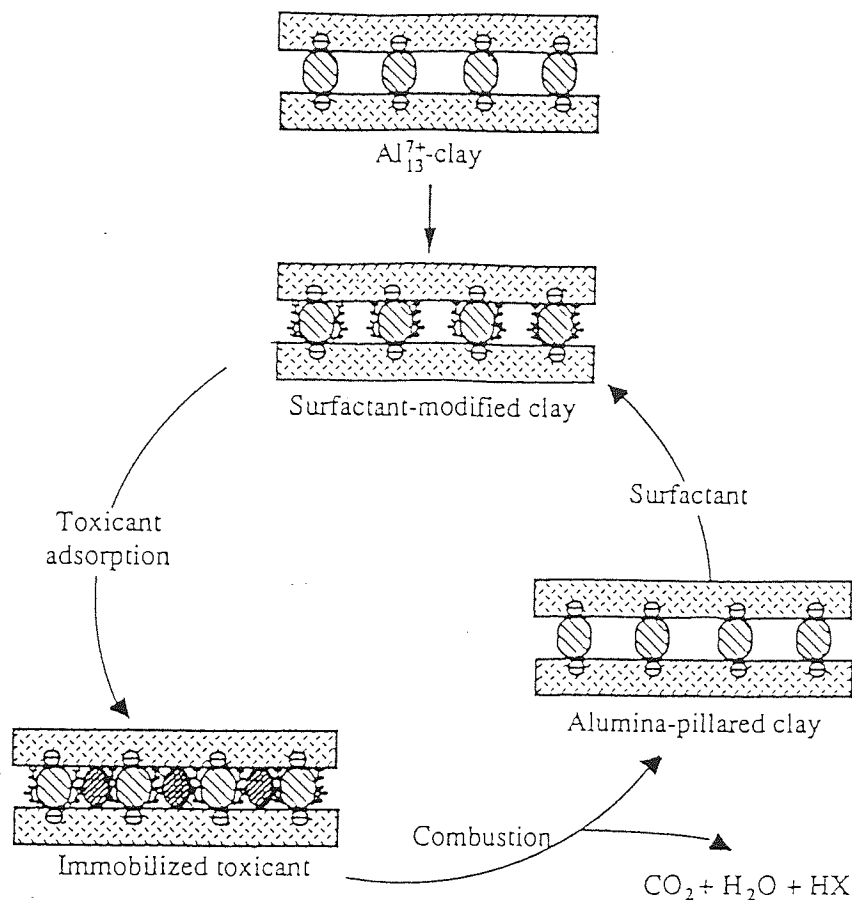


Figure 1.6 Scheme for the thermal recycling of a surfactant modified pillared clay adsorbent²⁶

1.4 Clay-organic/inorganic interactions

Section 1.3.4 briefly outlined some of the clay-organic/inorganic exchange reactions displayed by the smectite clays. Early references to clay-organic systems document attempts to react clays with organic cations²⁷ or neutralise acid-treated clays with organic bases such as amines^{20,28,27}. This section will deal specifically with the cation exchange interaction of montmorillonite with quaternary ammonium compounds; and both laponite and montmorillonite with transition metal complexes. Theng 1974²⁹ has excellently documented clay-organic interactions.

The terminology used in the literature for the description of the products of the cation exchange reaction of montmorillonite with quaternary ammonium compounds shows some variation: organo-clays is the most commonly used one, and quaternary ammonium exchanged clays is also used. Though the latter is the more descriptive of the two and not easily confused with the organic compounds one is attempting to adsorb, a short form would be more convenient. In this thesis the terminology which

will be used is that of Quat-clay. The Quat being the abbreviated form of the quaternary ammonium cation.

1.4.1 Quaternary ammonium cation exchanged smectites

1.4.1.1 Mechanism for the exchange reaction

The cation exchange of smectite clays by quaternary ammonium compounds has received much attention, and extensive research into the Quat/clay interaction has been documented by Theng²⁹ and Mortland³⁰.

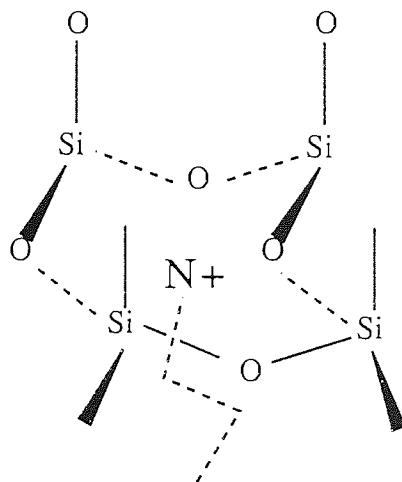
When a quaternary alkyl ammonium salt, Quat, of the type $R_4N^+X^-$ (where R = alkyl chain) is reacted with the smectite clay, the R_4N^+ ions exchange with the exchangeable cations. The consequences of this reaction are an increase in the basal spacing and a significant change in the surface properties of the clay; that is, the nature of the surface changes from hydrophilic to hydrophobic due to the presence of the alkyl (R) chains. The first reactions of this kind with defined organic cations were observed by Smith in 1934²⁰.

It has been shown that the amount of Quat taken up is dependant on the type of Quat and the type of clay. For montmorillonite, if the alkyl chain of the Quat is short, exchange will not occur beyond the cation exchange capacity (c.e.c.) of montmorillonite. However if the alkyl chain is long then exchange can and does occur beyond the c.e.c. This exchange in excess of the c.e.c. is due to van der Waals forces of attraction between the alkyl chains of the exchanged Quat and the alkyl chains of the Quat in close proximity of the clay²⁹.

Morel and Henin³¹ reported 'excess' uptake of long chained amines into montmorillonite, kaolinite, and sepiolite, the amount adsorbed beyond the c.e.c. increased with molecular weight. Cowan and White³² determined isotherms for the adsorption of primary n-alkylammonium cations (ethyl, C_2 through to tetradecyl, C_{14}) by sodium montmorillonite. They showed that the isotherms were Langmuir in nature, that is, the exchange reaction resulted in a strong interaction between the clay and the organic cation. The strength of interaction appeared to increase with molecular weight. This manifests itself as an initial slope and a plateau for adsorption, increasing with molecular weight. Above C_8 , adsorption beyond the c.e.c. of the clay occurred. This increase in adsorption with molecular weight was further confirmed by Theng et al.³³.

Comparison of the free energy of the exchange reaction³³, shows that, ΔG^m , increases in the order $Et_1 < Et_2 < Et_3$. When alkylammonium ions of the same weight are compared the order is $Et_1 < Me_2$, $Bu_1 < Et_2$ and $Pr_1 < Me_3$ (Where Me, Et, Pr, Bu correspond to methyl, ethyl, propyl, and butyl and the numbers denote mono, di-, tri, and tetra-alkyl derivatives). Here it is assumed that the increase in affinity with cation size is due to the increased contribution of van der Waals forces to the adsorption energy. The van der Waals contribution (cation-cation interaction) more than offsets the ability to form hydrogen bonds with the clay surface. The ability of the ammonium cations to form hydrogen bonds with the clay surface decreases in the order primary, secondary, tertiary. Thus the overall order of affinity can be summarised as $R_1NH_3^+ < R_2NH_2^+ < R_3NH^+$.

Exceptions to this series were found to be the small methyl derivatives (mono- through tetra-), which showed greater affinity than expected and the bulky R_4N^+ which showed less affinity than expected. This was explained by suggesting that the shape of the cation determines the extent to which cation-cation interaction or cation-clay interaction can occur (via van der Waals interactions). This interaction or lack of interaction may result from the ability of the cation to, what has been termed, 'key into' the oxygen surface of the clay. The methylammonium derivatives are obviously more able to do this than for example Bu_4N^+ . Figure 1.7 shows a schematic representation of keying.



Schematic view of the octahedral holes formed by the silicate layers in clays and the keying of ammonium cations

Figure 1.7 A schematic representation of the keying which may occur when quaternary ammonium cations exchange into clay materials

1.4.1.2 Arrangement of exchanged cations in the interlayer region.

When the basal spacing of the montmorillonite clay, the basal spacing of the exchanged clay and the minimum thickness of various cations (derived from the Catalin model³⁴) are compared, it is interesting to note that the basal spacing of the exchanged clay is significantly less than the sum of the basal spacing of the clay and the minimum thickness of the cation. Keying of the cations into the clay surface would result in such differences in basal spacing data²⁹.

Jordan³⁵ observed that the basal spacing of montmorillonite exchanged with n-alkylammonium cations of varying chain length increased dramatically between C₁ and C₂, remained steady at 13.6 Å (an interlayer separation of 4 Å) until C₁₀, and beyond C₁₀ the basal spacing rose to a plateau of 17.6 Å until C₁₈. The steps represent differences of 4 Å. Knowing the surface area per exchange site and the area covered by each amine oriented parallel to the clay layers, it was deduced that up to C₈, the cation fills up to half the area per exchange site, beyond C₈ more than half the exchange site is filled. Where up to half the area per exchange site only was used, the amine cation adsorbed on one surface can be fitted in the gaps between the cations lying on the opposite surface. Where more than half the exchange site is taken up this interlocked system cannot be obtained and double layers form.

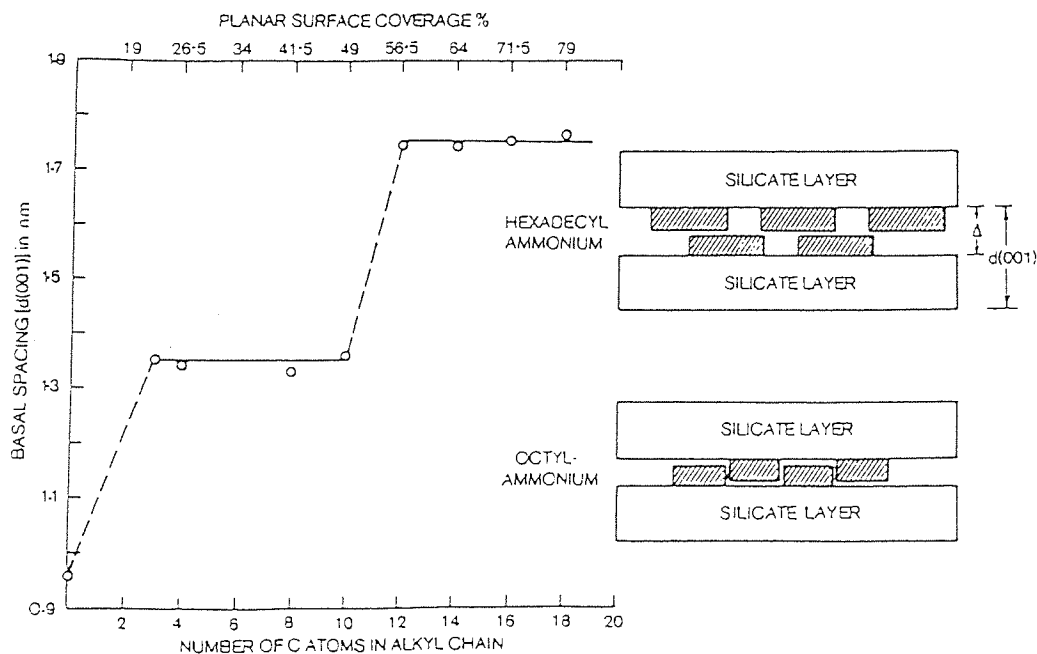


Figure 1.8 The variation in basal spacing with the number of carbon atoms in the alkyl chain with percentage of internal basal plane area occupied by the cation, in complexes of montmorillonite with primary n-alkylammonium ions (after Jordan³⁵)

When cations are exchanged beyond the cation exchange capacity, further steps are observed corresponding to an arrangement resulting from van der Waals forces, where it is suggested that the alkylammonium cations orient themselves vertical to the clay layers.

Basal spacings of montmorillonite with n-alkylpyridinium compounds give spacings indicating that the alkyl chains lie parallel to the silicate surface when a large alkyl group is present. When methyl- and ethyl- groups are present the results suggest that keying of the alkyl group takes place and that an additional interaction between the aromatic ring and the clay surface may be occurring.

1.4.1.3 Properties of quaternary ammonium cation exchanged montmorillonites

1.4.1.3.1 Stability of the quaternary ammonium cation exchanged montmorillonites

Once intercalated, quaternary ammonium exchanged cations are strongly retained. It was found that the replacement of the cations depended on both the basicity and size of the replacing cation. An increase in basicity leads to an increase in desorption and the smaller the cation the greater the ease of desorption³². Jordan³⁵ reported the effect of the organic medium on adsorption. He found that those of high polarity efficiently extracted a large concentration of the exchanged cations.

1.4.1.3.2 Water adsorption

The exchange of sodium or calcium by large quaternary ammonium cations results in a reduction in the water uptake by the montmorillonites^{27,36}. As a result of the exchange reaction, a large proportion of the clay surface becomes occupied by the organic cations, decreasing that available to water. In addition to this, the alkyl groups of the organic cations tend to repel the water molecules²⁷. The relationship observed between the proportion of organic cation present and the decrease in water uptake is now established³⁶.

In contrast to this, the presence of small quaternary ammonium cations actually enhances the uptake of water, polar organics, and non-polar organics, from the vapour or gaseous phases. This is attributed to the fact that the small cations take a relatively

small fraction of the clay mineral surface area and they are capable of propping open the silicate layers resulting in interlayer porosity²².

1.4.1.3.3 Adsorption of organic compounds from vapour and gaseous phases

Much work in the area of vapour phase organic compound adsorption followed the work of Barrer et al.²². Work by Barrer and Millington³⁷ observed increases in basal spacing when quaternary ammonium cation exchanged clays were intercalated with organic gases and vapours, for example n-heptane, benzene. It was deduced that both the final spacing, and the arrangement of the organic cations²⁹, was controlled by the organic vapour rather than by the quaternary ammonium cation. Following this work with similar systems Slabaugh and Hiltner³⁸ found that when they used quaternary ammonium cations of C₁₂, C₁₄, C₁₆ and C₁₈ the basal spacing increased stepwise with increase in partial pressure (concentration of gas/vapour). Below a certain partial pressure the basal spacings remained constant, this basal spacing corresponding to that of the quaternary ammonium cations arranged in a double layer in the interlayer region. Above this partial pressure there is a drastic increase in basal spacings, indicating a single layer arrangement of the ammonium cations with the chains standing perpendicular to the silicate surface.

The swelling is defined as a two step process³⁸, see Figure 1.9. Adsorption firstly occurs on the external surfaces of the exchanged clay and on any silicate surface available in the interlayer region via the polar sections of the molecule - no increase in basal spacing is observed. The second step involves the non-polar sections of the molecule and occurs at high adsorbate pressures. The alkyl chains of the quaternary ammonium cations appear to be displaced from the silicate surface creating new surfaces on which the organic molecules can adsorb, and liberate the quaternary ammonium alkyl chains from the organic molecules by which they were solvated. Thus polar molecules do not give rise to appreciable swelling, whereas those molecules possessing both polar and non-polar groups in a molecule are able to swell the exchanged clay further.

This gas/vapour adsorption property has enabled such complexes to be used as gas-chromatographic separation media: Principally methyl and ethyl ammonium exchanged montmorillonites have been used^{22,37}. Long chained ammonium compounds, trade name 'Bentones', have been used as stationary phases in gas-liquid chromatographic columns⁴⁰.

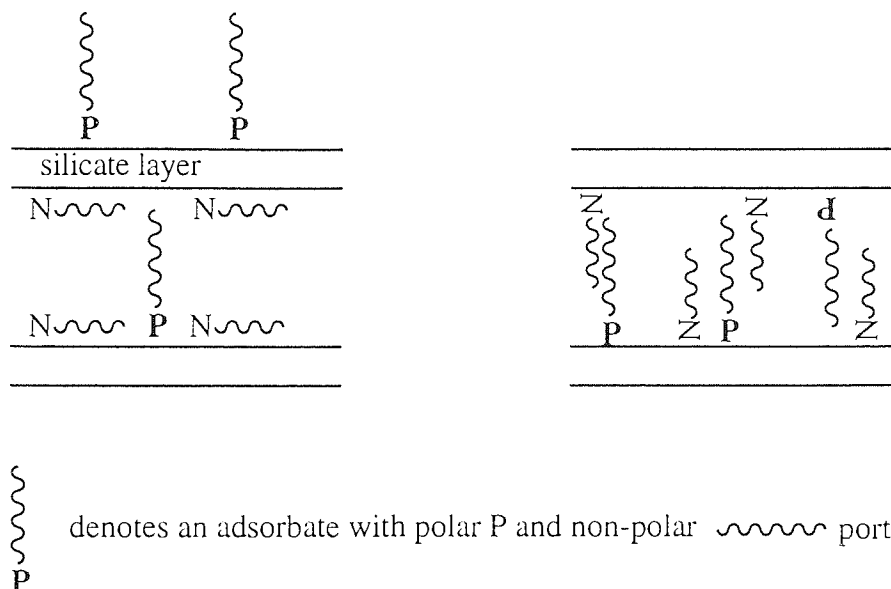


Figure 1.9 The two step process as proposed by Lagaly³⁹ for the adsorption of molecules possessing polar and non-polar sections onto clay materials

In dealing with clay-alcohol adsorption, Annabi-Bergaya et al.⁴¹ investigated the adsorption of methanol by smectites with different interlayer cations. Intermolecular (adsorbate-adsorbate) interactions had to compete with the solvation power of the interlayer cations creating adsorbate-adsorbent interactions. With lithium-montmorillonite as the adsorbent the methanol maintained its liquid like association. In calcium-montmorillonite, methanol solvated the calcium ion as a result of the greater charge density of this ion. Thus the interactions between the liquid molecules compete with the surface forces that break the intermolecular association in methanol. When a quaternary ammonium exchanged clay is used as an adsorbent, polar molecules such as methanol orient themselves around the alkyl chains in a way that optimises the screening of the charges on the nitrogen cations, favouring the clustering of polar molecules near the hydrocarbon chains. Thus, it is proposed that polar molecules adsorb in the interlayer space between alkyl chains and on the external surfaces Lagaly et al.,1983³⁹.

Investigations by Wolfe et al. 1985⁴² indicated that dodecylammonium and dodecyldiammonium cations lie flat in the interlayer region, whereas propylammonium orients perpendicular to the clay layers. Because of the similarity between the length of the dodecyldiammonium cations and the intercharge site distance, i.e. the distance between sites of highest density positive charge in the interlayer region, the cations lay flat between the charge sites and "locked" the clay layers together, disabling the ability for further expansion.

In parallel to the above work on vapour/gas phase adsorption studies, studies of adsorption from solution were being carried out. A detailed review of research in this area will be discussed in Section 1.6.

1.4.2 Transition metal complex exchanged smectites

The types of cation used for clay exchange reactions and therefore the modification of clays has recently grown to encompass transition metal complexes. Examples are 2,2'-bipyridyl complexes of iron(II) and copper(II), $[M(\text{bipy})_3]^{2+}$ (where $M = \text{Fe}, \text{Cu}$), exchanged into smectite clays⁴³; and metalloporphyrins exchanged into smectite clays, for example, tetrakis(1-methyl-4-pyridiniumyl)porphyrin iron(III), Fe(III)TMPyP, the Co(II) analogue⁴⁴ and manganese porphyrins¹⁹. As yet little work has been published in this field but this is set to change as research into clays as catalytic supports grows, and modified clays are considered as sorbents. The nature of the amine complexes will be discussed below.

1.4.2.1 Mechanism of exchange

The geometry of some transition metal complexes may render them useful for opening up and exposing clay mineral surfaces for sorption and catalysis, where reactions could be catalysed by outer sphere electron transfers. The interlayer openings produced could be as large as 8 Å compared to that of 4 - 5 Å commonly obtained for alkylammonium exchanged clays. It was as recently as 1977 that the first transition metal complex was reported to have been exchanged onto a clay surface. The work carried out by Berkheiser and Mortland⁴⁵, studied the exchange of 1,10-phenanthroline complexes of iron(II) and copper(II) onto hectorite. Both the 1,10-phenanthroline iron(II) complex, $[\text{Fe}(\text{phen})_3]^{2+}$, and the 1,10-phenanthroline copper(II) complex, $\text{Cu}[(\text{phen})_3]^{2+}$, are exchanged into the mineral readily, the larger charge and size differences possibly the driving force for the exchange reaction.

The $[\text{M}(\text{phen})_3]^{2+}$ cations were adsorbed beyond the c.e.c. of the clay as the salt, for example $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_2$ which was removed by washing with distilled water. Washing of the exchanged clay removed both salt intersalated into the interlayer region and, for example, NaClO_4 present in the interlayer region, a product of the exchange reaction, thus freeing silicate surface area. The exchanged clays were found to be stable at least for the duration of the studies. Similar observations were made for metal-2,2'-bipyridyl complexes $[\text{M}(\text{bipy})_3]^{2+}$, where $M = \text{Fe}, \text{Cu}^+, \text{Ru}^{43}$. In addition to these observations desorption of the salt $[\text{M}(\text{bipy})_3](\text{ClO}_4)_2$, where $M = \text{Fe}$ and Cu

was observed at high salt loadings. It is of interest to note that beyond the c.e.c. of the clay the associated anion will effect the adsorption of the salt. The intersalation of $[\text{Fe}(\text{bipy})_3]^{2+}\text{X}$, where X is the associate anion ClO_4^- , Cl^- , Br^- , or SO_4^{2-} , into hectorite clay was found to be affected by the anion present. $[\text{Fe}(\text{bipy})_3]\text{SO}_4$ shows the greatest tendency towards intersalation. $[\text{Fe}(\text{bipy})_3](\text{ClO}_4)_2$ shows an adsorption maximum where the salt is taken up in excess of the c.e.c. of the clay, but desorption occurs to maintain cation exchange at the c.e.c of the clay⁴³.

1.4.2.2 Arrangement in the interlayer region

The fully exchanged $\text{M}(\text{phen})_3^{2+}$ -hectorites exhibited basal spacings of 17.4 Å. Fractional exchange yields a low angle reflection corresponding to 12 Å which decreases with increase in fraction of c.e.c. of complex exposed to the clay. This suggests that exchange occurs in a given interlayer, before occurring in successive interlayers. If exchange occurred uniformly throughout the mineral a constant 17.4 Å would be obtained⁴⁵. This non-uniformity is due to hectorite not possessing uniform layer charge, thus the complex cations may preferentially fill the interlayers with highest charge density before filling any others. The cations are 8 Å along the C_3 symmetry axis. When the C_3 axis is perpendicular to the silicate sheets, a 17.6 Å spacing should result, which is the case. Basal spacings of 18 Å are obtained for $[\text{M}(\text{bipy})_3]^{2+}$, this is in accordance with the value of 8 Å expected for monolayers of cations oriented on the on the silicate surfaces with their threefold axis perpendicular to the silicate sheets.

1.4.2.3 Properties of transition metal complex exchanged smectites^{43,45}

$[\text{Fe}(\text{phen})_3]^{2+}$ and $[\text{Cu}(\text{phen})_3]^{2+}$ were not displaced from the interlayer silicate surface by either Mg^{2+} ions, in the form of MgCl_2 , or tetrapropylammonium cations. On exposure to $[\text{Ni}(\text{phen})_3]^{2+}$, a small amount of exchange occurred and $[\text{Fe}(\text{phen})_3]^{2+}$ was displaced from the clay, this was accompanied by a significant concentration of $[\text{Ni}(\text{phen})_3]^{2+}$ being adsorbed onto the clay in excess of the c.e.c.

Dinitrogen, N_2 , adsorption occurs at the surfaces that are unoccupied by the complex cations. Large surface areas are obtained which are the result of the propping open of the silicate layers by some 8 Å; this enables multilayer adsorption of gases/vapours to occur. Lower surface areas were observed for $[\text{Cu}(\text{phen})_3]^{2+}$ -hectorite and $[\text{Cu}(\text{bipy})_3]^{2+}$ -hectorite; this was attributed to the partial collapse of the interlayers as a

result of loss of one of the "phen" or "bipy" ligands to produce $[\text{Cu}(\text{phen})_2]^{2+}$ and $[\text{Cu}(\text{bipy})_2]^{2+}$ as evidenced by ESR.

Vapour adsorption isotherms of water and benzene onto $[\text{M}(\text{phen})_3]^{2+}$ exchanged hectorites, where $\text{M} = \text{Cu}$ and Fe , resulted in Type II isotherms (Section 1.6 defines isotherm types) resulting in relatively strong adsorbate-adsorbent interactions. Adsorption of water by $[\text{M}(\text{bipy})_3]^{2+}$ exchanged hectorites, where $\text{M} = \text{Fe}$, Ru and Cu , resulted in Type III isotherms, indicating weak adsorbate-adsorbent interactions. For the $[\text{Fe}(\text{phen})_3]^{2+}$ and $[\text{M}(\text{bipy})_3]^{2+}$ hectorites investigated in this study, two different types of water were found to be present: water weakly hydrogen bonded to the silicate oxygens and water associated with the complex metal cations. For adsorption of benzene by $[\text{Fe}(\text{phen})_3]^{2+}$ -hectorite, it was postulated that interaction occurred via the π - π electrons of benzene and phenanthroline ligands, the orientations of the benzene being parallel to the ligands.

1.5 Adsorption by montmorillonite and modified montmorillonites

Section 1.5.1.3. described the adsorption of gases/vapours by montmorillonite and modified montmorillonites. Quat-clays have shown an ability to selectively adsorb organic compounds from water and organic media. This selectivity could well be enhanced to ensure the adsorption of particularly problematic molecules from waste streams (Sections 1.7.2.3 and 3.9 describe in more detail why such an adsorbent is needed). The problem of water pollution and water remediation is a challenging one in which novel methods are needed to ensure high water quality, therefore this section will deal principally with adsorption of various compounds from water.

1.5.1 Mechanisms and Classification of adsorption

1.5.1.1 Definitions

Adsorption is the accumulation of one or more components in an interfacial layer. An example of adsorption is condensation of a gas, or the adsorption of a solute, onto a free surface. Examples are carbon dioxide condensed into charcoal layers, or a solution of benzene adsorbed onto a clay mineral. The term used is different from that of absorption which suggests penetration into the mass of the absorbing lattice. The counterpart of adsorption is desorption which describes the loss of components from the interfacial layer.

The solid is termed the adsorbent, and the gas or solute the adsorptive. On accumulation at the interfacial layer the adsorptive is termed the adsorbate.

The term sorption will be used to embrace both adsorption and absorption.

Many adsorbents of high surface area are porous and with such materials it is often useful to distinguish between the external and internal surface. The external surface and internal surfaces are difficult to define. Sing et al.⁴⁶ have suggested that external surfaces include those facing outwards, the surfaces of cracks which are wider than they are deep. The internal surfaces then comprise of the walls of the cracks, pores and cavities which are deeper than they are wide and which are accessible to the adsorptive. For the purpose of studies of clay adsorption the external surface will be defined as the area surrounding the agglomerates or particles and the internal surface as the interlayer regions of the clay.

Adsorption may occur such that all the adsorbate molecules are in contact with the adsorbent surfaces, such adsorption is termed monolayer adsorption. When only a fraction of the adsorbate molecules are in contact with the adsorbent surfaces, multilayer adsorption is said to have occurred.

The relation, at constant temperature, between the amount adsorbed and the equilibrium pressure of the gas, or equilibrium concentration of the solute, is known as the adsorption isotherm.

1.5.1.2 Classification of adsorption isotherms

1.5.1.2.1 Gases

Sing et al⁴⁶ have summarised the classification of adsorption of gases by solid adsorbents. Types I - V were originally proposed by Brunauer, Deming, Deming and Teller and is commonly referred to as the Brunauer, Emmett and Teller⁴⁷ (BET) classification. Figure 1.10 shows the types.

The Type I isotherm is concave to the equilibrium pressure axis and the amount adsorbed approaches a limiting value. Such an isotherm may result from microporous solids (pore widths < 2 nm or 20 Å), for example activated carbons, molecular sieve zeolites. The limiting uptake is governed by the accessible micropore volume rather than the internal surface area.

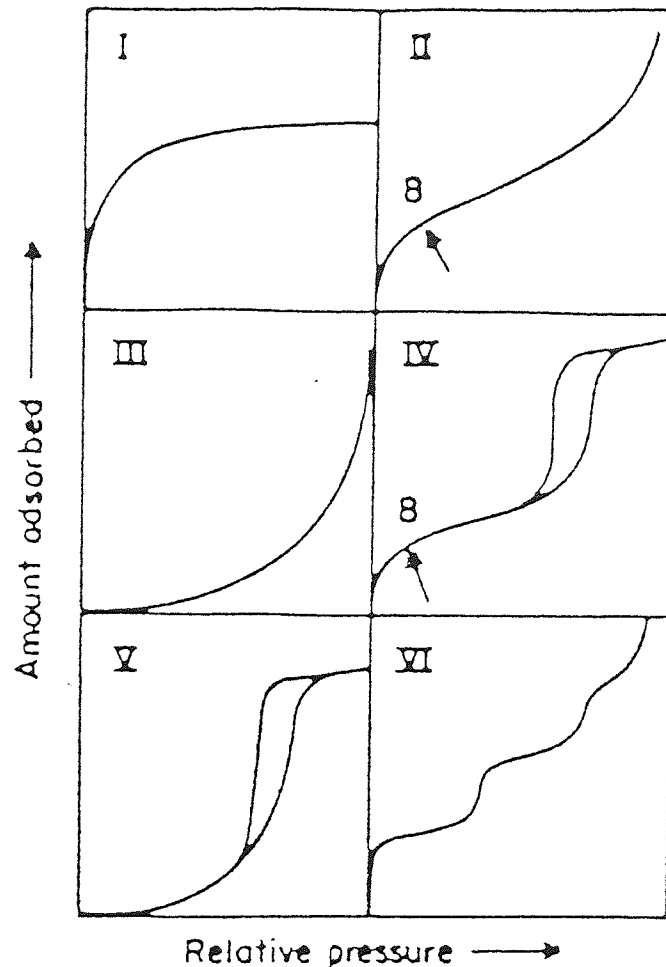


Figure 1.10 Types of adsorption isotherm, after Sing et al.⁴⁶

The Type II isotherm is normally obtained with a non-porous or macroporous solid (pore size approximately 500 Å). The Type II isotherm represents unrestricted monolayer-multilayer adsorption. Point B indicates where the beginning of an almost linear section where monolayer coverage is complete and multilayer adsorption begins.

The Type III isotherm is convex to the equilibrium pressure axis over its entire range, such isotherms are not common, but where they occur they are indicative of weak adsorbate-adsorbent interactions.

The Type IV isotherm is characterised by a hysteresis loop (the isotherm for adsorption is not the same as that obtained from desorption), thus adsorption is not reversible. As Type II isotherms, the initial part of the curve is due to monolayer-multilayer adsorption. Such isotherms are obtained when capillary condensation takes place in the mesopores (pore size 20 Å - 500 Å).

The Type V isotherm is uncommon, it is related to the Type III isotherm in that the adsorbate-adsorbent interaction is weak.

The Type VI isotherm, consists of steps the nature of which are dependent on the system and the temperature. The steps represent successive layer adsorption on a uniform non-porous surface, the step heights represent the monolayer capacity for each adsorbed layer.

The classification detailed above was designed primarily for the classification of adsorption of gases onto solids. The same classification can be used to describe observations of adsorption of solutes onto solids.

1.5.1.2.2 Solutes

Giles et al. in 1960⁴⁸ described their own classification of solution adsorption isotherms. The types observed (eighteen in all) and the explanation postulated have a close parallel with the isotherms of the BET classification and can be grouped into the BET classification. The BET classification enveloping both classifications, and being somewhat more concise, is commonly used to describe both gaseous and solution adsorption. Deviations or additional information, compared to the gaseous BET classifications, on the characteristics of the solution isotherm types are given below, with the Giles et al. classification also given.

For adsorption from solution Type I - H2 - isotherms are well known. The initial slope of the isotherm results from the presence of a solute which has such an affinity for the solid that it is completely or almost completely adsorbed. The adsorbed species may be ionic micelles, polymeric materials or compounds able to displace other compounds from the surface.

Type II - L3 - As more solute is taken up, there is progressively less chance that a bombarding solute molecule will find a suitable site on which it can be adsorbed. This also applies to the latter stages of the other isotherm types.

Type III - S1 - The initial part of this curve results from a mechanism opposite to that described for Type II isotherms. The more solute there is already adsorbed, the easier it is for additional amounts to become adsorbed via van der Waals interactions.

Type IV - L4 - similar to Type II as described above.

Type V - S2 - similar to Type III as described above.

Type VI - S4 - stepped version of Types II and IV.

Type C - Partitioning - The availability of adsorption sites remains constant at all concentrations up to saturation. Thus the shape of the isotherm is linear. The constant partitioning of solute between solution and substrate right up to the maximum adsorption characterises partitioning. Conditions favouring partitioning include the solute having a higher affinity for the adsorbent than for the solvent. The linearity suggests that the number of sites for adsorption remains constant. Thus as more solute is adsorbed, more sites must be created. This could arise when the solute has a higher attraction for the adsorbent than the solvent itself has and the solute may be able to penetrate into the structure of the adsorbent in regions not already penetrated by the solvent.

Besides these six (seven for solutions) isotherms there are borderline cases which may be difficult to assign to one type. Thus one isotherm may have characteristics of more than one type of isotherm class or may be difficult to fit to any of the types. In the case of monolayer coverage of solute, it is not necessarily the case that the solute molecules are close packed or that the monolayer is entirely solute molecules, there may be solvent also present. The monolayer may well consist of clusters of solute molecules adsorbed on the most active sites.

1.5.2 Adsorption of organic compounds by amine and ammonium modified clays from aqueous solution

1.5.2.1 Early studies

1.5.2.1.1 The nature of the adsorbent - comparison of amine and ammonium derivatives

The adsorption of organic molecules from aqueous solution by modified clays was first documented by Cowan and White in 1962⁴⁹. They investigated the adsorption of phenols by a series of n-primary aliphatic amine derivatives (C₂ - C₁₈) and tertiary amine derivatives (C₁₂ - C₁₈). They suggested that the main factors affecting adsorption were: the nature of the sites available for adsorption; the nature of the adsorbate molecules; spatial consideration; thermodynamic quantities; and solubility of the adsorbate in the solvent.

Maximum phenol adsorption was found to occur when dodecylammonium (as the primary ammonium cation) exchanged bentonite was present as the adsorbent, an increase or decrease in alkyl chain length reducing adsorption. It was suggested that phenol was adsorbed onto the interlamellar sites via two mechanisms. The first mechanism was thought to be non-polar, van der Waals interactions between the aliphatic chains of the ammonium cation and the benzene ring of the phenol. The second mechanism involved polar interactions between the hydroxyl group of the phenol and the exposed hydrophilic clay surface via electrostatic interactions or hydrogen bonding. Increasing the amine chain length will increase interactions via van der Waals type forces, but decrease that via polar interactions. Results suggested that both factors may be operative and adsorption occurs at both the hydrophilic and organophilic areas of the clay.

Monolayer coverage in an interpenetration fashion, as is said to occur when the smaller primary ammonium cations ($C_1 - C_{10}$) exchange onto the clay surface³⁵, leads to some phenol being adsorbed. However, the larger primary ammonium cations ($C_{12} - C_{18}$) needing to arrange in a bilayer fashion expose a greater proportion of mineral surface (see Figure 1.8 - Jordan³⁵). It seems reasonable to assume that maximum adsorption occurred at C_{12} because sites were available for both types of interaction to occur, a longer alkyl chain would have resulted in the coverage of the mineral sites available for phenol adsorption.

Studies of the nature of the adsorbate centred on the substituted phenols. Two adsorption series were observed:

4-hydroxymethylbenzene (p-cresol) > 3-hydroxymethylbenzene (m-cresol) >
2-hydroxymethylbenzene (o-cresol), see Figure 1.11,

and

1,2-dihydroxybenzene (pyrocatechol) > 1,3-dihydroxybenzene (resorcinol) >
1,4-dihydroxybenzene (hydroquinone), see Figure 1.12.

By considering electron distributions it was observed that the highest electron density is observed when the methyl and hydroxyl groups attached to the benzene ring are remote, and when the hydroxyl groups of the second series are close to each other. Thus, it was concluded that for maximum adsorption the charge density of the adsorbate molecule must be localised.

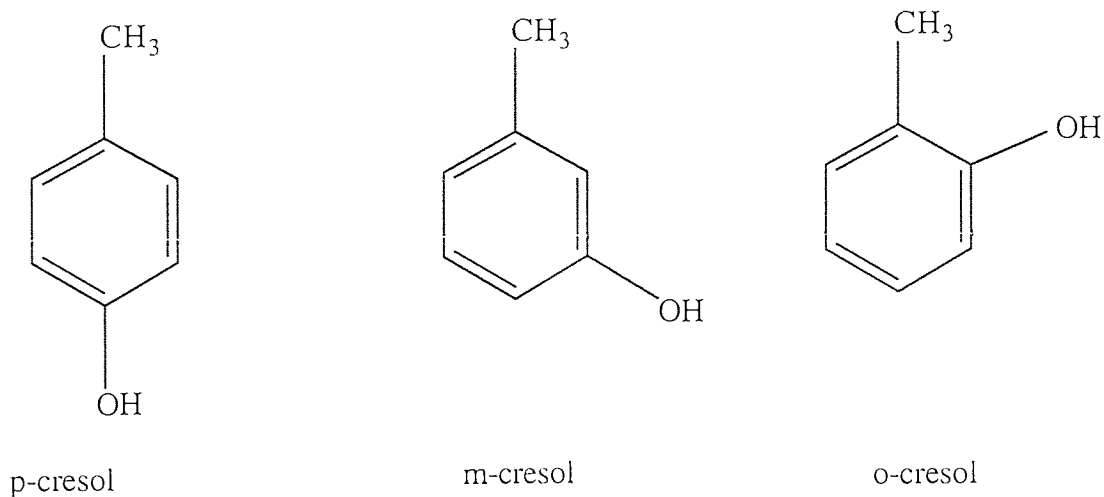


Figure 1.11 Cresols used in the Cowan and White study

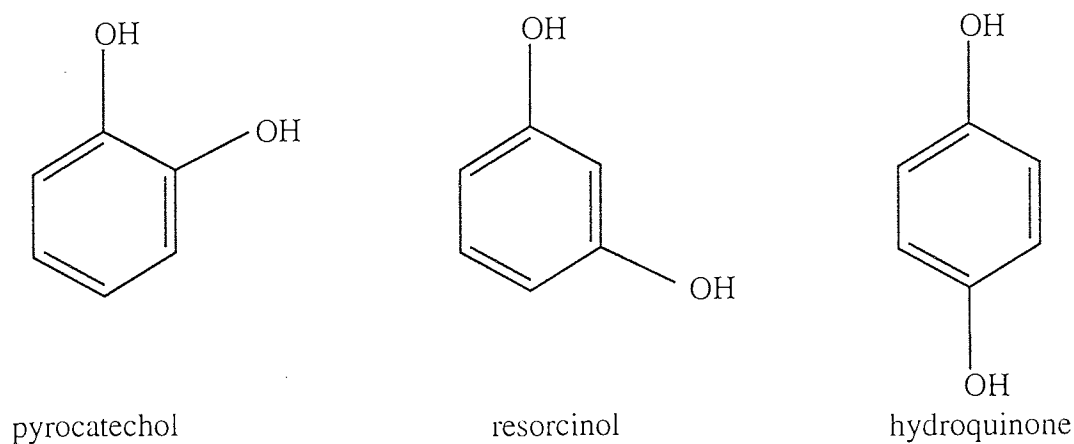


Figure 1.12 Dihydroxybenzenes used in the Cowan and White study

Work by Street and White 1963⁵⁰, extended their investigations of the adsorption of phenol by including quaternary ammonium exchanged clays in their list of adsorbents. They concluded that amine modified clays when compared to quaternary ammonium exchanged clays of the same carbon content (wrt carbons in the alkyl chains) were less effective as adsorbents for phenol.

1.5.2.1.2 Ammonium compound type and the adsorption of phenols

Comparison of dimethyloctadecyl amine modified clay with dimethyldioctadecyl ammonium exchanged clay for adsorption of phenols confirmed previous findings⁴⁹, that organophilic properties alone do not continually increase the extent of adsorption. However the increase in the extent of adsorption was seen to increase with quaternary ammonium cation content, suggesting that in this case the balance of hydrophilic/hydrophobic adsorption sites is not a factor in the adsorption of phenol.

The controlling factor was postulated to be the carbon/nitrogen ratio of 29:1 of the quaternary ammonium cation.

Street and White⁵⁰ concluded that with the primary amines the balance between alkyl chain length and exposed mineral surface appears to be important; for the tertiary amines it appeared to be the ratio between alkyl chain length and ethoxy chains (which the tertiary amines used in this study contained); and in the quaternary ammonium compounds the carbon/nitrogen ratio. Common to all these is the ratio between a polar (mineral surface, ethoxy chains, nitrogen charge) and a non-polar component (alkyl groups), suggesting this balance is needed for the adsorption of phenol from aqueous solution.

Comparisons between primary and quaternary ammonium exchanged clays were made by Cowan 1963⁵¹. Here the study involved adsorption of phenol and m-cresol by tetradecylammonium bentonite and the results were compared with results previously obtained for dodecylammonium bentonite. Dodecylammonium bentonite exhibited typical adsorption behaviour - adsorption decreased with increasing temperature, characteristic of an exothermic process, tetradecylammonium bentonite showed abnormal behaviour, the degree of adsorption with temperature being variable. Partial molar heats of adsorption were calculated.

Adsorption of phenols from dilute solutions may involve the expansion of the silicate layers. Expansion was said to depend on available interlayer space, size and concentration of adsorbate; and work needed to expand the clay layers to allow intercalation. The adsorption with dodecylammonium has been summarised above. Adsorption with tetradecylammonium appeared to occur by a slightly different process. The process of adsorption changes from endothermic to exothermic over a relatively small change in surface coverage. Here it is proposed that before intercalation can occur the clay lattice must undergo expansion to accommodate the adsorbate molecules, and the work involved in carrying out such a process is in excess of that liberated by adsorption. Once the expansion has occurred to the minimum critical distance, the amount of interlayer surface greatly increases and adsorption of the phenol can then proceed as for dodecylammonium bentonite.

1.5.2.1.3 Adsorbate functional group and its effect on adsorption

Further investigations into the adsorption of a variety of organic compounds by octadecyltrimethylammonium-montmorillonite, were undertaken by Street and White 1963⁵². The variety of compounds reflected differences in functionality. The

presence of the phenol group and the decrease in solubility of the compounds in water were observed to enhance adsorption; acidity/basicity did not noticeably effect adsorption. No relationship was found between adsorption and functional group. The final basal spacings do not reflect the extent to which adsorption has occurred. It was suggested that the orientation of aniline in the interlayer region was perpendicular to the silicate layer because a large basal spacing was observed for the adsorbent-adsorbate system. The quaternary ammonium cations were thought to remain parallel to the silicate throughout the adsorption process.

1.5.2.1.4 The thermodynamics of adsorption

The entropy change ($-\Delta S_m$) for the adsorption processes involved in the adsorption of phenols by n-primary amine modified clays, was found to become more negative with increasing amount of amine present on the clay surface, Cowan and White⁴⁹. The greater the amount of amine present, the less space there is available for bifunctional adsorption of the phenols and hence the more ordered such molecules are when adsorbed. More dilute solutions of phenol were observed to give a greater entropy change on adsorption.

In the adsorption of phenols by tetradecylammonium and dodecylammonium exchanged bentonite the partial molar heats of adsorption were found to be proportional to ammonium ion content at high levels of phenol adsorption⁵¹. This leads to the conclusion that the ammonium cations are sites for adsorption. The paper unfortunately had no XRD data to confirm these theories.

Another important factor that may affect adsorption is solubility. Adsorption has been shown to be inversely proportional to solubility⁴⁸. An adsorbate having little or no affinity for a particular solvent and greater affinity for an adsorbent will be adsorbed to a greater extent than another adsorbate showing greater affinity for the same solvent. However, for the adsorption of hydroxymethylbenzenes and dihydroxybenzenes by dodecylammonium exchanged bentonite, no link between solubility of the adsorbate and adsorption is observed and it was concluded that the solubility effect is overridden by bonding and steric factors⁴⁹.

1.5.2.2 Modern concerns regarding water quality and the adsorption of organic compounds by ammonium modified clays from aqueous solution

1.5.2.2.1 Selectivity

In spite of the work of Cowan et al. and Street et al., outlined above, bentonite had limited use, unmodified, as a coagulant in the purification of water and waste water. Bentonite was investigated specifically to adsorb organic compounds from water supplies. It was the work of McBride et al.², that revitalised the work of the sixties, though no doubt the rise of concern in the state of water supplies had a major part in initiating these studies. These studies, as in those of Cowan and White, involved the modification of clays to enhance adsorption of organic compounds from water supplies. McBride et al. showed that different clay-organic complexes have widely varying adsorption properties for benzene, phenol, and chlorobenzenes. McBride et al. demonstrated that adsorption onto tetramethylammonium (TMA) exchanged smectites is greatly favoured by small planar molecules (phenol, benzene) but not by the larger chlorinated benzenes. The interactions occur via π electron interactions with the silicate oxygens. TMA cations are small rigid tetrahedra that do not occupy significant space in the interlamellar regions of the clay, i.e. a significant amount of the silicate surface remains exposed. The larger hexadecyltrimethylammonium (HDTMA) cations are able to adsorb the chlorinated benzenes. Results suggested that the chlorinated benzene molecules are too large to enter into the interlamellar regions of the TMA clay, and that sorption may only occur because of the additional swelling afforded by the HDTMA cations. Therefore tailoring may be designed to accommodate the steric nature of a given pollutant, while eliminating the adsorption of non-targeted compounds.

Studies by Stul et al.^{53,54} suggested that in the adsorption of alcohols from dilute solutions by primary quaternary ammonium cation exchanged clays, the process closely parallels that of the partitioning between organic solvent and water in bulk solution. It was proposed that hydrogen bonds form between the OH group of the alcohol and the NH_3 group of the quaternary ammonium cation. The alcohol appeared to adsorb principally by displacement of water from the clay mineral surface. Association between alcohol molecules is also observed in these systems.

Wolfe et al. 1985⁴² studied alkylammonium systems for adsorption of mixtures of organic pollutants. The ammonium compounds investigated were dodecylammonium, which proved a good adsorbent in the work of Cowan⁵¹; dodecylidiammonium, due to the formation of pillars with mica-type clays reported by Weiss⁵⁵; and

propylammonium, which yields relatively large free interlamellar volumes when exchanged with montmorillonite, Barrer and Millington 1967³⁷.

With dodecyldiammonium-montmorillonite no adsorption of the organic compounds was observed. The cation appeared to bind the clay layers together and prevent expansion. At high organic concentrations the dodecylammonium cations 'dissolved' in the pollutant and oriented perpendicular to the silicate surface, thereby helping to expand the clay layers and expose the silicate surfaces for adsorption. At low concentrations of pollutant the propylammonium montmorillonite had a larger free interlayer volume and thus became the better adsorbent. Overall the ammonium salts of straight chain hydrocarbons selected by Wolfe et al. did not significantly improve the adsorptive capacity of natural montmorillonite. The relatively poor performance of these tailored clays may be explained by the tendency of the flexible hydrocarbon end of the ammonium salts to lie flat along the interlamellar plane. The adsorptive capacity of the tailored clay is thus reduced by the obstructions created by the hydrocarbon chains.

The tailoring of clays for adsorption of specific molecules was again exemplified by Mortland et al. 1986⁵⁶. Adsorption isotherms were obtained for phenol and a series of chlorinated analogs adsorbed onto quaternary ammonium exchanged clays of varying hydrophobicities from both aqueous and hexane solutions. Organo-clays with relatively high hydrophobicities (hexadecyltrimethylammonium and hexadecylpyridinium exchanged montmorillonites) adsorbed phenols from water in proportion to their solubilities, which can be interpreted as a measure of their hydrophobicities. Thus adsorption increased phenol < chlorophenol < dichlorophenol < trichlorophenol. The isotherms obtained also reflected an increase in adsorbate-adsorbent interaction with hydrophobicity. For the less hydrophobic Quat-clays, trimethylammonium-, and tetramethylammonium-montmorillonite, phenol was adsorbed but the interaction was typical of weak adsorbate-adsorbent interactions. The two Quat-clays, containing relatively small cations, do not cover the interlayer surface of the clay mineral. It is possible that the now partially hydrophilic and partially hydrophobic clay was only able to adsorb compounds with similar properties. The size and shape of the phenol and chlorophenol was also suggested as a factor that may affect adsorption, where interlayer adsorption occurred.

1.5.2.2.2 Comparison with granular activated carbon

Work by Cadena and Jeffers¹ emphasised the importance of a water miscible, inexpensive and non-toxic ammonium cation to be added to the clay. In their studies of adsorption by TMA-smectite, results were compared with the industrial adsorbent granular activated carbon, GAC. The rate of adsorption and effect of pH was also studied. The selectivity of TMA-smectite may present the greatest asset of tailored clay adsorption; GAC has not proved as effective with respect to selectivity. However, the adsorption capacity of GAC is greater than that of TMA-smectite. TMA-smectite is highly selective for benzene, while adsorption of the methylbenzenes is several orders of magnitude lower than for those of benzene. TMA-montmorillonite removes benzene from solution at a faster rate than GAC due to the large number of particles present in clay suspension. The variation in adsorption over the pH range expected from natural waters is minimal.

1.5.2.2.3 Hydrophobicity

In a similar study to that of Mortland et al. 1986, Boyd et al. undertook a study of the effect of hydrophobicity on the adsorption of pentachlorophenol⁵⁷. The study involved quaternary ammonium cations with a range of hydrophobicities: those with high hydrophobicities such as dioctadecyldimethylammonium (DODMA) and HDTMA and those with low hydrophobicities, for example TMA. Pentachlorophenol is relatively hydrophobic and was adsorbed by the more hydrophobic Quat-clays, i.e. DODMA and HDTMA exchanged clays. The mineral surface is obscured by these large cations. The adsorption process for the more hydrophobic clays was described as a partitioning of the pentachlorophenol between the water and hydrophobic environment provided by the alkyl groups, which may be envisaged as a bulk organic solvent like hexane or octanol. Similarity between the organic matter partitioning coefficient and the octanol water partitioning coefficient substantiated the partitioning theory. The use of smaller organic cations which are less hydrophobic, leave mineral surfaces exposed. The mineral surfaces are occupied largely by water. Pentachlorophenol is not capable of displacing water from the mineral surface and the organic moieties resulting from the presence of the small TMA cations do not act as an effective partitioning medium for pentachlorophenol.

1.5.2.2.4 The effect of clay layer charge and aqueous media on adsorption

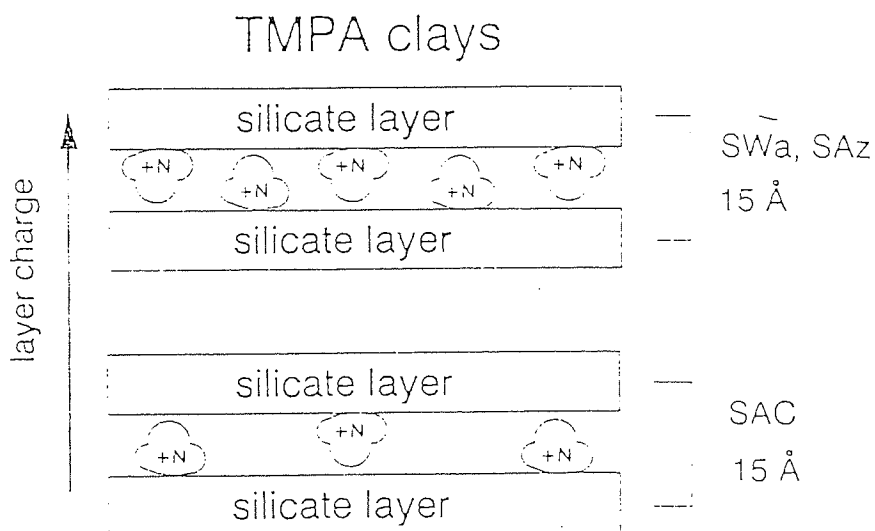
Lee et al.⁵⁸ made direct comparisons between adsorption of benzene, toluene, and o-xylene vapours by dry tetramethylammonium-smectites (TMA-smectites) and adsorption as solutes from water by wet TMA-smectites. The effect of clay layer charge on adsorption was investigated by using a high charged clay - Arizona smectite and a low charged clay - Wyoming smectite to produce the TMA-smectites. On exchange, the arrangement of the TMA cations in the interlayer region of the high charged smectite will expose less of the silicate surface to the adsorbate species than in the case of the low charged smectite. This is due to the fact that in the original clays, the low charged smectite contained a lower proportion of exchangeable cations than the higher charged clay. Therefore on exchange the interlayer can be envisaged as being more crowded in the high charged clay, reducing the possibility of other species to interact with the silicate surface. This work gave a clearer indication of the factors affecting adsorption.

Adsorption of organic vapours by the TMA-smectite was strong due to interactions with both the aluminosilicate mineral surfaces and the organic moieties of the TMA cations in the interlayers. The organic molecules arrange themselves in either a tilted orientation or one parallel to the silicate layer. The free mineral sites are preferred over smaller sites where the organic may have to orient in a tilted fashion with less favourable energetic interactions. As the molecular size of the adsorbate increases, the molecule may be forced to take up a more vertical orientation. Such steric constraints lead to lower overall uptake. The closer packing of the TMA cations in the high charge exchanged clay lead to the low charge exchanged clay exhibiting greater adsorption capacities, due to possessing greater free mineral surface area than the high charge clay.

Comparison of adsorption from the vapour and aqueous phase indicated that the hydrated samples had lower adsorption capacities. This probably resulted from hydration of the TMA cations or the silicate mineral sites in the interlayer region. Hydration occurring in the free mineral sites would leave only the TMA sites for the adsorption of benzene, or the hydration of the TMA cations would leave only the clay surface sites available for adsorption, either or both result in reduction of organic molecules adsorbed. This hydration would also occur, in addition to the reduced free mineral site already present, in the high charge clay, and thus adsorption by this clay is further reduced.

Competitive adsorption between benzene and toluene onto TMA-smectite (low charge) indicated that benzene was able to compete effectively with toluene for adsorption sites, but toluene was unable to do so with benzene. This suggests that the adsorption of toluene was restricted because benzene preferentially occupied the interlamellar regions of the clay. Possible reasons for this were not discussed.

Although much work has been in the field of adsorption of organic compounds onto clays, and many isotherms obtained, the nature of the adsorptive interaction was, and to a certain extent, still is poorly understood. A step forward was made by Jaynes and Boyd 1991⁵⁹ when they undertook the investigation of the nature of the adsorptive interaction of aromatic hydrocarbons with trimethylphenyl-smectite, TMPA-smectite. TMPA-smectites derived from smectites of different charge densities, resulted in TMPA-smectites with different TMPA contents (Figure 1.12).

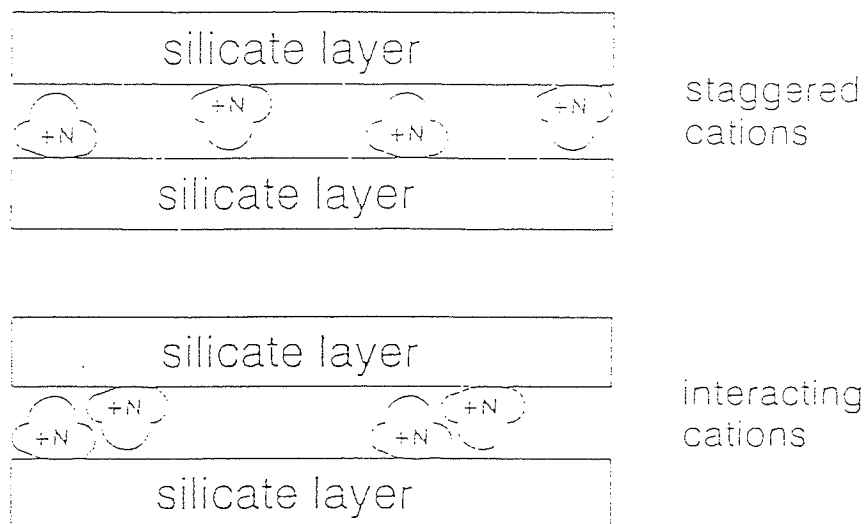


The upper diagram shows the possible arrangement in a high charged clay, the lower the possible arrangement in a low charge clay.

Figure 1.12 TMPA cations arranged in the interlayer region of clays with different layer charge, after Jaynes and Boyd⁵⁹

Benzene, toluene, ethylbenzene, propylbenzene, and butyl benzene and naphthalene uptake from water by the TMPA-smectites yielded Langmuir or type I isotherms. The amount of organic adsorbed was inversely proportional to layer charge and TMPA content and directly proportional to surface area. This suggests that adsorption occurs at the interlayer siloxane surface of the mineral and that the TMPA simply acts to pillar the clay, propping the layers open. The replacement of TMPA cations in the interlayer region controls the size of the adsorptive sites. Arrangement of the TMPA molecules in the interlayer region may occur in a different way to that postulated by Barrer and

Perry⁶⁰. It was suggested that the TMPA cations may interact via π - π interactions of the phenyl groups, allowing more siloxane surface for adsorption (Figure 1.13). Evidence for adsorption via interactions of the planar surface of the adsorptive molecule and the clay surface was obtained, in that as the planar area of the adsorbed molecule increased, the clay surface area occupied by each molecule also increased. The preferential adsorption of hydrophobic organic molecules from water demonstrates that the siloxane surfaces are hydrophobic in nature.



The interactions between interlayer organic cations and the size of adsorption sites as postulated by Barrer and Perry (upper diagram), and as postulated by Jaynes and Boyd (lower diagram).

Figure 1.13 The interactions between interlayer organic cations and the size of adsorption sites.

The partitioning behaviour of HDTMA-clays was further investigated by testing the effectiveness of clays with different charge densities as sorbents of alkylbenzenes (Jaynes and Boyd 1991⁶¹). Adsorption increased with basal spacing and organic carbon content. These properties result from the closer packing of the HDTMA in the high charge clays. Due to more cation exchange sites present in the high charge clays, a greater concentration of HDTMA will be present and the cations will arrange themselves in a position almost perpendicular to the silicate layers Lagaly 1982⁶². This is in contrast to the work with the more compact organic cations that expose mineral surfaces and adsorb via those surfaces.

1.5.3 Adsorption of inorganic compounds from aqueous solution

To date investigations of the adsorption of inorganic compounds from aqueous solution by montmorillonites modified or not, has not been published in the literature. The only inorganic molecules studied have been those involved in the investigation of interlayer cation effects on the properties of clays. This has been briefly described in section 1.3.4.

1.6 Industrial applications of clays

1.6.1 The industrial use of clay minerals

Clays are an essential component of soils, to which we owe our survival. They are also the raw materials for some of mankind's most ancient and essential artefacts: pottery, bricks, tiles etc. They are formed by the weathering and decomposition of igneous rocks and occur typically as very fine particles.

China clay or Kaolin, which is predominantly kaolinite, is particularly valuable because it is essentially free from iron impurities and therefore white. In 1974 approximately half of the world's production of kaolinite was used for paper filling or paper coating, and one-quarter was used for various fire-bricks and refractories. When kaolinite is mixed with a small amount of clay-mica and quartz, a fine-grained, highly plastic material is produced. This material is known as ball clay and is used for production of china, crockery, earthenware, tiling, sanitary ware and electrical porcelain.

Properties of muscovite mica include perfect basal cleavage, toughness, elasticity, transparency, high dielectric strength, chemical inertness, and thermal stability to 500 °C. Sheet mica is used for furnace windows, for electrical insulation (condensers, heating elements), and in vacuum tubes. Some uses for ground mica are as fillers for rubbers and plastics; and for insulating boards.

Talc, unlike the micas, consists of electrically neutral layers without the interleaving cations. It is valued for its softness, smoothness, and dry lubricating properties, and for its whiteness and chemical inertness. Its most important applications are in ceramics, insecticides, paints and paper manufacture, cosmetics and toilet preparations.

1.6.2 Uses of smectite clays

Smectites can be divided into three groups with regard to commercial usage; sodium smectites, calcium smectites and fuller's or acid earths. The largest users of smectite clays have been the foundry, oil well drilling and iron ore pelletising industries.

Fuller's earth is a calcium montmorillonite. The name derives from its early use (Cyprus - 5000 BC) for the fulling or cleansing of woollen cloth from its natural oils and greases. It has a high absorptive and adsorptive capacity, and pronounced cation exchange capacities which allow it to be converted to sodium montmorillonite (bentonite). It is used mainly as an oil and grease absorbent and as pet litter.

Bentonite (sodium-montmorillonite) is extensively used as a drilling mud. This application is based on the thixotropic properties of its aqueous suspensions. Thus, replacement of Ca for Na in the montmorillonite greatly enhances its ability to swell in one dimension by the reversible uptake of water; this effectively cleaves the clay particles causing a separation of the lamellar units to give a suspension of very finely divided, exceedingly thin plates. These plate like particles form a gel with thixotropic properties. This thixotropy is widely used in civil engineering applications, in oil-well drilling, and in non-drip paints. Many types of organic and inorganic additives are used to improve or regulate the properties of drilling muds, the effectiveness of which depends on the surface, colloidal and ion exchange properties of the smectite clays used.

The plasticity of bentonite is also used in mortars, putties, and adhesives, in the pelletising of iron ore, and in foundry sands. In terms of annual tonnage the major use of smectite clays is in foundry moulding sands. Smectites are mixed with sand and water to make the sand plastic and cohesive so that it can be moulded. The smectite clay must give the sand sufficient strength to maintain the shape of the cavity before, during and after the pouring of the hot metal into the mould.

Calcium smectite clays that have been acid treated, and Fuller's earths, are used for the filtration of animal and mineral oils and greases; for decolourising vegetable oils; and sodium smectites are used for clarifying wines, beers and fruit juices.

Small volume uses include atomic waste disposal, emulsifiers, inks, paints, catalysts, soaps, ceramics, and water clarification.

1.6.3 Uses of organophilic clays

Organophilic clays find a diverse range of applications in, for example, cosmetics, inks, polishes, chromatography, dispersions of hydrophilic polymers in oil, and catalysis. For practical and industrial uses quaternary alkylammonium cations are preferred to primary alkylammonium cations because effects due to hydrolysis - alkylammonium/alkylamine equilibrium - are absent, and desorption of free alkylamine is strongly reduced. The four areas of largest application are drilling fluids, paints, greases and fibreglass resins.

Drilling fluids remove drill cuttings, stabilise the hole, prevent blow outs, support the drill string and casing, transmit hydraulic power to the bit, and lubricate the drill string and bit. Drilling fluids are usually water-based, but oil-based muds are being increasingly used for use in water sensitive formations, in soluble salt formations and at high temperatures as they offer additional protection from corrosion and are reusable. A good organo-clay mud will help to stabilise the water/diesel oil/organo-clay emulsion; render the cuttings wettable; provide stable rheological and colloidal properties up to depths of 5000 m where the pressure could be 10^8 Pa and the temperature 230 °C.

In paints, organoclays play a vital role in stabilising the colloidal system by preventing pigment settling, reducing separation of liquid components, enhancing application properties and controlling absorption into porous substrates. The thixotropic properties of the paint can be accurately controlled by adjusting the type and quantity of organoclay. During application the high viscosity falls rapidly, enabling a thin film to be readily formed. Once applied, the film must regain viscosity sufficiently rapidly to minimise sagging, but not so rapidly that brushwork imperfections do not smooth out.

Greases are lubricating oils which have been gelled. The gelling agent - an organoclay- serves to increase the apparent viscosity of the oil and make the oil into a thixotropic fluid, this property being essential for the application.

Fibreglass resin is a 50 wt% solution of low molecular-weight unsaturated polyester in styrene. By adding an initiator and catalyst, the styrene cross-links the polyester to give a tough thermoset plastic. The liquid resin needs to be thixotropic in order to suspend additives and fillers during prolonged storage; prevent separation of fibreglass while the resin is curing; prevent sagging while the resin is curing on an inclined mould; enable easy pumping and spraying of the liquid resin. Fumed silica is the most

widely used thixotropic agent, but recent advances in organophilic clay technology have seen increasing use of clay-based thixotropes for this purpose.

1.7 Water pollution and current methods of treatment

1.7.1 Water Pollution

Water pollution results from both natural phenomena and man's activities. Pollution can be classified by four categories⁶³: chemical, physical, physiological and biological. Biological forms of pollution include vectors of water-borne diseases (for example virus, bacteria, protozoa) and biological growths caused by the discharge of waste materials into water (for example excessive growths of algae on waste discharges which contain nutrients).

Colour, turbidity, temperature, suspended solids, foam and radioactivity come under the category of physical pollution.

Examples of physiological pollution are problems of taste and odour. Very small concentrations of substances can impart an undesirable taste to water. Chlorophenols, for example, can be tasted at a concentration of 0.001 mg/litre. Many of these taste and odour producing compounds have the ability to taint fish. Thus, a very small quantity of phenol in the water may completely eliminate the use of fish for food because of the bad taste imparted by the chemical.

Chemical materials that may be discharged into receiving water may be broadly classified into organic and inorganic pollutants. Discharge of inorganic materials can result in changes of pH caused by soluble salts or toxicity caused by heavy metals. The major consideration with respect to organic materials is the depletion of dissolved O₂ and its resultant effect on the biota. Biochemical reactions and the exertion of a BOD (biochemical oxygen demand) are the characteristics of organic wastes that are of significance to the O₂ balance in water. Other examples of the effects of organic material pollution which cause concern are oil and its tendency to form films; taste and odour producing substances such as phenols; compounds such as pesticides; and compounds that are known to restrict growth or cause death of fish and other aquatic life, yet their effect on humans is unknown.

1.7.1.1 Groundwater pollution

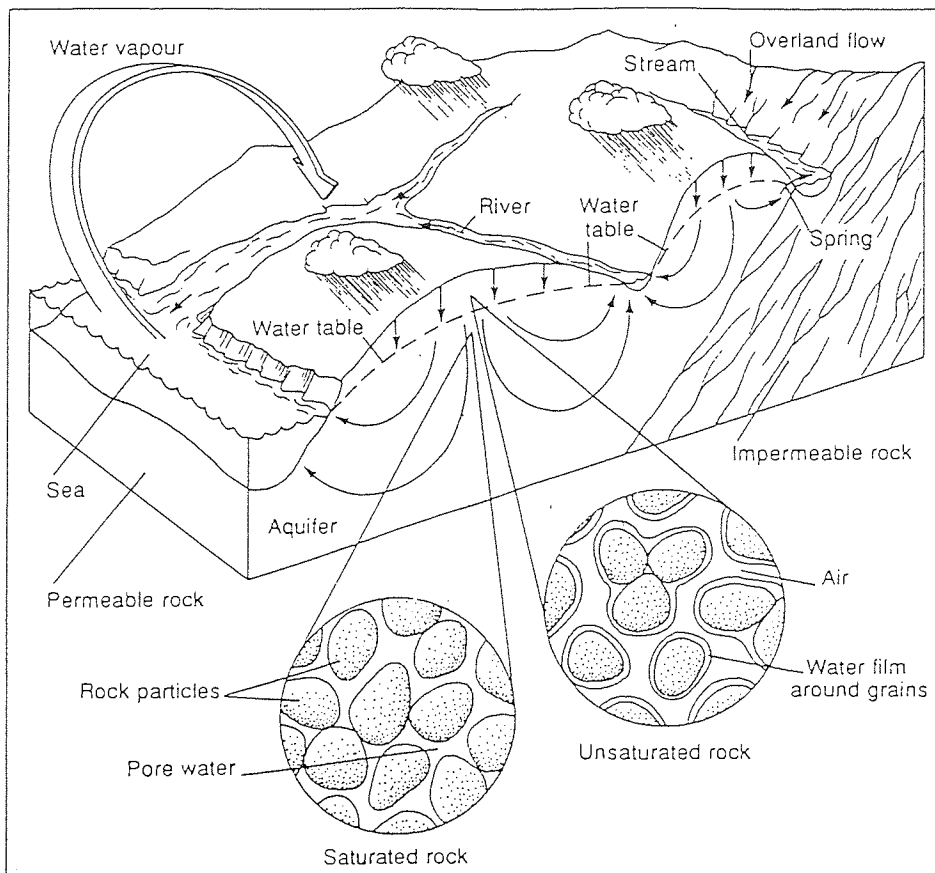
Groundwater is contaminated by a wide range of contaminants as a result of domestic and industrial wastes. Significant quantities of chemicals can reach the ground water in five different ways:

1. Seepage through unlined lagoons and other surface impoundments.
2. Improper landfilling. Organic chemicals and heavy metals have been detected at significant concentrations in the underlying soil and groundwater in close proximity to landfills.
3. Improper surface and subsurface disposal. This arises due to indiscriminant disposal of wastes into wells, pits, and abandoned mine shafts. This can lead to the elimination of vegetation and contamination of surface waters via runoff and/or direct discharges.
4. Leaks in pipes, process equipment and storage tanks.
5. Accidental spills.

In soil-groundwater systems, water is responsible for the transport of contaminants. The layer of soil near the surface is called the unsaturated zone. As its name suggests it is not completely saturated with water (the water present is often called soil water). Water transports the contaminant through the unsaturated zone towards the saturated zone (Figure 1.14). The upper surface of the saturated zone is known as the water table. The percolation rate is a function of the number and size of voids in the soil, i.e. the pore space. The percolation rate will vary as the soil layers change, a fine clay generally reducing percolation rate and a coarse sand increasing percolation rate. The percolation rate may also be affected by the presence of a contaminant.

An aquifer yields water from the unsaturated zone. There are two types of aquifer: confined (or artesian) and unconfined. The water table forms the upper surface of an unconfined aquifer, while an artesian aquifer is confined by a layer of relatively impermeable material (Figure 1.14). The ability of a geological formation such as an aquifer to store water is determined by porosity (volume of voids per unit volume - the greater the porosity the greater the water storage capacity) and permeability (the volume of water discharged per unit area per unit time) properties.

The concentration of chemicals in the groundwater may be reduced by various physical, chemical and biological reactions such as: adsorption onto soil surfaces, volatilisation from the soil, biodegradation, and chemical degradation. Adsorption in this case refers to the accumulation of a contaminant at the surface of soil particles. The degree of adsorption and type of chemical interaction depends on the chemical



Overhead and underfoot: water soaks into the ground to collect within an aquifer, where the rock is permeable. When the pores are full, the rock is saturated

Figure 1.14 The water cycle - a detailed diagram of the paths of water in the ground. After Price⁶⁴

properties of the contaminant and the composition of the soil (the organic matter and clay content of the clay are particularly important). Volatilisation from soil is not restricted to volatile compounds. The volatilisation rate will be dependant upon vapour pressure and water solubility. Biodegradation occurs by the breaking down of organic compounds with micro-organisms. These micro-organisms are capable of converting contaminants into inorganic substances such as CO₂, H₂O and mineral acids. Chemical degradation results from chemical reactions such as oxidation, hydrolysis and reduction. Adsorption or the presence of clay minerals may effect the rates of these reactions. Clays are well known as catalysts and the immobilisation of a contaminant may facilitate reactions. Degradation will vary with pH, soil composition, presence of iron and aluminium oxides, presence of metal cations, soil moisture and temperature.

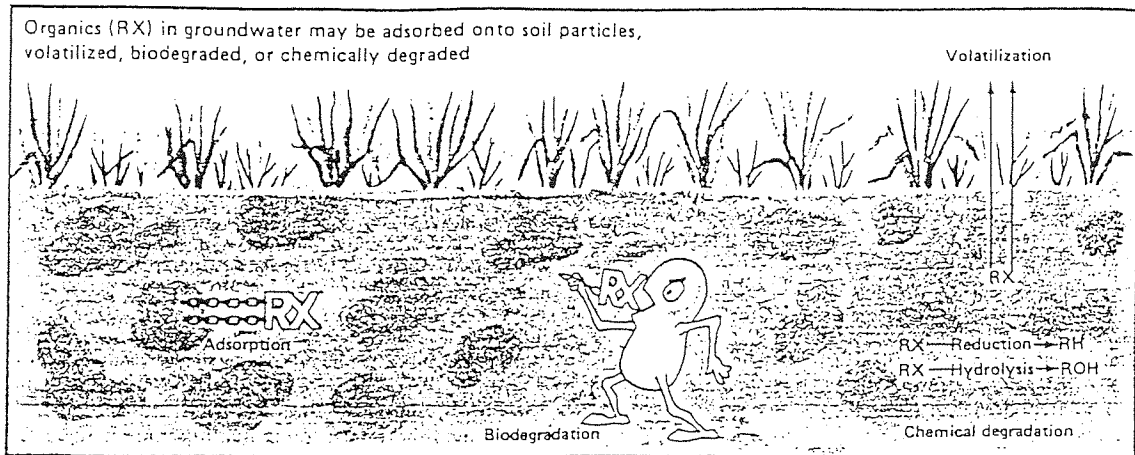


Figure 1.15 The fate of contaminants on exposure to land. After Dragun et al.⁶⁵

1.7.1.2 Hazardous wastes

Hazardous wastes are not clearly defined and a uniform definition has not been obtained throughout the EEC. In the UK they are defined as special wastes but include other chemicals in the category of difficult wastes.

Special wastes are defined as those which may be difficult or dangerous to dispose of because of their physical and chemical characteristics. These wastes are either medicinal products available only on prescription, or materials listed as being dangerous to human life, or having a flash point of 21 °C or less⁶⁶.

Difficult wastes, is a term introduced by Waste Management paper number 26⁶⁷ which sets out a long list of wastes covering all special wastes under the 1989 regulations and includes other wastes. The term is "...used to include wastes which would in certain circumstances be harmful in either the short or long term to the environment. It also includes wastes whose physical properties present handling problems."⁶⁸

Primary sources of hazardous waste are shown in Table 1.1

Table 1.1 Primary sources of hazardous waste

Source	Example
Industrial	chemical manufacturing, manufactured products, formulating, extractive industries (mining, oil/gas production)
Municipal	waste treatment facilities, power generation
Hospital	infectious and biohazardous
Reclamation	land and buildings
Nuclear	
Agricultural	

In 1979 the U.S. Environmental Protection Agency (E.P.A.) compiled a list of 129 priority pollutants frequently found in industrial waste waters and the number of primary point sources (that is, industries) contributing to the presence of a particular pollutant in the waste water⁶⁹. The priority pollutants were divided into nine groups: metals, asbestos, total cyanides, pesticides, compounds extracted under acidic conditions, compounds extracted under alkaline conditions, neutral extractable compounds, total phenols, and purgeable compounds. They were grouped as such to develop sampling and analytical experiments.

1.7.2 Current methods of treatment and/or disposal

In dealing with hazardous wastes the following processes must be considered: generation, storage, treatment, disposal and transportation. Methods of treatment and disposal will be discussed herein.

1.7.2.1 Methods for disposal

The method chosen for final disposal will be affected by the type of material under consideration. The material must be thoroughly evaluated before and after treatment so that its hazardous and non-hazardous (toxicity, flammability, corrosivity, reactivity, radioactivity, persistence), and physical-chemical properties (pH, solubility, volatility, physical form, vapour pressure, reactivity, thermal stability, decomposition properties) are understood in order to reach a decision for final disposal. Factors such as availability, geographic, transport, economic must also be considered.

Options for disposal (disposal of the final material) include landfills, secure landfills (burial), ocean dumping, underground injection and natural storage areas (caves, shale beds). Associated with these options are specific technical considerations, such as waste solidification and containerisation, containment techniques, monitoring, and sampling. Local, geographical and hydrological considerations include position of a landfill in relation to aquifers. There is escalating cause for concern over the contamination of ground water supplies with regard to landfill disposal.

1.7.2.2 Landfill and leachates

Landfill - the disposal of waste in the ground - is the predominant method of disposal in the UK. Over 90% of the total quantity of controlled wastes is disposed of in this way, either directly or after some form of pre-treatment. 70% of chemical industry's waste is disposed of in this way. The UK is fortunate in that the many clay and other mineral extraction sites are particularly suitable for landfill. However, the difficulty in obtaining such sites increases as environmental awareness grows⁶⁶.

Co-disposal involves the joint deposition of industrial and household wastes. It aims to use the natural bacteriological and chemical mechanisms involved in the degradation of domestic wastes to aid the subsequent breakdown of the industrial materials. The UK is practically alone in its use of this method of disposal. The method of co-disposal has been said to eventually render hazardous wastes as safe; the method is economically viable and there is no evidence of groundwater pollution. Arguments against this method are lack of study of the method, especially regarding environmental impact; co-disposal has the potential to spread contamination over a large area; and while it has been accepted that this method works for certain mixes of waste, inadequate work has been carried out to determine the capacity of a landfill to cope with and treat specific wastes and hence to make co-disposal work in practice. Unfortunately there has been a failure to follow Her Majesty's Inspectorate of Pollution guidelines for co-disposal at all landfill sites⁶⁶.

In the USA, co-disposal of hazardous wastes is not permitted, and hazardous wastes are normally landfilled, after treatment, in containment landfills designed to be totally secure.

1.7.2.2.1 Environmental impact of landfill

There is evidence that a large number of landfill sites, mainly the older ones, cause local contamination of the groundwater around them. Once contamination of the

groundwater has occurred it is rarely possible to rehabilitate the resource and landfill sites are the most significant threat to groundwater for some authorities. Environmental monitoring at many sites is currently inadequate.

The gradual absorption of water by solid wastes in landfills occurs until the absorption capacity of the waste is exceeded. Any further additions of water result in the release of leachate. Contamination occurs due to the generation of leachate. Leachate is a liquid derived from water contained within or which comes into contact with a waste body⁷⁰. It contains suspended solids, the soluble components of waste and the soluble products of the degradation of the waste. The composition will vary with the stage that the degradation process has reached and the type of waste in the site. The degradation of waste can be divided into three broad phases:

1 The initial decay process. Aerobic decomposition occurs readily due to the presence of trapped air in the waste. Eventually anaerobic decomposition takes over as the oxygen supply becomes depleted. Carbohydrates, for example are hydrolysed and then fermented producing organic acids. The leachate from this decay process therefore contains high levels of organic acids, it has a low pH, it will contain ammonium ions derived from the breakdown of nitrogen compounds, and chloride ions.

2 The methanogenic phase. The organic acids formed in the initial decay process are broken down into methane and carbon dioxide which are evolved as landfill gas. The relative ammonia concentration increases as nitrogen compounds continue to be degraded and the chloride levels tend to remain constant.

3 The post-methanogenic phase. After methanogenesis has effectively ceased the leachate components will be the same as those in the methanogenic phase but the concentrations will have significantly decreased. Biological processes will have stopped and any principal changes will be due to dilution from infiltration. The degree of infiltration will depend on the quality of the lining and capping.

Leachate composition will vary from site to site depending on the composition of the landfill and the amount of water contained within, or coming into contact with, the waste and the decay time. Constituents of leachate include organic, ammonia, chloride, metallic and sulphate compounds; red list substances and dissolved gases.

The organic carbon compounds present in the leachate have significant effects on watercourses where the compounds are broken down aerobically causing dissolved oxygen levels in the watercourses to fall and threaten the water ecosystem. The amount of organic carbon present in the leachate will affect the method of treatment and suitability of the leachate or effluent for discharge into the watercourse. Ammonia is

toxic to fish and is not discharged into surface water bodies other than in very low concentrations.

Leachate contains many simple ions of which chloride is in highest concentration. This causes a problem to aquatic species and can be prejudicial to other water uses. Leachate often contains low levels of sulphate. The major problem is the reduction to hydrogen sulphide, a toxic gas with an all too distinct odour.

During the methanogenic stage landfill conditions result in heavy metals being insoluble and therefore levels of dissolved metals being low. High concentrations of these metals can be toxic to many organisms. Red list substances are known for their toxicity and persistence in the environment. Substances in this list include organochlorine pesticides, mercury and cadmium.

Examples of dissolved gases include methane, carbon dioxide, and hydrogen sulphide. These are generally removed using an aeration process to prevent build up of explosive, asphyxiating or toxic gases in the sewer. Landfill gas is a major pollutant problem associated with domestic waste. In 1986 a house was blown up at Loscoe in Derbyshire by gas which had migrated from a landfill. 700 - 800 landfill sites are close to housing and require urgent attention because of methane gas generation. Landfill gas problems are associated mainly with older sites, especially those which have closed down. Modern private sector landfill sites are constructed with internal piping for collecting and venting methane gas in a controlled manner, and the gas collected is, in some cases, used to produce electricity.

There has been a general trend towards operating landfill sites on the basis of containment to prevent leachate polluting groundwater and also to avoid problems of landfill gas migration. Creating a site with a high degree of containment, however, results in the accumulation of leachate at the base of the site. As the level of the leachate builds up the "head" of liquid increases and there is an increased risk of leakage. In addition, gas extraction becomes more difficult as the depth of the unsaturated waste layer decreases. Hence there is a need to minimise the volume of leachate produced by diverting any groundwater which may enter the site, by diverting surface waters and reducing the ingress of rainwater; and/or to remove the leachate from the base of the site and to treat or dispose of it in an environmentally acceptable way⁷⁰.

1.7.2.3 Methods for pre-treatment

Prior to final disposal, waste, or leachate removed from landfills via drainage systems, may undergo pre-treatment. The treatment systems are split into three main stages, primary treatment, secondary treatment and tertiary treatment. The choice of treatment method will be dictated by the material to be disposed, availability of treatment (which tends to demand the consideration of transport costs) and the availability of secure dump sites.

Primary treatment is designed to pre-treat waste or leachate in preparation for a secondary treatment process. The treatment is normally adequate to allow discharge to sewer but not for discharge into a watercourse. Methods include solids settlement, holding/mixing lagoons and aeration. Secondary treatment is designed to achieve a second stage reduction in waste or leachate concentrations by further removal of contaminants, usually by biological methods. The constituents and concentrations of the resulting waste will determine how the waste will be discharged. Tertiary treatment is designed to improve the quality of the waste so that it is suitable for discharge or disposal. Tertiary methods are listed in Table 1.2

1.7.2.3.1 Recover/recycle/reuse

Recover/recycle/reuse includes the recirculation of leachate whereby the landfill acts as an anaerobic bioreactor and further decomposes the leachate. Another method is that

Table 1.2 Tertiary treatments used in Waste management

Method	Example
recover/recycle/reuse	
thermal treatment	incineration
chemical/physical	neutralisation, precipitation, ion exchange, hydrolysis, oxidation / reduction, flocculation, activated carbon adsorption, dialysis, evaporation, reverse osmosis, ammonia stripping
biological treatments	biodegradation using micro-organisms
solidification/stabilisation	using cements or resins to fix pollutants

of spray irrigation of grassland and woodland. This method is not widely practised but involves the use of low strength waste or leachate with high nitrogen:carbon ratio. 'Treatment' occurs in the upper horizons of the soil where the waste may evaporate or precipitate; be 'sorbed' or oxidised; undergo ion exchange, nitrification, denitrification or be taken up by plants. The waste moves through the soil towards groundwater in the way described in Section 1.7.1.1, and it is therefore important that an aquifer is not in close proximity to the site chosen.

1.7.2.3.2 Thermal treatment

Thermal treatment involves the pyrolysis or incineration of waste to reduce detoxification and/or volume. This process can be used for organic chemicals and heavy metals.

1.7.2.3.3 Chemical/physical treatment

Chemical/physical treatments usually involve the injection of a substance that will degrade or immobilise the contaminants. The most effective use of this treatment is where there are a few compounds with similar chemical characteristics. Treatment suitable for one type of waste may not be suitable for another and thus a combination of treatment may be needed. Such processes result in separation, volume reduction and in the case of chemical processing, detoxification. Organic and inorganic chemicals and heavy metals can be treated in this way.

Activated carbon adsorption involves the exposure of waste to carbon which has been produced as a porous, high surface area solid. Contaminants within the leachate are adsorbed by the carbon. The carbon needs to be regularly replaced. The disposal of the carbon and effluent is at present being addressed as the cost of the process is high. The process is well suited for the removal of organics, especially non-volatile organics which are difficult to remove by air stripping. At best, adsorption can achieve 99% removal of the organic contaminants but the costs of the process do not always make the use of the process viable.

1.7.2.3.4 Biological treatments

Biological treatments create conditions suitable for sufficient microbial activity to degrade contaminants to less toxic products. The technique is most efficient for the treatment of organic chemicals.

1.7.2.3.5 Solidification/Stabilisation

Solidification/ Stabilisation involves the mixing of wastes with materials to produce a strong, impermeable solid. This method is widely used for the pre-landfill treatment for *inorganic* hazardous wastes. It is especially useful in situations where the chemical detoxification of a hazardous waste stream is either not possible or prohibitively expensive. It involves mixing liquid or semi-solid wastes with binders to produce a solid which is structurally sound and relatively impermeable. Binders often consist of ordinary portland cement (OPC) or OPC with fly ash, kiln dust, other pozzolanic and industrial by-products. Sometimes polymers are used. The aim is to treat the waste stream so that it is safe for transportation, storage, burial, and to reduce mobility of the toxic constituents. The lack of interaction between the binders often used and the *organic* toxic compounds has adverse effects on cement hydration (see Section 1.7.2.4.3), microstructural properties and engineering properties, which renders this method inadequate for the disposal of waste containing organic compounds⁷¹⁻⁷⁴.

Recent work by Montgomery et al.^{72,73} has involved the enhancement of this technique using suitable additives to allow the treatment of inorganic wastes with organic components (up to 15% by volume) thus providing an alternative to the expensive aforementioned methods of pre-treatments and disposal. The additives used were quaternary ammonium ion exchanged clays, or Quat-clays. These were chosen as pre-solidification agents due to their ability to adsorb organic compounds from water, see Sections 1.4 and 1.5. Initial work⁷³ used Wyoming Bentonite clay exchanged with a quaternary ammonium salt to adsorb a range of phenols from an aqueous solution. The mixture was then solidified with OPC. Tests on the solidified samples showed that the Quat-clays provided an interface between the phenols and the OPC matrix, and enhanced retention of the phenols.

Subsequent work⁷⁴ involved the use of Quat-clays to adsorb/stabilise typical organic-contaminated industrial wastes, previously little work had been carried out on real wastes. The amount of organic compound adsorbed by the Quat-clay from each waste was determined. Varying mixes of waste, clay and OPC were developed to obtain the best range of mixes giving optimum waste retention on solidification. The Quat-clay adsorbed the organic constituents of the industrial waste very effectively. Solidification yielded an homogeneous solid with good structural properties and leaching of organics was low. Such results strongly suggest that there is great potential for use of this method in treatment of waste both as a pre treatment and as an in situ treatment of contaminated soils.

Soundararajan⁷⁵, investigated the solidification/stabilisation product by various analytical techniques. Evidence for interactions between various organic compounds and the clay component of the solidification/stabilisation material was put forward. DSC was used to investigate the ease with which vaporisation of the organics and decomposition of the matrix would occur. It was found that the ease of vaporisation was much more difficult on solidification, sometimes requiring twice the energy of vaporisation of the organic alone. When the waste was vaporised it was found to fragment or polymerise (as evidenced by GC/MS). Minimal leaching was observed for the investigated systems.

One disadvantage of this method of disposal was observed when Leigh Environmental's Sealosafe process, a method based on the solidification model, was used for disposal at a Walsall site in 1989. Some time after burial, the solidification agent was found not to have solidified⁷⁶ due to the presence of organic compounds.

1.7.2.4 Cements and the properties that influence solidification / stabilisation

For detailed background on cements and cement chemistry the reader is referred to general texts such as those by Czernin⁷⁷, Akroyd⁷⁸, and Taylor⁷⁹.

1.7.2.4.1 Background

Structural cement belongs to the class of 'hydraulic cements', or cements which harden by reacting with water and give a water-resistant product. Portland cement, aluminous cement and slag cement are typical of this class of hydraulic cements. The major constituents of hydraulic cements are CaO (lime), SiO₂ (silica), Al₂O₃ (alumina) and Fe₂O₃ (ferric oxide).

1.7.2.4.2 Portland Cement

When a mixture of lime and silica is heated in the presence of alumina and ferric oxide, tricalcium silicate is produced. On cooling the product solidifies into dark, stone-hard, dense lumps known as Portland cement clinker. The cooling process is rapid so as to produce a grindable product. Though the reaction described above is the main reaction which occurs, other products are produced. The main compounds entering into the composition of Portland cement are listed in Table 1.3

Table 1.3 The composition of Portland cement

Compound	Cement abbreviation	Formula	Percentage present
Tricalcium silicate	C ₃ S	3CaO.SiO ₂	54.1
Dicalcium silicate	C ₂ S	2CaO.SiO ₂	16.6
Tricalcium aluminate	C ₃ A	3CaO.Al ₂ O ₃	10.8
Tetracalcium aluminoferrite	C ₄ AF	4CaO.Al ₂ O ₃ .Fe ₂ O ₃	9.1

Minor constituents of Portland cement clinker include water and magnesium oxide. It is the presence of magnesium oxide that gives the cement its characteristic greenish-grey colour. Gypsum, CaSO₄, is added to portland cement for the purpose of regulating setting time. Alkalis present in Portland cement are represented as K₂O and Na₂O. Manganese and titanium are present in very low concentrations. A certain amount of unreacted calcium oxide will be present and as a result of this there will also be a small amount of calcium hydroxide. Below a certain concentration, the presence of each these constituents is harmless.

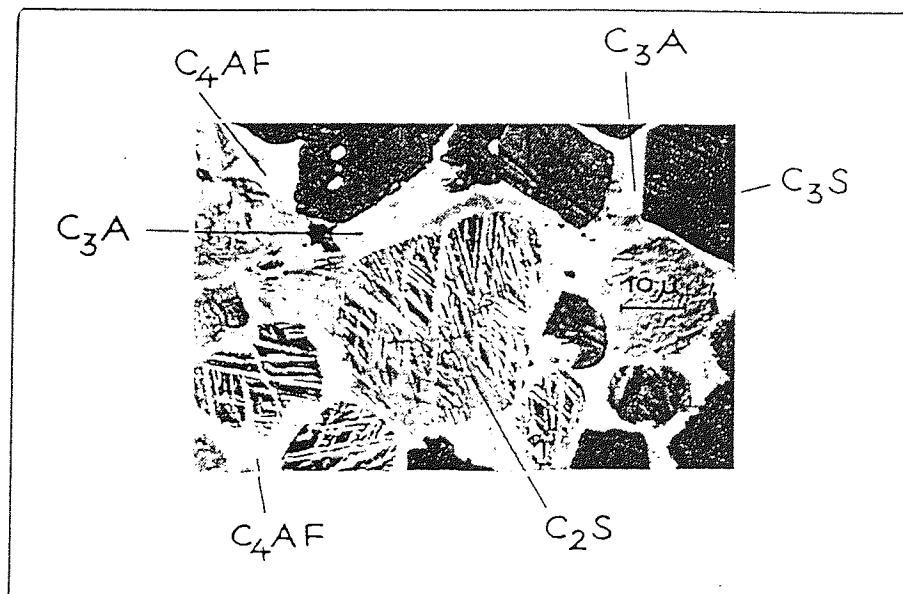
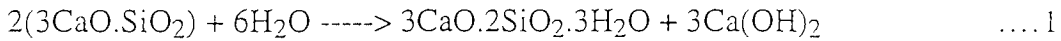


Figure 1.16 Etched Portland cement clinker. After Czernin⁷⁷

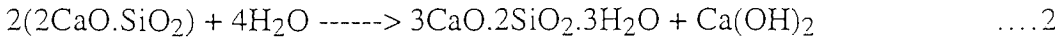
1.7.2.4.3 Hydration of Portland cement

Equations 1 - 4 describe the hydration process of Portland cement:

Tricalcium silicate



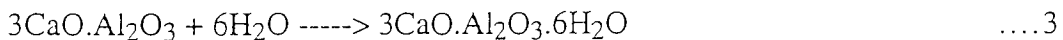
Dicalcium silicate



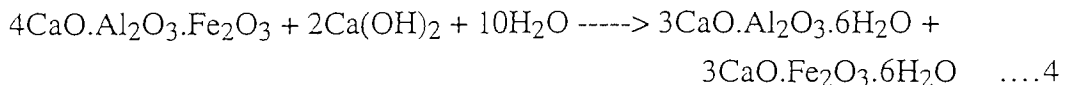
From both tri- and dicalcium silicate the final product of cement hydration leads to the formation of tricalcium disilicate hydrate. This colloidal compound is termed "tobermorite" because it is practically identical to the rare, naturally occurring mineral of that name.

The hydration process of the aluminate compounds is less well ascertained, but the product is known to be hydrated tricalcium aluminate and tricalcium ferrite. Suggested equations to represent the reactions are:

tricalcium aluminate

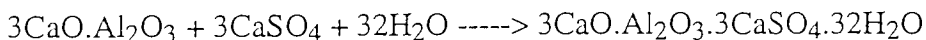


tetracalcium aluminoferrite



The latter two processes involve hydration without any lime being released.

These four reactions only fully set-in after all the gypsum has completed its reactions. Gypsum reacts with the aluminate components, and is precipitated as insoluble water-rich, calcium sulphoaluminate (ettringite)

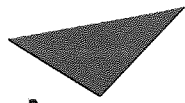


There is little difference in the water binding capabilities of the two calcium silicates and thus the ratios of dicalcium silicates to tricalcium silicates will not have a significant effect on the water binding abilities. The same is true of the aluminate compounds and thus water binding abilities can only be changed by significantly altering the silicate and aluminate components.

The principal constituent of hydrated Portland cement is the tobermorite gel. The adhesion of the tobermorite particles to each other and to the embedded aggregates is responsible for the strength of the cement which is due to the formation of Si-O-Si-O bonds. The following electron microscope photographs (Figure 1.17) show the hydration of Portland cement over 28 days. Diagram 1 shows the cement grains shortly after mixing with water; 2, the mix after one hour. Here, worm like structures can be seen growing on the surface of the grain towards the water-filled capillary space. Note that we do not see individual crystals but the cement gel. Diagram 3 shows that after 24 hours the capillary space is filled up to a greater degree and in Diagram 4, after 28 days, the gel is now more consolidated and denser than before, filling all the available capillary space and bonds between the original cement grains, which now appear to be joined at the contact surfaces.

The calcium hydroxide released during the hydration of the silicates, precipitates as relatively large crystals and contributes little to the bonding of the cement grains.

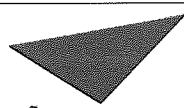
The cement gel represents a high-strength material which belongs to the class of rigid gels. The gel contains water, bound chemically by cement constituents. The water content corresponds to 25 % of the weight of the cement, 10% of which is able to be driven off by heating at 105 °C. The remaining water is termed "gel water".



Aston University

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Figure 1.17 Electron microscope photographs showing the hydration of Portland cement over 28 days⁷⁷



Aston University

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Figure 1.17 Electron microscope photographs showing the hydration of Portland cement over 28 days⁷⁷

1.7.2.4.4 Composite cements

A composite cement is a hydraulic cement composed of Portland cement and one or more inorganic materials that take part in hydration reactions. The most important of these inorganic materials, or mineral additions, are pulverised-fuel ash, ground granulated blast furnace slag (GGBFS), natural pozzolans and microsilica. The mineral addition may be ground together with the cement clinker and gypsum, or mixed with Portland cement when the latter is being used. Mineral additions may be broadly categorised as pozzolanic materials or latent hydraulic cements. Neither type reacts significantly with water in the absence of other substances. Pozzolanic materials are often high in SiO_2 and often in Al_2O_3 and low in CaO .

Blastfurnace slag is formed as a liquid at 1350 - 1550 °C in the manufacture of iron. If cooled sufficiently rapidly to below 800 °C, a wet, sandy material is produced which when dried and ground is called ground granulated blastfurnace slag and often contains over 95% glass. The composition of the slag varies considerably between plants, depending on the operation of the plant, but that of a given plant is unlikely to vary much unless the source of the ore is changed.

The percentage composition of the main constituents of slag is generally as follows in Table 1.4:

Table 1.4 The percentage composition of the main constituents of slag

Main constituents	Per cent	Minor constituents	Per cent
SiO_2	28-38	MgO	0-16
Al_2O_3	8-18	CaS	0-5
CaO	35-45	MnO	< 1
		FeO	< 1
		Fe	< 1
		alkalis	< 1

Latent hydraulic cements have compositions between those of pozzolanic materials and Portland cement. They act as hydraulic cements if mixed with water and a minimal amount of some other substances that serve as a catalyst. GGBFS is a latent hydraulic

cement. When mixed with Portland cement, hydration of the GGBFS is catalysed by the $\text{Ca}(\text{OH})_2$, this modifies the products of the Portland cement clinker.

In the slag cement composite, the slag reacts considerably more slowly than the tricalcium silicate, and strength development is therefore slower to an extent that increases with the proportion of slag. For equal 28 day strengths, replacement of a Portland cement by one containing 65% of slag can lower the compressive strength by almost half at 2 days, but increase it by about 12% at 91 days.

The principal hydration products of the slag cement are essentially similar to those given by pure Portland cements, but the quantities of $\text{Ca}(\text{OH})_2$ present are significantly lower than that which would be produced by the Portland cement fraction if no slag was present. The process of hydration is also similar - layers of the hydration product forming at the boundaries of the slag grains and slowly extending inwards.

1.7.2.4.5 Properties of hardened cements

Hardened cements have high mechanical strength, are partially elastic, are susceptible to shrinkage, chemical attack, thermal expansion/contraction, cracking and creep, are slightly porous, and can be thermally conductive. The property of porosity is briefly discussed here as it is this property that will dictate the ability of the cement to retain the hazardous compounds in the process of solidification/stabilisation technology.

Permeability / Porosity

When cement is mixed, extra water is added over and above that required for hydration of the cement in order to give the cement sufficient workability. In addition, air is trapped during mixing, a small amount of which cannot be removed even by prolonged vibration. The cement paste is an impermeable material, but it is riddled by a mass of capillaries, often interconnected, so that the concrete is inherently permeable. The permeability is of relatively low order, comparable to that of clay. The capillaries are formed during compaction, which causes water to rise and so form channels. Some water is trapped below the aggregate particles, while some fills the pore spaces between the cement particles. Hydration of the cement produces a gel which tends to fill the water voids and to decrease the permeability, although the voids are never completely eliminated. Incomplete curing or allowing the concrete to dry out during hydration increases the porosity, so that complete and thorough curing is necessary to ensure low permeability.

Permeability will be affected by the quantity and composition of the cement, aggregate and water. Thorough mixing, complete compaction and proper curing will ensure low permeability. Highly porous constituent materials will form cements with high permeability, but fine materials must also be present in the mixture to fill voids and produce maximum density. Increase in water content will lead to a cement with high permeability, but enough water must be added to allow for adequate workability.

For immature pastes, that is pastes that are days old, comparisons of the porosities of Portland cement and slag cement show that the porosity of the slag cement is greater than that of the Portland cement. This is due to the slow reaction of the mineral addition. In comparison of the more mature pastes, that is, those cured for more than 90 days, the slag cement has a greater distribution of fine porosity than the Portland cement. The reasons for this are not yet clear. This decrease in porosity displayed by the slag cements decreases the permeability to water, and decreases the diffusion of chloride ions out of cement pastes into saline solutions⁸⁰.

1.8 Objectives

1.8.1 Hazardous Wastes

Section 1.7.1.3 outlines the nine groups containing the 129 priority pollutants. The groups of hazardous wastes to be investigated in this work are compounds in the total phenols group and compounds in the metal groups. More specifically phenol and chlorinated phenols, and organotin compounds. Table 1.5 lists the priority pollutants in these groups. Letters w, s, b represent the environmental compartment in which the pollutant can be detected - water, sediment or biota. Numbers represent the pollutant category. Categories 1 and 2 are of most concern because they are persistent and may bioaccumulate or enter food chains. Categories 3 and 4 include pollutants that are persistent but nonaccumulative and are toxic in direct exposure. Category 5 includes those pollutants that are non-persistent, and consequently tend to remain toxic only over short time periods or at limited distance from the pollutant source.

Chlorinated phenols such as 2,4,6-trichlorophenol and 4-chloro-3,5-dimethyl-phenol are manufactured for use as germicides. Bakelite is produced from the condensation of phenol with methanal. Phenols result in water supplies primarily from industrial waste discharges. Of the 11 phenols and cresols on the pollutant list, three appear to remain in the water column, whereas the remaining eight are all of significance in sediments. It should be noted that pentachlorophenol and 2,4-dimethyl phenol may also

bioaccumulate and thus their high category ranking. Phenols are objectionable in respect to taste and odour, 0.001 ppm present in a water supply may be tasted. Phenol and its chlorinated congeners are toxic and they are powerful irritants. In acute phenol poisoning, the main effect is on the CNS, though damage to the kidneys, liver, pancreas, spleen, and edema of the lungs may result.

The organotin compounds utilised in the work to be covered in Chapter 5 are bis(tributyltin) oxide and triphenyltin chloride. The first recorded use of organotin compounds was as stabilisers for vinyl resins in 1936. The study of their biological effects in the 50s lead to their use as insecticides and fungicides. Triphenyltin compounds have been widely used to combat a range of fungal diseases since the early 1960s, these compounds also possess antifeedant properties. Tributyltins are also used for the preservation of materials such as wood, as disinfectants and in antifouling paints.

Table 1.5 The phenol group and the metal group of priority pollutants After EPA⁸¹

Metals and inorganics	Rank/Compartment	Phenols and cresols	Rank/Compartment
Antimony	3,w	Phenol	3,w
Arsenic	1,s,b	2-chlorophenol	3,w
Beryllium	3,w	2,4-Dichlorophenol	5,w
Cadmium	1,s,b	2,4,6-trichlorophenol	3,s
Chromium	1,s,b	Pentachlorophenol	1,s,b
Copper	1,s,b	2-Nitrophenol	3,s
Cyanides	1,w	4-Nitrophenol	3,s
Lead	5,s,b	2,4-Nitrophenol	3,s
Mercury	1,s,b	2,4-Dimethylphenol	1,s,b
Nickel	1,s,b	p-Chloro-m-cresol	3,s
Selenium	1,s,b	4,6-Dinitro-p-cresol	3,s
Silver	1,s,b		
Thalium	1,s,b		
Zinc	1,s,b		

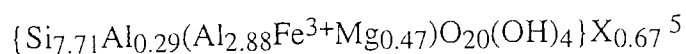
In the late 60s, the poisoning of wounded North American soldiers followed after they had been carried on wooden stretchers which had been treated with a fungicide preparation of triphenyltin hydroxide⁸². The studies carried out after this incident lead to the restricted use of organotins in North America and mainland Europe. In the U.K. cases of poisoning have also been recorded.

Tributyl tin compounds have been used in antifouling paints to control fouling and boring organisms on ships and small boats. The tributyl tin compounds are the active biocidal agents in the paint. When the link between high concentrations of tin compounds found in oysters and high boating activity was made in France, in 1982⁸³, the use of organotin on most boats under 25 metres was banned. Paint manufacturers have responded to this by marketing new formulations of tributyl tin where tributyl tin is chemically bound to the polymers within the paint and, theoretically, is then released at a controlled rate when it reacts with water, thus reducing the amount of tin released into the environment. This consideration is particularly important when the debris is disposed of. Regulation has already be set in place regarding sales of organotin-containing paints and regarding safe water concentrations⁸³.

Both tributyltin and triphenyltin compounds are toxic to fish and are shown to be carcinogens to mice and rats⁸⁴. Mammalian toxicity is manifested as having detrimental effects on the nervous system and produces edema of the white matter of the brain and spinal cord⁸². Further legislation will lead to a restriction in use and disposal in the very near future.

1.8.2 Clays selected for investigation as adsorbents

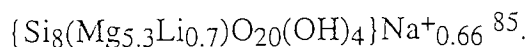
The availability, high surface area, facile cation exchange, high adsorption capabilities and high selectivity when modified and low cost of Wyoming bentonite makes this mineral a good candidate for adsorption processes. Montmorillonite, derived from Wyoming bentonite, is a naturally occurring mineral. It has an ideal formula



where X is the exchangeable ion.

Laponite, a synthetic hectorite belonging to the group of smectites, is also investigated. It has a cation exchange capacity significantly lower than that of montmorillonite and thus a difference in adsorption capacities may be observed. The purest form of laponite is laponite RD. The advantage of laponite RD is that its chemical composition

is known and therefore the exact cation exchange capacity can be determined from both its formula and established experimental methods. The idealised formula is



Laponite is used in industry but the economic viability of its use in the waste treatment is not a strong one.

1.8.3 Project Objectives

Granular activated carbon (GAC) is a common adsorbent used in the removal of hazardous pollutants from aqueous solutions. GAC adsorption is a non-selective process. Competition between pollutants of varying hazard categorisations often occurs, which may result in non-hazardous compounds being adsorbed over hazardous compounds. Thus the capacity to remove hazardous pollutants is reduced. The literature to date, in the field of modified clays as adsorbents, has lead researchers to believe that these clays are viable alternatives to GAC for use in the target treatment of hazardous pollutants.

The major objective of this work was to further explore the nature of the adsorbate-adsorbent interactions resulting from the adsorption process. It was decided to expand upon the work of Mortland et al. 1986⁵⁶ by firstly, investigating the adsorption of fluorophenols using recently developed Sonically Induced Nuclear Magnetic Resonance (SINMR) methods. Unfortunately these SINMR methods are not yet ready to analyse such products as would be produced from the adsorption process.

The second method of expansion was by moving the adsorption process some steps closer to that which industry would consider viable by investigating the adsorption of more than one phenolic compound, by more than one organo-clay. Results of this study are detailed in Chapter 3. Also discussed in Chapter 3 is the use of organoclays as additives for solidification/stabilisation waste treatment and the effect of different cements on the retention of hazardous compounds in the matrix.

The result of studies undertaken at Michigan State University, under the supervision of Professor Stephen Boyd are presented in Chapter 4. This study investigates the effectiveness of a new quaternary compound, tetramethylphosphonium bromide, as a cation capable of modifying the clay surface such that it is able to adsorb hazardous organic compounds.

In Chapter 5, investigation is made of the adsorption of organometallic compounds, specifically organotin compounds, by the modified clays already developed in previous work with the phenols. Until very recently there was little work being carried out in the field of adsorption of metallic compounds but this is being resolved as legislation relating to the disposal of metals and heavy metals tightens.

Chapter 6 discusses preliminary studies of the exchange of transitional metal complexes, of the form $[M(\text{bipy})_3]^{2+}$, onto clays and their ability to adsorb phenols.

Finally, Chapter 7 documents the attempts to introduce conditions suitable for charge transfer interactions between synthesised quaternary ammonium compounds and 2,4,6-trichlorophenol. In theory the charge transfer interactions will supplement the established methods of interactions with the clay surface and interactions with the ammonium compounds.

Chapter 2

Standard methods for preparation and analytical techniques

2.1 Chemicals and materials used

2.1.1 Chemicals and solvents

Chemicals and solvents were obtained from Aldrich Chemical Company, British Drug Houses or Lancaster Synthesis Limited, exceptions are listed below. Common solvents were supplied by the Chemistry department and were dried where necessary and stored over molecular sieves. Analytically pure solvents were used without further purification.

2.1.2 Clay minerals

Montmorillonite was supplied via Akzo Nobel by Steetley Minerals Ltd. as Wyoming Bentonite this has a c.e.c. of 69 meq/100 g. Montmorillonite SAC was supplied by the American Colloid Company. This has a c.e.c. of 90 meq/100 g. Laponite RD was obtained from Laporte Industries, the c.e.c. is 73 meq/100 g.

2.1.3 Cementitious materials

Ordinary Portland Cement (OPC) and Ground Granulated Blast Furnace Slag (GGBS) were obtained from Blue Circle via the Civil Engineering Department.

2.2 Preparation of Wyoming Bentonite for use in exchange reactions

2.2.1 For exchange via shaker method

Wyoming bentonite as supplied contains mineral impurities. These impurities were removed by adding 350 cm³ distilled water to 12 g clay in a 500 cm³ conical flask and shaking on a mechanical shaker overnight. The flask was then removed from the shaker and the contents allowed to settle. After settling the dispersed clay - montmorillonite - is then decanted from the flask, bottled and stored. The impurities were dried and weighed.

2.2.2 For exchange via the microwave oven

The montmorillonite is prepared as described in Section 2.2.1. It is then dried in a evaporating dish which is placed in a 80 °C oven. The resulting montmorillonite is then ground to a particle size of 210 µm and stored for use.

2.3 Analytical Techniques

2.3.1 Atomic Absorption spectrophotometry (AA)

Atomic absorption measurements were carried on a Perkin Elmer 360 instrument. Standard sodium nitrate solution was used for sodium analysis.

2.3.2 Elemental Analysis

Elemental analysis for carbon, hydrogen and nitrogen were carried out by Medac Ltd, Department of Chemistry, Brunel University.

2.3.3 Fourier Transform Infra-red spectroscopy (FTIR)

Infra-red spectra in the range 4000-500 cm⁻¹ were recorded on a BIO-RAD FTS-40A Fourier Transform Infra-red spectrometer. Either KBr discs or NaCl plates were employed for analysis of organic compounds.

For analysis of clays and modified clays Diffuse Reflectance Fourier Transform Infra-red and Near Infra-red Spectroscopy was employed. The samples were prepared in cylindrical holders as a sample/KBr mix and analysed in the 5000 - 500 cm⁻¹ region.

2.3.4 High Performance Liquid Chromatography

HPLC data was obtained using a Varian 9065 Polychrom Spectrophotometer with a Varian 9010 solvent delivery system.

2.3.5 Melting Points

A Gallenkamp electrically heated melting point apparatus with a mercury thermometer was used to determine all melting points.

2.3.6 Methylene Blue dye titration for the determination of cation exchange capacity

5 g clay slurry (2.5 - 3.0 wt%) were first made up to 20g with distilled water. The methylene blue dye adsorption capacity was then determined by titration with standard 0.01M methylene blue dye solution. Increments of 1 cm³ or less of the titrant were each followed by a shaking of the flask.

The course of the titration was followed by periodically spotting a drop of the titrated slurry onto a filter paper. The end point was indicated when excess dye appeared as a sky-blue colouration radiating from the normally darkly-dyed solids in the centre. This was reconfirmed by running the spot test after a two minute waiting period.

2.3.7 Mössbauer spectroscopy

Mössbauer analyses were conducted by Professor F.J. Berry, Chemistry Department, The Open University.

2.3.8 Nuclear Magnetic Resonance Spectroscopy (NMR)

Solution

¹H and ¹³C solution spectra were recorded at Aston University using a Bruker AC-300 MHz instrument .

Solid - Magic Angle Spinning

Solid samples were also analysed on this instrument with a solid state probe. Samples were spun at the magic angle at approximately 4 kHz. ²⁹Si spectra were measured at a frequency of 59 MHz.

Tetramethylsilane was used as the internal reference for all spectra.

2.3.9 Secondary Ion Mass Spectrometry (SIMS)

Positive and negative SIMS analysis were conducted on a VG Scientific ESCALAB 200-D instrument fitted with a standard SIMS quadrupole (800 amu) and using a 3 keV Argon beam.

2.3.10 Ultraviolet/Visible spectrophotometry (UV)

Ultraviolet/Visible solution spectra were obtained from a Pye Unicam SP1800 spectrometer using 1 cm quartz cells.

2.3.11 X-Ray Diffraction Spectroscopy (XRD)

Of particular interest was the d(001) reflection. This is also known as the d, or basal, spacing. Any change in the interlamellar region will appear as a change in the basal spacing. XRD results were provided by Akzo Nobel, Littleborough and the Department of Geology, Keele University courtesy of Dr. Rowbotham.

2.3.12 X-Ray Photoelectron spectroscopy (XPS)

Analysis was carried out the VG Scientific ESCALAB 200-D instrument using MgK α (1253.6 eV) radiation. Deconvolution techniques were employed where appropriate, the process terminating when the simplest fit with a satisfactory χ^2 value was obtained.

Chapter 3

The adsorption of phenolic compounds by quaternary ammonium exchanged smectite clays and the study of solidification/stabilisation as a pre treatment to the landfilling of chlorinated phenols.

3.1 Introduction

Research involving the tailoring of organo-clays, or Quat-clays, for possible use as clay barriers, or to be used as alternatives to activated carbon in treatment by adsorption, is a rapidly expanding field. The reaction between quaternary ammonium compounds of the type $\text{RN}(\text{CH}_3)_3^+\text{X}^-$ and smectite clay is that of exchange of the exchangeable cation present in the clay with $\text{RN}(\text{CH}_3)_3^+$ ions. When exchanged onto montmorillonite clay, the resulting Quat-clay shows an affinity towards particular organic compounds, and different types of adsorption isotherms are observed. Much recent work has focused on the adsorption of organic pollutants.

Akzo chemicals manufacture quaternary ammonium compounds of the type $\text{R}(\text{CH}_3)_3\text{N}^+\text{Cl}^-$, where $\text{R} = \text{C}_{16/18}$, and became aware of the studies of the adsorption characteristics of this type of compound when exchanged onto clays. This, combined with the tightening of legislation on the disposal of the phenols as a group, and on pentachlorophenol in particular, prompted Akzo chemicals to consider a new application for their Quat-clays. Research at Akzo, Littleborough has involved the study of the adsorption of pentachlorophenol by various tallow ammonium exchanged clays.

To reduce leaching from landfills the Quat-clay may be applied to act as a barrier. Research has been carried out to further reduce leaching by mixing the adsorbed organic, quaternary exchanged clay with cement⁷². Section 1.7 describes this research.

3.1.1 Adsorption of phenolic compounds

Section 1.5 described the developments in the research on clays as adsorbents from the studies of Smith in 1934²⁰ to those of Jaynes and Boyd 1991⁵⁹. After almost 60 years of research there are still many questions about the mechanisms by which organic compounds adsorb onto Quat-clays. What has been observed, however, is the selectivity of different Quat-clays for different organic compounds. The selectivity is

dependant on many different factors for different adsorbents and adsorbates. Factors such as solubility of the adsorbate⁵⁶, size restrictions of both the adsorbent and the adsorbate², extent of silicate layer screening⁵⁸, and the solvent from which the adsorption is studied⁵⁶, are all known to influence adsorption.

Mortland et al.⁵⁶ studied the adsorption of phenols and chlorinated phenols from water by hexadecyltrimethylammonium exchanged montmorillonite, HDTMA-montmorillonite; hexadecylpyridinium exchanged montmorillonite HDPY-montmorillonite and trimethylphenylammonium exchanged montmorillonite, TMPA-montmorillonite. Chemical formulae of the Quats are shown in Table 3.1 below.

Table 3.1 The quaternary ammonium compounds used in the studies of Mortland et al.⁵⁶

Chemical name	Chemical formula	Quat
Hexadecyltrimethylammonium bromide	$C_{16}H_{33}N(CH_3)_3^+Br^-$	HDTMA ⁺ Br ⁻
Hexadecylpyridinium chloride	$C_5H_5NC_{16}H_{33}^+Cl^-$	HDPY ⁺ Cl ⁻
Trimethylphenylammonium chloride	$C_6H_5N(CH_3)_3^+Cl^-$	TMPA ⁺ Cl ⁻

This work has shown that in the adsorption of phenols and chlorinated phenols by a range of Quat-montmorillonites, specificity is observed. When R of $RN(CH_3)_3^+$ is a long alkyl chain, for example $C_{16}H_{33}$ -, the adsorption of the chlorinated phenols occurs via a partitioning process, typified by a linear isotherm. However, when R is a more compact organic group, for example the phenyl group C_6H_5 -, adsorption of the phenol will occur but not that of the chlorinated phenols. The adsorption isotherms obtained are of Types III, V, or C, which are typical of weak adsorbate-adsorbent interactions.

3.1.2 Objectives

Mortland et al.⁵⁶ studied the adsorption of phenol, 3-chlorophenol, 3,5-dichlorophenol and 3,4,5-trichlorophenol by montmorillonites exchanged with the Quats listed in Table 3.1. He concluded that the montmorillonites exchanged with the long chained Quats were better adsorbers of the chlorinated phenols and the montmorillonites exchanged with the short chained Quats were better adsorbers of

phenol. The findings are detailed in Section 3.4. The work of the adsorption isotherm study was to be extended by examining the adsorption of a different group of phenols. The phenols were phenol, 2-chlorophenol, and 2,4,6-trichlorophenol. These phenols are of particular concern as regards pollution and disposal. The study will test the conclusions drawn by Mortland for the chlorinated phenols as a group. Adsorption characteristics of Quat-laponites were also studied.

Bi Quat-clays were prepared and their adsorption characteristics compared to those of single Quat-clays. This direction was taken because an industrial stream or contaminated water may contain a number of organic compounds. The results of adsorption onto a single Quat-clay suggest there is selectivity towards the organics used. It would be useful, therefore, if more than one contaminant could be adsorbed at a time. However, before modelling a waste stream or contaminated water with a number of phenols in the laboratory, it was decided to examine whether the adsorption of one organic was affected by the presence of another Quat-clay in the system. The study of these systems could provide a useful step towards systems which would be industrially viable.

This chapter will also describe preliminary studies into the use of stabilisation/solidification technology for the safe disposal of organic compounds, specifically phenols. The established method using ordinary Portland cement (OPC) will be compared to that of slag cement, i.e., ground granulated blast furnace slag mixed with ordinary portland cement (GGBS/OPC).

The objectives of this chapter were:

(i) to verify the phenol adsorption results of Mortland by preparing fully exchanged montmorillonites;

(ii) to study the adsorption characteristics of another smectite clay - laponite - by preparing new exchanged laponites with the following Quats: hexadecyltrimethyl ammonium bromide ($\text{HDTMA}^+\text{Br}^-$), hexadecylpyridinium chloride (HDPY^+Cl^-), trimethylphenyl ammonium chloride (TMPA^+Cl^-). The use of laponite (with lower clay layer charge) may result in different adsorption properties than those observed for exchanged montmorillonites. The Quats were chosen to represent the different characteristics of the Quats used by Mortland and should reflect the effect of chain length and aromatic ring system on adsorption of phenolic compounds.

Analysis of the initial clays and exchanged clays was made by X-Ray Diffraction (XRD), Silicon-29 Magic Angle Spinning Nuclear Magnetic Resonance (MASNMR),

and the usefulness of Fourier Transformed Infra-red and Near Infra-red (FTIR, FTNIR) and X-ray Photoelectron Spectroscopy (XPS) as analytical tools were studied;

(iii) to measure the adsorption of phenols and chlorophenols onto the Quat-clays by monitoring Ultraviolet-Visible spectra (UV-Vis). The phenols and chlorophenols were chosen to demonstrate the effect of the presence of the chlorine constituent on the amount of phenol adsorbed and the resulting interaction, but they differed slightly from those of Mortland because they are phenols and chlorophenols commonly found in industrial waste streams⁶⁹, i.e. phenol, 2-chlorophenol and 2,4,6-trichlorophenol were used;

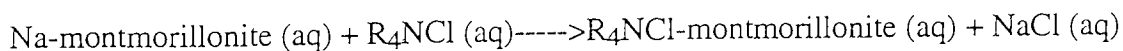
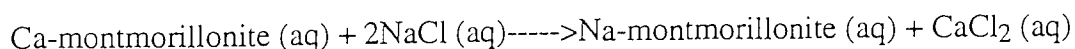
(iv) to examine fluorophenol adsorption, with the intention of using Sonically Induced Nuclear Magnetic Resonance as an analytical tool;

(v) To conduct preliminary studies on the attenuation of chlorophenols by exchanged clays and cement solidified exchanged clay mixes.

3.2 Preparation of exchanged Quat-montmorillonites

3.2.1 Exchanged montmorillonites: Preliminary studies

The standard method for the laboratory preparation of Quat-clays involves two steps. Firstly, the conversion of the montmorillonite clay to sodium-montmorillonite by washing in sodium halide solution. The calcium and potassium ions, in the case of montmorillonite, are removed by washing the resulting sodium-montmorillonite until it is halide free. Secondly, the addition of the Quat, at between two and five times the c.e.c of the clay, to the sodium-montmorillonite slurry. The resulting Quat-clay is then washed in distilled water to remove the sodium halide from the clay. The following equations summarise the reaction:



It can be seen that the standard method of preparation of the Quat-clay requires repeated washing and separation procedures; such procedures are facilitated by use of high speed centrifuges which were not available for this study, or the use of dialysis equipment which is time consuming. Both procedures are unlikely to be used by

equipment which is time consuming. Both procedures are unlikely to be used by industry for the production of materials to be used for waste disposal. Thus it was decided to work with the montmorillonite clays using a simpler procedure for the preparation of the Quat-clays. Exchange reactions were conducted bearing in mind the findings of Breakwell⁸⁶ which suggest that negligible concentrations of Ca²⁺ cations are displaced during exchange and thus the total c.e.c. of the clay is due to the Na⁺ cations. Exchanging an excess amount of Quat onto the clay was avoided, reducing the need for repeated washing and therefore time for preparation.

The effect of using the modified method of preparation of Quat-montmorillonites, which will be described in Section 3.2.2, on the adsorption efficiency of the Quat-clays will be discussed in Section 3.4.

To achieve fully exchanged Quat-smectites the c.e.c. of the clays must be known. From the clay c.e.c. the amount of Quat required to satisfy the c.e.c. can be calculated and thus fully exchanged clays prepared. The equation used to calculate this quantity can be found below:

$$\text{wt (g) quaternary ammonium compound required to satisfy the c.e.c} = \frac{\text{meq of clay/100 g} \times \text{wt clay used (kg)} \times \text{RMM Quat}}{\text{activity of Quat} \times \text{valency of Quat}}$$

The c.e.c.s of laponite, bentonite and montmorillonite are quoted in the literature as: laponite 73 meq/100 g, bentonite (as supplied) 70 meq/100 g and montmorillonite (component of bentonite) 80-100 meq/100 g. The c.e.c.s of the clays were determined in the laboratory, by the method described in Section 2.3. and found to be 73 meq/100 g, 69 meq/100 g and 90 meq/100 g respectively. The activity of the Quat refers to the percentage purity of the Quat.

Montmorillonite was prepared as described in Section 2.2.1. Initial studies for the modification of the procedure for the preparation of quaternary ammonium exchanged montmorillonites, involved the use of HDTMA⁺Br⁻ at varying proportions of the c.e.c. The amount of sodium released during the reaction was determined. Each reaction was carried out in duplicate, one product was washed with 100 cm³ distilled water and the other remained unwashed. Two of the washed samples were submitted for XRD analysis. It was found that the basal spacings (d(001)) were comparable with those found in the literature⁵⁶. However, the amount of Quat added to the clay did not result in the release of a proportional amount of sodium cations when the products were washed with 100 cm³ distilled water Table 3.2.

Table 3.2 The relationship between fraction of HDTMA⁺Br⁻ added for the exchange reaction and the sodium released

HDTMA ⁺ Br ⁻ added (g)	Percentage exchange Na ⁺ (AA)	Basal spacing (Å)
0.8	21	/
1	24	17.31
1.7*	21	17.65

* Added at the c.e.c. of the clay

When the product was washed with 1 dm³ of distilled water, an increase in the amount of sodium released was observed. The effect of washing on sodium release for HDTMA⁺Br⁻ exchanged montmorillonite (HDTMA-montmorillonite) is shown in Table 3.3.

Table 3.3 The effect of washing on sodium release for HDTMA*-montmorillonite.

amount of distilled water used in washing (dm ³)	Percentage exchange Na ⁺ AA	basal spacing (Å) ^a
0.1	21	17.65
1.0	75	18.01

* Added at the c.e.c. of the clay

^a basal spacing of montmorillonite = 12.44 Å

These experiments show that on exchange at the c.e.c of the clay and washing with a considerable amount water, a Quat-clay with basal spacing of 18.01 Å is obtained, this is as expected from literature values⁵⁶. Washing with only 10% of this amount of water, suggested only 21% exchange had taken place which is clearly not the case from the basal spacing results. Such results highlight the importance of washing in the preparation of Quat-clays if sodium analysis is to be used as an indication of

exchange. Washing will also ensure the thorough removal of ion pairs, NaCl and unreacted HDTMA⁺Br⁻ in the case of the HDTMA exchanged clay, from the product which may otherwise impair the adsorbent properties.

Percentage exchange was monitored by sodium release on washing. 100% exchange was initially taken to correspond to the amount of sodium present according to the ideal formula of montmorillonite: $[\text{Si}_8\text{Al}_{3.33}\text{Mg}_{0.67}\text{O}_{20}(\text{OH})_4]0.67\text{X}$, where X is (are) the exchangeable cation(s). The exchangeable cations in montmorillonite are calcium and sodium. It has been shown by Breakwell⁸⁶ that during the exchange reaction involving the Quats, the release of calcium ions from the interlayer region of the clay is negligible compared with that of the sodium cations. It was therefore initially assumed that X was wholly sodium cations. When the experiments above were repeated with the HDTMA cation and montmorillonite at varying multiples of the cation exchange capacity, the HDTMA-montmorillonite products were washed until three successive washings contained less than 1% Na⁺ ions, the results are shown in Table 3.4.

Table 3.4 Results from the exchange reaction between HDTMA⁺Br⁻ and montmorillonite beyond the c.e.c and the accompanying release of Na⁺ cations

n multiple of c.e.c	percentage exchange ($\pm 8\%$) (Na ⁺ AA)
0.5	35
1	75
2	80
2.5	80

The results show that even when the c.e.c. is exceeded, only 80% of the assumed Na⁺ ion content is released from the interlayer region. From the ideal formula of montmorillonite, 0.1 g Na⁺ ions were expected to be displaced per 5 g of montmorillonite clay when full exchange is achieved. It can be seen that when HDTMA⁺Br⁻ is added at 2.5 times the c.e.c. only 80% of the predicted exchanged occurs. This would suggest that the assumption is incorrect and only 0.08 g of Na⁺ ions are displaced per 5 g of montmorillonite clay when full exchange is achieved.

Subsequent percentage exchange data for montmorillonite exchange reactions will be based on the fact that 0.08g sodium cations are displaced per 5 g montmorillonite when full exchange occurs.

3.2.2 Preparation of fully exchanged montmorillonites

HDTMA, HDPY, and TMPA exchanged montmorillonites were prepared as follows: The montmorillonite slurry (prepared as described in Section 2.2.1) and the amount of Quat needed to satisfy the c.e.c. of montmorillonite were placed in a 500 cm³ conical flask and shaken for 1 week on the mechanical shaker. The product was filtered, washed with 1 dm³ distilled water/5 g clay and air dried. The filtrate was retained and analysed by sodium Atomic Absorption (which yields information on sodium release and therefore the extent of exchange in the reaction) and X-ray Diffraction (XRD) analysis (which indicates a change in the interlayer distance of the clay). The results are tabulated in Table 3.5.

The reaction was found to be accelerated considerably by heating to 60 °C. This method is used in industry: The clay suspension was prepared as outlined in Section 2.2.1. The mixture was heated, with stirring to 60 °C and kept at 60 °C for 30 minutes. The ammonium compound was then added to satisfy the cation exchange capacity (c.e.c.) of the clay and the mixture stirred for one hour. The resulting product was cooled, washed, filtered and air dried as for the reaction at ambient temperature. The resulting Quat-montmorillonites prepared at 60 °C have the same properties as those prepared at ambient temperatures with respect to basal spacing, sodium exchange and appearance.

3.2.3 Characterisation of the fully exchanged montmorillonite clays

The Quat-montmorillonites were characterised using X-ray diffraction (XRD), Atomic absorption (AA), silicon-29 magic angle spinning nuclear magnetic resonance (²⁹Si MASNMR) and X-ray photoelectron spectroscopy (XPS).

3.2.3.1 XRD - Quat arrangement in the interlayer region and the degree of exchange

The basal spacings (d(001)) shown in Table 3.5, suggest that fully exchanged clays have been synthesised and agree with literature values, HDTMA-montmorillonite 18 Å

⁵⁶ and TMPA-montmorillonite 14.8 Å⁵⁹. The results suggest that in HDTMA-montmorillonite and the HDPY-montmorillonite the Quats are arranged in bilayers as shown in Figure 3.1, as described in Section 1.4.1. The TMPA molecules in TMPA-montmorillonite are assumed to be arranged in a monolayer as described in Section 1.5.2.2.

Table 3.5 Quat-montmorillonites washed with 1 dm³ water - percentage exchange and basal spacing results

Quat*	Exchange (%) (± 8%)	Basal spacing(Å)
HDTMA+Br ⁻	94	18.01
HDPY+Cl ⁻	75	17.30
TMPA+Cl ⁻	74	14.24

* Quat added to satisfy the c.e.c of montmorillonite

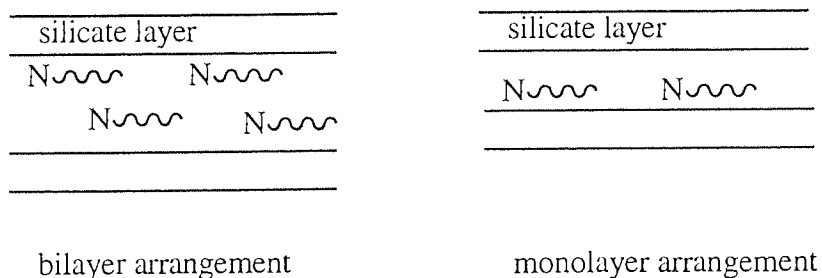


Figure 3.1 Arrangement of Quats in the interlayer region of smectite clays after Lagaly⁶²

3.2.3.2 AA

Table 3.5 shows the basal spacing and percentage exchange results as obtained from sodium AA analysis.

As stated in Section 3.2.1 percentage exchange data for montmorillonite exchange reactions will be based on the fact that 0.08g sodium cations are displaced per 5 g montmorillonite when full exchange occurs.

The percentage sodium release detected in the washings of the products suggest significantly less than the 94% exchange (observed for HDTMA-montmorillonite) has taken place for the HDPY- and the TMPA-montmorillonites. The reason for this is not clear. The exchange reactions for the three Quats with montmorillonite were repeated several times, the percentage release of sodium ions given in Table 3.5 being the average of the results. In all cases the Quats were added at the c.e.c and yet there is a disparity of some 16% between highest and lowest sodium release values. The values of the c.e.c. of the clays were obtained by established methods and there is no reason to doubt the results of those analyses. This is supported by the results of the exchange reactions for laponite clays, where the chemical formula is known. When the Quat is added at the c.e.c of the laponite, 90-100% sodium release is observed. This suggests that c.e.c results are correct but the amount of sodium expected to be released as a product of montmorillonite exchange reactions varies with the Quat used. The presence of the $\text{Ca}^{2+}/\text{K}^{+}$ in montmorillonite may play a part. It is probable that the arrangement of the Quats around the $\text{Ca}^{2+}/\text{K}^{+}$ ions affect the extent of the exchange reaction. Both Quats with aromatic groups are exchanged to a lesser degree than the HDTMA Quat. The presence of the aromatic group may restrict possible orientations in the interlayer region containing $\text{Ca}^{2+}/\text{K}^{+}$ ions and thus restrict the extent of exchange.

3.2.3.3 FTIR

Montmorillonite and the Quat-montmorillonites were analysed by FTIR employing KBr discs. The spectra are shown in Figure 3.2. The characteristic peaks of the montmorillonite used in this study are listed in Table 3.6. The assignments are obtained from studies by Farmer⁸⁷ and Marcel/Beutelspach⁸⁸.

The spectrum of the HDTMA-montmorillonite was identical to that of the montmorillonite spectrum except for the presence of two sharp peaks at 2920 cm^{-1} and 2843 cm^{-1} and two sharp peaks at approximately 1500 cm^{-1} . These are present due to the stretching of C-H bonds and C-N or C-C bonds respectively.

For HDPY- and TMPA-montmorillonites similar observations were made, the spectra essentially being an addition of the two precursors. A narrowing of the peak at 1050 cm^{-1} was observed for the HDPY-montmorillonite product.

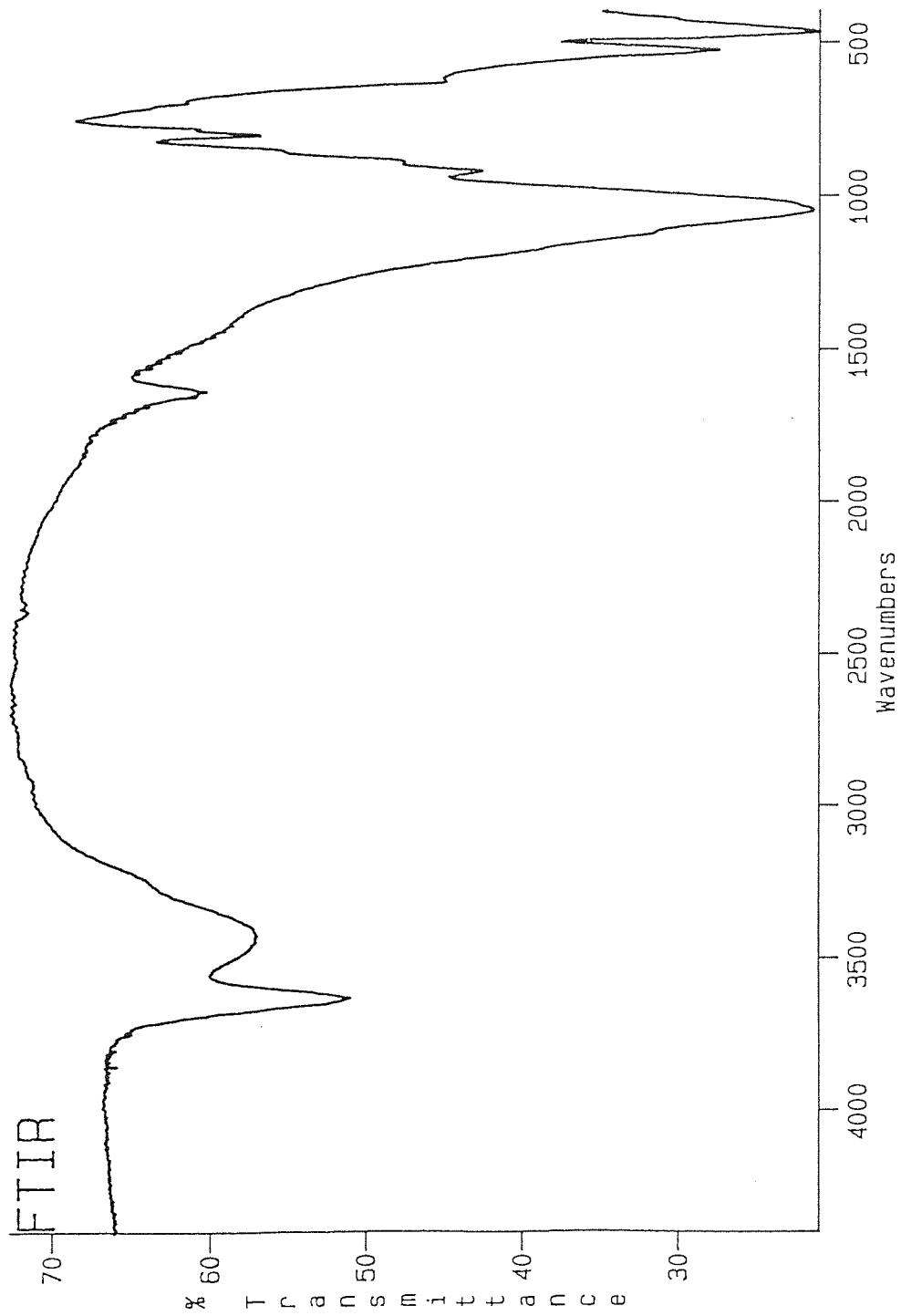


Figure 3.2a FTIR spectrum of montmorillonite

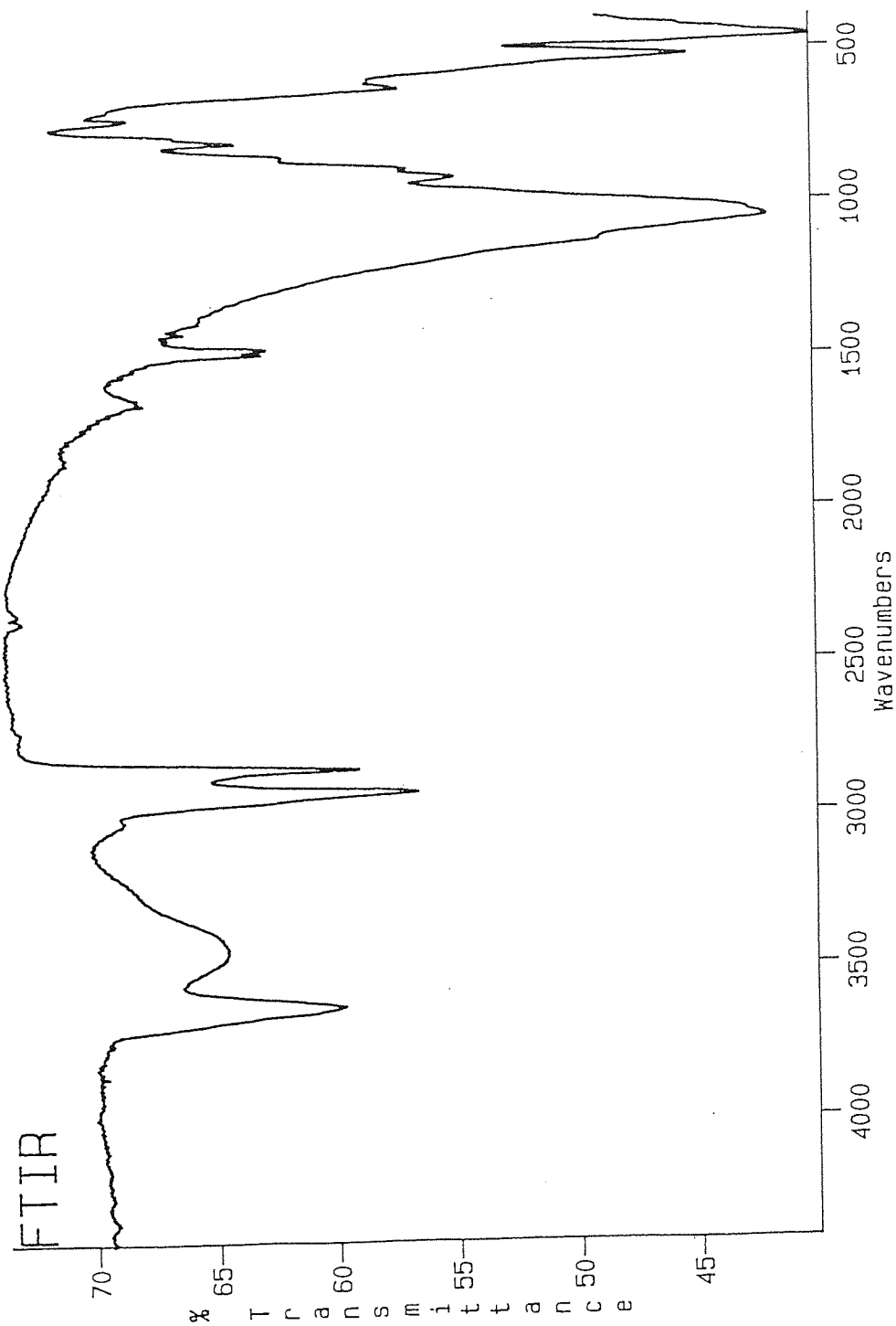


Figure 3.2b FTIR spectrum of HDTMA-montmorillonite

Table 3.6 Characteristic FTIR absorptions and assignments for montmorillonite

wave number	assignment
3638 cm ⁻¹ - sharp	OH stretching, (Al ³⁺ or Mg ²⁺)-OH,
3220 cm ⁻¹ - broad	hydrogen bonded water,
1640 cm ⁻¹ - sharp	HOH deformation (hydration)
1050 cm ⁻¹ - broad	stretching vibrations of Si-O and Si-O-Si,
920 cm ⁻¹ - sharp	deformation of OH attached to 2Al ³⁺ ,
889 cm ⁻¹ - sharp	deformation of OH attached to Fe ³⁺ and Al ³⁺ ,
855 cm ⁻¹ - sharp	deformation of OH attached to Al ³⁺ and Mg ²⁺ ,
800 cm ⁻¹ - sharp	Si-O deformation
620 cm ⁻¹ - sharp	
522 cm ⁻¹ - sharp	
468 cm ⁻¹ - sharp	

When primary ammonium cations such as the octadecylammonium cation (C₈H₁₇NH₃) are exchanged into montmorillonite clays, changes in the spectrum of the clay can be observed, Slosiarikova et al.⁸⁹. The most intense IR bands of dioctahedral smectites occur in the range 1000 - 1200 cm⁻¹ which corresponds to the Si-O and Si-O-Si vibrations. The FTIR spectrum of the octadecylammonium exchanged clay shows that when full exchange occurs, a reduction in the Si-O peak intensity is observed and the presence of a shoulder is observed at 1110 cm⁻¹. It is suggested that the presence of the primary ammonium cation results in a change in the arrangement of the SiO₄ tetrahedra in a manner that is distinguishable by the FTIR experiment. The N-H stretching vibrations for the primary ammonium cation are also seen to shift to a higher wavenumber when exchanged into the montmorillonite. The two observations made by Slosiarikova et al.⁸⁹, are not found to occur when the quaternary ammonium cations HDTMA, HDPY and TMPA are reacted with montmorillonite. The FTIR experiment is not sensitive to changes in the N-C bond strengths. The arrangement of the SiO₄ tetrahedra in the montmorillonite clay is not affected by the exchange reactions conducted in this study.

3.2.3.4 Diffuse reflectance FTNIR

FTNIR experiments were carried out as described in Section 2.3. Figure 3.3 shows the spectrum of montmorillonite. The additional characteristic peaks, in the region 5000 cm^{-1} to 4000 cm^{-1} , of the montmorillonite used in this study are listed in Table 3.7 below, assignments are obtained from studies by Hunt et al.⁹⁰ and Clarke et al.⁹¹.

Table 3.7 Characteristic FTNIR absorptions and assignments for montmorillonite in the $5000 - 4000\text{ cm}^{-1}$ region

wave number	assignment
4760 cm^{-1} - broad	
4500 cm^{-1} - sharp	AlOH combination vibration
4120 cm^{-1} - broad	MgOH and FeOH combination vibrations

The advantages of the Diffuse reflectance FTNIR spectra over the established FTIR method for obtaining spectra are:

- i) the increased clarity of the spectra and improved peak resolution and
- ii) the increased information on the octahedral layer of the smectite clays.

Unfortunately, none of these advantages prove to be useful in the analysis of the montmorillonite clay and the Quat-montmorillonite product. Indeed on carrying out FTNIR analysis on the montmorillonite, HDTMA-montmorillonite and TMPA-montmorillonite, no differences in the NIR region (5000 cm^{-1} to 4000 cm^{-1}) were detected between the three samples.

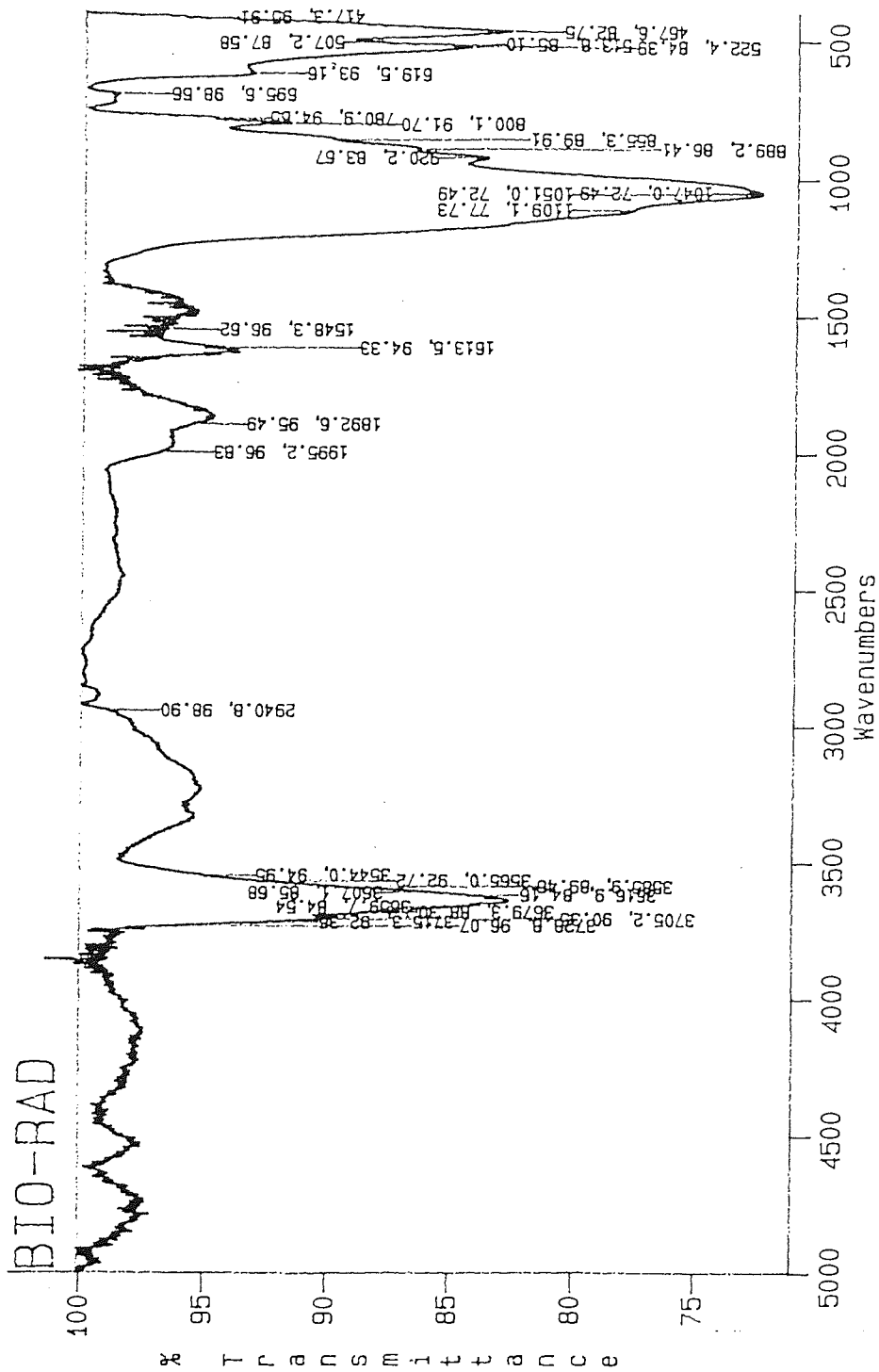


Figure 3.3 Diffuse reflectance FTNIR spectrum of montmorillonite

3.2.3.5 ^{29}Si MASNMR

^{29}Si MASNMR of bentonite has two characteristic peaks. That furthest upfield being termed Q^4 and that downfield, Q^3 . The terms Q^3 and Q^4 refer to the environment of the silicon atoms in the sample. The Q^4 peak results from the presence of $\alpha\text{-SiO}_2$ in the clay, where the silicon shares oxygens with four other silicon atoms. When silicon shares oxygens with three other silicon atoms (as found in the silicate layer of montmorillonite) a Q^3 peak is observed in the spectra. Figure 3.4 shows a typical ^{29}Si MASNMR spectrum of bentonite clay. The Q^4 and Q^3 resonances are typically found at -107.5 ppm and -92.9 ppm respectively when tetramethylsilane is used as the reference.

^{29}Si MASNMR spectra of bentonite and HDTMA-montmorillonite, both before and after washing, were determined and compared. Samples from the same reaction were submitted on three different occasions. It was found the Q^3 resonance for the exchanged clays (both washed and unwashed) occurred at 93.5 ± 0.1 ppm and the Q^4 resonance at 107.7 ± 0.1 ppm. Washing of the exchange clay had no effect on the position of the Q^4 and Q^3 resonances. Thus, the shift differences in the Q^3 resonances between the bentonite clay and the exchanged montmorillonites are significant when compared to the shift differences observed for replicate determinations of exchanged clay samples from the same reaction. Table 3.8 displays the ^{29}Si MASNMR results.

Table 3.8 Summary of the ^{29}Si MASNMR analysis of HDTMA-montmorillonite

Material	Q^3 (ppm) ± 0.1 ppm	Q^4 (ppm) ± 0.1 ppm
Bentonite	-92.9	-107.5
Washed HDTMA-montmorillonite	-93.5	-107.6

Table 3.8 shows the results of the ^{29}Si MASNMR experiments for HDTMA-montmorillonite. The Q^4 peak remains invariant towards the exchange reaction, as expected. The Q^3 peak is seen to shift upfield from -92.9 ppm for bentonite to -93.5 ppm for washed, exchanged montmorillonite. This results from the sodium cation present in the bentonite clay deshielding the silicon atom to a greater extent than the quaternary ammonium cation. Thus the Q^3 peak is sensitive to the exchange reaction

confirming basal spacing and AA results which show that an exchange reaction has occurred in the interlamellar region.

3.2.3.6 XPS

XPS is a surface sensitive technique able to detect atoms down to 50 Å beneath the surface of a material. It has been shown to be able to distinguish between the various precursors and their products from reactions with clays^{92,93}. Here, it will be demonstrated that the Quat-montmorillonites may be characterised by XPS. Tables 3.9 and 3.10 display results of XPS analysis. Table 3.9 shows the results of the Br(3d), binding energy analysis of the various exchanged montmorillonite materials. HDTMA⁺Br⁻, NaBr and various NaBr exchanged clays were used as standards. This was to obtain additional support for the complete exchange of the HDTMA cation onto montmorillonite clay and to ensure no excess HDTMA⁺Br⁻ was present, trapped in the clay matrix.

Table 3.9 XPS Br(3d) data for exchanged montmorillonites

Sample	Br(3d), Binding energy (± 0.2 eV)
HDTMA ⁺ Br ⁻	67.00
HDTMA-montmorillonite washed 100 cm ³ water	74.4, due to Al(2p)
HDTMA-montmorillonite washed 1 dm ³ water	68.2
NaBr-montmorillonite washed 200 cm ³	68.3
NaBr-montmorillonite washed 600 cm ³	/*
NaBr (reference)	68.7

* Br undetected in this sample.

The results suggest that any Br present in the HDTMA-montmorillonite is probably in the form of NaBr. Thus, even after thorough washing, not all the sodium is washed from the product. The absence of a peak at 67.00 eV for the Quat-montmorillonite product shows that it is unlikely that Quat ion pairs are in the product. This is important for the application of the Quats-clays to adsorption as any adsorbate may preferentially react with the Quat ion pairs and not the Quat-clay adsorbent. The peak found at 74.4 eV was found to be due to the aluminium from the clay. The absence of

(*) 29Si MASNMR
100 MHz
100°C
1000000

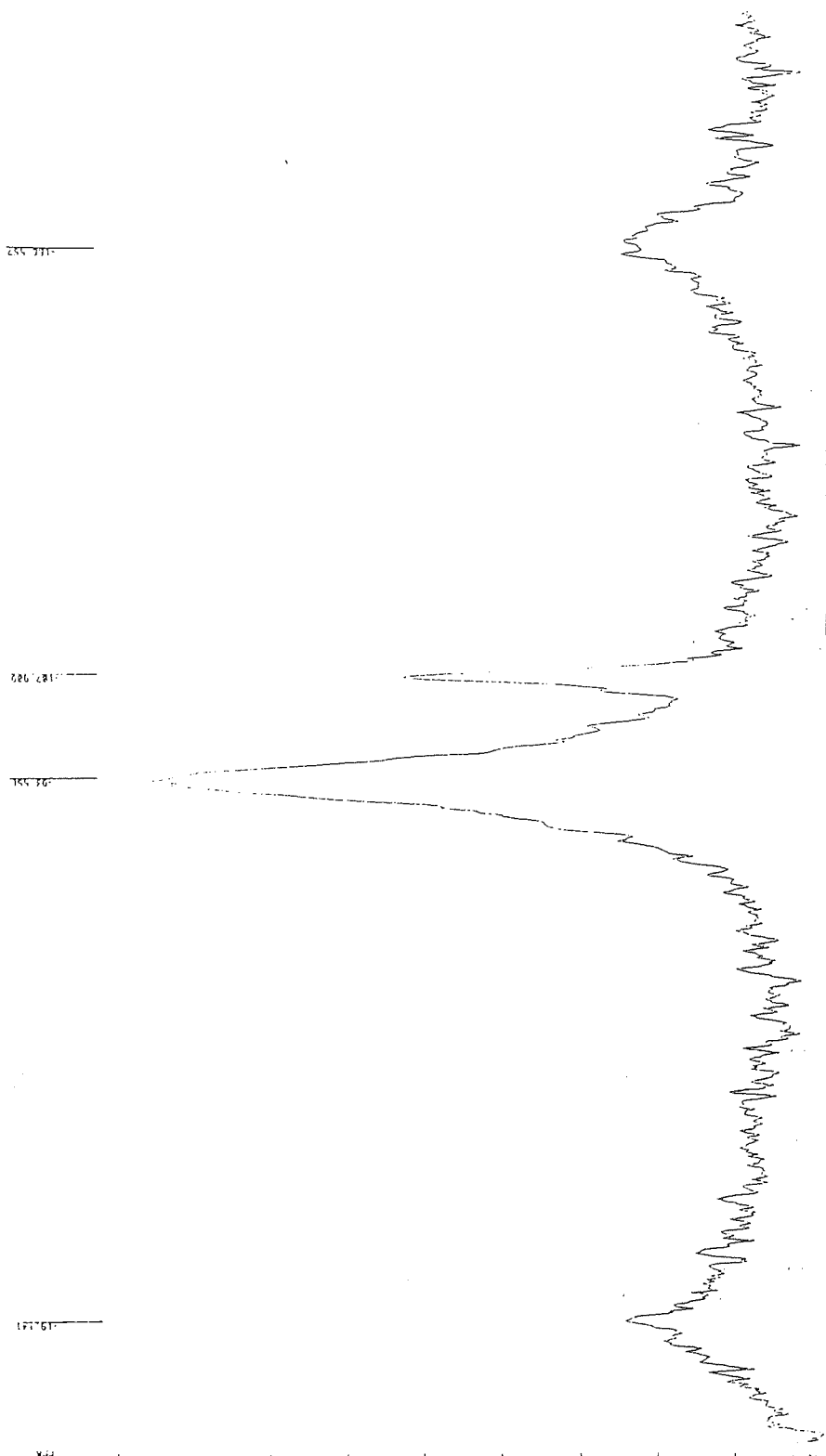


Figure 3.4 ^{29}Si MASNMR spectrum of bentonite clay

peaks due to the presence of Br in the HDTMA-montmorillonite washed with 100 cm³ distilled water was unexpected.

Table 3.10 shows the results of the N(1s), binding energy experiments. These experiments were carried out to investigate the effect of exchange on the N atom of the quaternary ammonium cation.

Table 3.10 XPS N(1s) data for exchanged montmorillonites

Sample	N(1s), binding energy (eV \pm 0.2)
HDTMA+Br ⁻	401.8
HDTMA-montmorillonite washed 100 cm ³ water	402.6
HDTMA-montmorillonite washed 1 dm ³ water	402.6
	two peaks - 399.3, 402.5

The binding energy of the nitrogen in the Quat and the nitrogen in the Quat-montmorillonite product differs by 0.8 eV.

The results suggest that the interaction between the nitrogen and the silicate layer is stronger than that between N and Br in the Quat precursor. This is not surprising as the Quat precursor exists as ion pairs, and it is possible that the oxygen of the silicate is able to act as a gegen ion with greater polarising properties than the Br⁻ ion. Interaction between the oxygen of the silicate layer and the nitrogen of the Quat may be via hydrogen bonding. This may result in the N-C bonds becoming stronger in the Quat when exchanged into the interlayer region than before exchange. Such increase in the N-C bond strength was unable to be detected by FTIR. This shows that XPS can be useful as an alternative tool for the characterisation of these Quat-clays.

The analysis for N yields results that suggest that on exchange a small percentage of the Quat (RN(CH₃)₃⁺) dissociates to the amine (RN(CH₃)₂). The peak at 402.5 eV arising from the presence of the exchanged Quat and that at 399.3 eV arising from the presence of any amine⁹⁴. However, work by Ashcroft et al.⁹⁵ has shown that a change in the state of surface atoms can be induced by the very nature of the experiment, i.e., the bombardment of the surface by X-rays induces a surface reaction

yielding products not originally typical of the surface. A repeat of the N(1s) XPS analysis of HDTMA-montmorillonite sample resulted in a peak at 402.5 eV only.

3.2.4 Exchanged montmorillonites - Conclusions

Exchanged Quat-montmorillonites were prepared without conversion to the sodium-montmorillonite, and by addition of the Quat at the c.e.c. only. The basal spacings of the resulting Quat-montmorillonites were comparable to those quoted in the literature. Studies of sodium release on exchange suggested that the quantity of sodium ions released depended on the Quat. Exchange with HDTMA⁺Br⁻ resulted in the highest sodium ion release, followed by the HDPY⁺Cl⁻ and the TMPA⁺Cl⁻ which displace similar quantities of sodium ions.

²⁹Si MASNMR spectrum of montmorillonite and the exchanged montmorillonites show the silicon atom to be sensitive to the presence of the Quats in the interlayer region. Shifts of 0.6 ppm were observed for the Q³ resonance when spectra of montmorillonite and HDTMA-montmorillonite materials were compared. Characterisation of HDTMA-montmorillonite by XPS Br(3d) suggests that washing of the Quat-smectite product removes the unexchanged HDTMA⁺Br⁻. Results from the N(1s) XPS analysis show that there is a change in the environment of the nitrogen atom on exchange, N(1s) HDTMA-montmorillonite exhibiting a higher binding energy than N(1s) HDTMA⁺Br⁻. This increased binding energy may be due to the interaction of the N in the exchanged clay, with the O of the silicate layer. The O atom is more electronegative than Br, resulting in the higher binding energies of the core electrons of the nitrogen atoms. This may lead to an increase in the N-C bond strengths within the Quat.

3.3 Preparation of exchanged Quat-laponites by the Wet method

There is no established method for the preparation of exchanged laponite RD clays, though Vansant and co-workers^{96,97} have studied the exchange reactions of laponite CP. The method of exchange used in their work was devised to facilitate study of the thermodynamics of exchange and is not dissimilar to those used in the synthesis of Quat-montmorillonites. That is, the conversion of the clay to the sodium form and the exchange in excess of the c.e.c.

3.3.1 Exchanged laponites: Preliminary studies

In conjunction with initial studies of montmorillonite (Section 3.2), parallel studies of the synthesis of HDTMA exchanged laponites were conducted. Experiments were carried out in ethanolic media, using 1.4 g (the amount required to satisfy the c.e.c.), 2 g, 3 g, and 5.6 g of HDTMA⁺Br⁻. All experiments were carried out in duplicate and one HDTMA-laponite sample of the pair was washed with 100 cm³ ethanol, the other remained unwashed. This ethanolic wet method used to obtain HDTMA exchanged laponite was one based on that used by the clay research group at Aston for the pillaring of laponite with organometallic compounds⁹³. The percentage exchange observed for reactions at different c.e.c.s is shown in Table 3.11.

Table 3.11 Percentage exchange observed for washed HDTMA-laponite products prepared in ethanolic solution

HDTMA ⁺ Br ⁻ added (g)	Na ⁺ exchanged (%)
1.4 (at c.e.c of clay)	1
2	13
3	23
5.6*	21

* For this experiment a basal spacing of 14.71 Å was recorded. The basal spacing of unreacted laponite was found to be 14.0 Å.

The low percentage of Na⁺ ions detected in the filtrate and significant increases in basal spacing (Table 3.11) in the presence of high HDTMA cation concentrations, suggest that as for the Quat-montmorillonites, large quantities of solvent will be needed for the removal of sodium cations from the Quat-laponite product. However, washing with large quantities of ethanol was not desirable, thus subsequent exchange reactions were carried out in distilled water as for the synthesis of Quat-montmorillonites.

The ²⁹Si MASNMR spectrum of laponite RD has two characteristic peaks the one furthest upfield being termed Q³ and that downfield, Q². The Q² peaks result from the presence of silicon sharing oxygen with two other silicon atoms. The presence of silicon sharing oxygens with three other silicon atoms results in a Q³ peak. In the case

of laponite, the Q² peak results from the presence of a silicon atom at an edge site and Q³ from the presence of a silicon atom within the silicate layer.

Samples of laponite and exchanged HDTMA-laponite in an ethanolic media were submitted for ²⁹Si MASNMR. A similar experiment to that described in Section 3.2 was conducted to assess the errors incurred in the ²⁹Si MASNMR experiment. ²⁹Si MASNMR spectra of laponite and HDTMA-laponite, both before and after washing with ethanol, were determined and compared. Samples from the same reaction were submitted on three different occasions. It was found that the Q² and Q³ resonances for the laponite clay were highly variable, compared to those of the bentonite clay. The results are tabulated in Table 3.12. It can be seen that the Q³ is sensitive to the exchange reaction but the Q² is not.

Table 3.12 Summary of ²⁹Si MASNMR results of laponite materials

material	Q ² ppm	Q ³ ppm
laponite	84.1 ± 0.4	94.4 ± 0.3
HDTMA-laponite	84.8 ± 0.3	94.9 ± 0.06
washed HDTMA-laponite	84.4 ± 0.3	94.9 ± 0.1

Table 3.13 Summary of ²⁹Si MASNMR results of exchanged laponite products

Sample	Q ² ± 0.4 ppm	Q ³ ± 0.3 ppm
Laponite	-84.72	-94.22
HDTMA-laponite washed	-84.65	-94.93

The results of the analysis of the laponite exchange reaction are presented in Table 3.13 and examples of the spectra can be found in Figures 3.5a and 3.5b. As can be seen from the MASNMR results in Table 3.13, the Q² peak is insensitive to the

exchange reaction. The Q^3 peak however, is sensitive to the exchange reaction as can be seen in its upfield shift from -94.22 ppm to -94.93 ppm. This is consistent with the increase in basal spacing observed, though not consistent with the percentage of sodium ions detected in the filtrate.

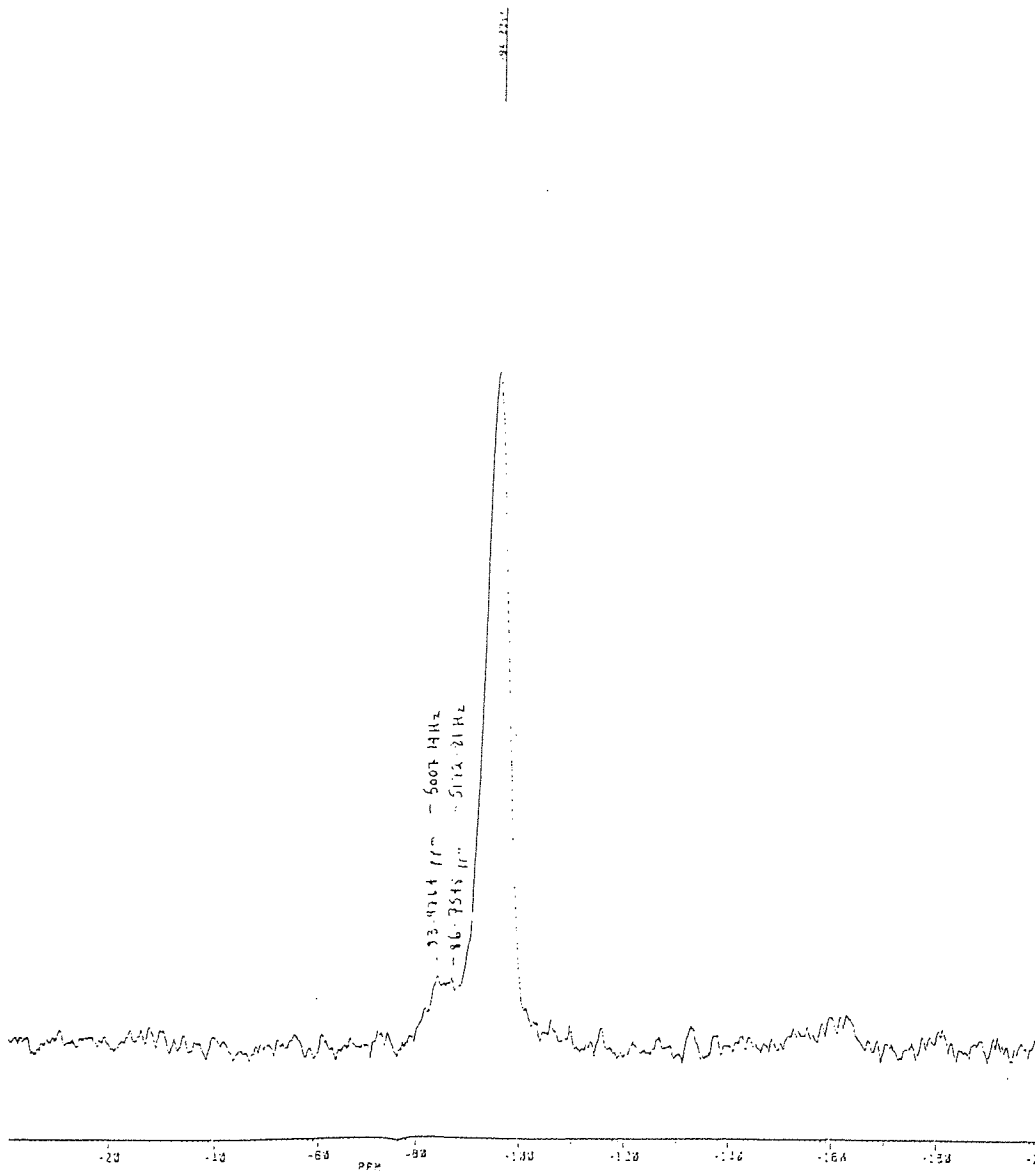


Figure 3.5a ^{29}Si MASNMR spectrum of laponite

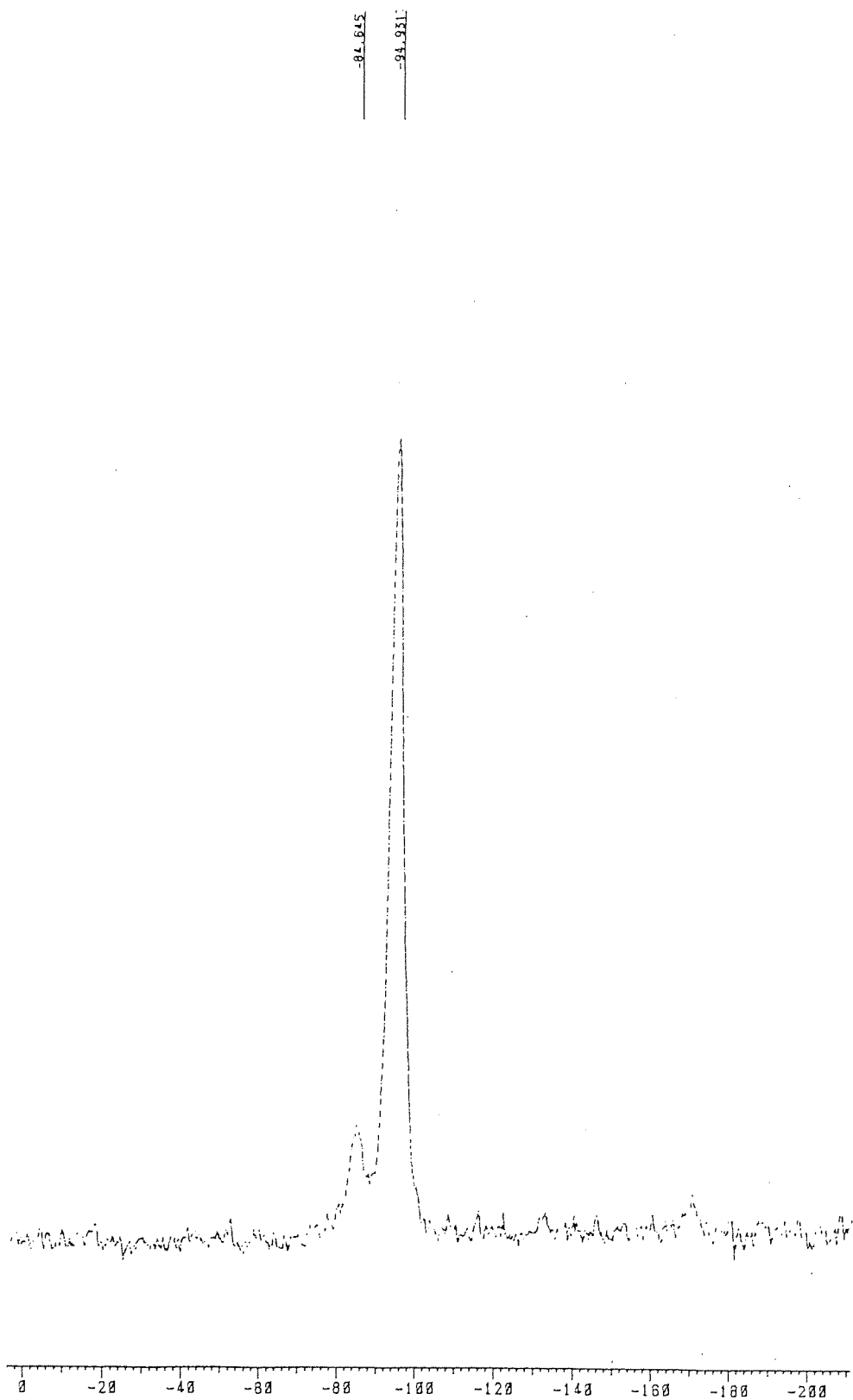


Figure 3.5b ^{29}Si MASNMR spectrum of HDTMA-laponite

3.3.2 Preparation of fully exchanged laponites

The problem of detection of sodium displacement in the exchange reactions of montmorillonite clays was resolved by thorough washing of the Quat-clay product. The results in Table 3.14 show the percentage sodium displaced during the preparation of HDTMA-laponite in aqueous solution and the effect of washing HDTMA-laponite on further displacement.

Thus the method used for preparation of Quat-laponites was as follows: a 200 cm³ aqueous solution of the amount of Quat required to satisfy the c.e.c. of laponite was placed in a 500 cm³ conical flask and 2.5 g laponite added. The flask was then stoppered and shaken at ambient temperature for 1 week. The product was filtered, washed with 1 dm³ distilled water/5 g laponite and air dried. The filtrate was retained and analysed by Na⁺ atomic absorption. The reaction was carried out in duplicate. One sample was washed with 1 dm³ of distilled water, the other remained unwashed. Atomic absorption measurements were made of the filtrate of the unwashed experiment and of the combined filtrate and washings of the washed experiment. Table 3.14 shows the results.

Table 3.14 HDTMA-laponite exchanged in aqueous solution

Experiment	% Na ⁺ exchanged (± 8%)
HDTMA-laponite unwashed	89
HDTMA-laponite washed	100

Applying the conditions of the bentonite exchange reaction to laponite exchange reaction has yielded extremely encouraging results with respect to sodium atomic absorption results. These results suggest that a high percentage of exchange can be achieved and detected even before washing the product (Table 3.14) and when the product is washed 100% exchange can be observed.

When the percentage exchange results of the washed (100 cm³ ethanol) HDTMA-laponite products (Table 3.12) and the unwashed (aqueous solution) HDTMA-laponite products (Table 3.14) are compared at equal c.e.c.s of exchange, 1% and 89% sodium

cations are displaced respectively. This would suggest that in the former reaction, which occurs in ethanol solvent, two reactions may occur. These two reactions are the exchange reaction of laponite with HDTMA cations or the solvation of the sodium cations of laponite with ethanol. It appears that the sodium cations are preferentially solvated by ethanol at low HDTMA concentrations. As the concentration of HDTMA cations increases, the displacement of the sodium cations increases. The results of this reaction could be confirmed by the thorough ethanolic washing of the HDTMA-laponite synthesised in ethanolic media, and measurement of the sodium ions released.

3.3.3 Characterisation of fully exchanged laponites

The Quat-laponites were characterised using Atomic absorption (AA), X-ray diffraction (XRD), silicon-29 magic angle spinning nuclear magnetic resonance (^{29}Si MASNMR) and X-ray photoelectron spectroscopy (XPS).

3.3.3.1 Atomic Absorption (AA)

The percentage exchange observed for the HDTMA-laponite reaction in aqueous solution is as one would expect. Calculations are facilitated by the knowledge of the chemical formula of the laponite clay. This known, the accurate sodium content can be calculated and thus the amount expected to be released on exchange. Table 3.15 shows the percentage exchange occurring when HDTMA, HDPY, and TMPA cations react with laponite clay. As in the case of montmorillonite, the percentage of sodium released varies with the Quat used for the reaction. The spread of the sodium release is again 16%. In the case of the montmorillonite both TMPA and HDPY cations exchanged to the same degree. For the laponite the HDPY cation is seen to exchange to a lesser degree. Again orientation is thought to govern the percentage exchange, as it is the Quats which have aromatic groups present that deviate from the 100% exchange expected.

3.3.3.2 X-ray Diffraction (XRD)

As with the AA results, the XRD results show that exchange is affected by the presence of aromatic groups. The Quats containing aromatic groups yield exchanged laponites with basal spacings in the order of 14.7 - 14.8 Å and the HDTMA-laponite has a basal spacing of 14.0 Å. This confirms previous theories that the alkyl group

lies flat against the silicate layer in the exchange reactions between the HDTMA cations and the smectite clays³⁵. In the reactions between HDPY and TMPA, the orientation

Table 3.15 Percentage exchange and basal spacing results from the synthesis of Quat-laponites washed with 1 dm³ distilled water

Quat*	Exchange % (± 8%)	Basal spacing (Å)
HDTMA+Br ⁻	100	14.01
HDPY+Cl ⁻	74	14.77
TMPA+Cl ⁻	92	14.71

* Quat added to satisfy the c.e.c of laponite
laponite d(001) = 12.95 Å

of the aromatic group is flat and parallel to the silicate layer⁵⁹. For all the Quat laponites, the Quats are arranged in a monolayer in the interlayer region hence basal spacings of 14 - 15 Å, rather than the 14 - 18 Å observed for the Quat-montmorillonites where the Quats take up either a monolayer or bilayer arrangement⁶².

3.3.3.3 29-Silicon magic angle spinning nuclear magnetic resonance (²⁹Si MASNMR)

Samples were not submitted for ²⁹Si MASNMR analysis, however, typical spectra can be seen in Section 3.6.2.3.

3.3.3.4 X-ray Photoelectron Spectroscopy (XPS)

Here, it will be demonstrated that the Quat-laponites may also be characterised by XPS (Section 3.2.3 showed the characterisation of exchanged montmorillonites could be achieved). Tables 3.16 and 3.17 display results of XPS analysis. Table 3.16 shows the results of the Br(3d) analysis of HDTMA-laponite. A washed sample of HDTMA-laponite was sent for XPS analysis along with samples of HDTMA⁺Br⁻ and NaBr, which were sent as a standards. This was to obtain additional support for the complete exchange of HDTMA onto montmorillonite clay and to ensure no excess HDTMA⁺Br⁻ was present, trapped in the clay matrix. The spectra are shown in Figures 3.6a - c.

Table 3.16 XPS analysis of bromine in HDTMA-laponite

Sample	Peak centre Br(3d) binding energy (± 0.2 eV)
HDTMA+Br ⁻	67.00
HDTMA-laponite	/*
NaBr reference	68.7

* Br undetected in this sample

Bromine was not detected in the Quat-laponite product. This suggests that all the Quat present, is present as the exchanged cation, neither HDTMA⁺Br⁻ or NaBr are present in the HDTMA-laponite product. This is important for the application of the Quat-clays to adsorption as described in Section 3.2.3.

Table 3.17 XPS analysis of nitrogen in HDTMA-laponite

Sample	Peak centre N(1s) binding energy (± 0.2 eV)
HDTMA+Br ⁻	401.8
HDTMA-laponite	402.8

Table 3.17 shows the results of the N(1s) XPS experiments. These experiments were carried out to investigate the effect of exchange on the N atom of the quaternary ammonium cation.

The binding energy of the nitrogen in the Quat-laponite product is 1.0 eV greater than in the Quat before exchange. This can be attributed to stronger cation anion interactions and/or greater N-C bond strengths as described in Section 3.2.3. The amine peak that was initially observed for the HDTMA-montmorillonite product was not observed in the HDTMA-laponite spectrum.

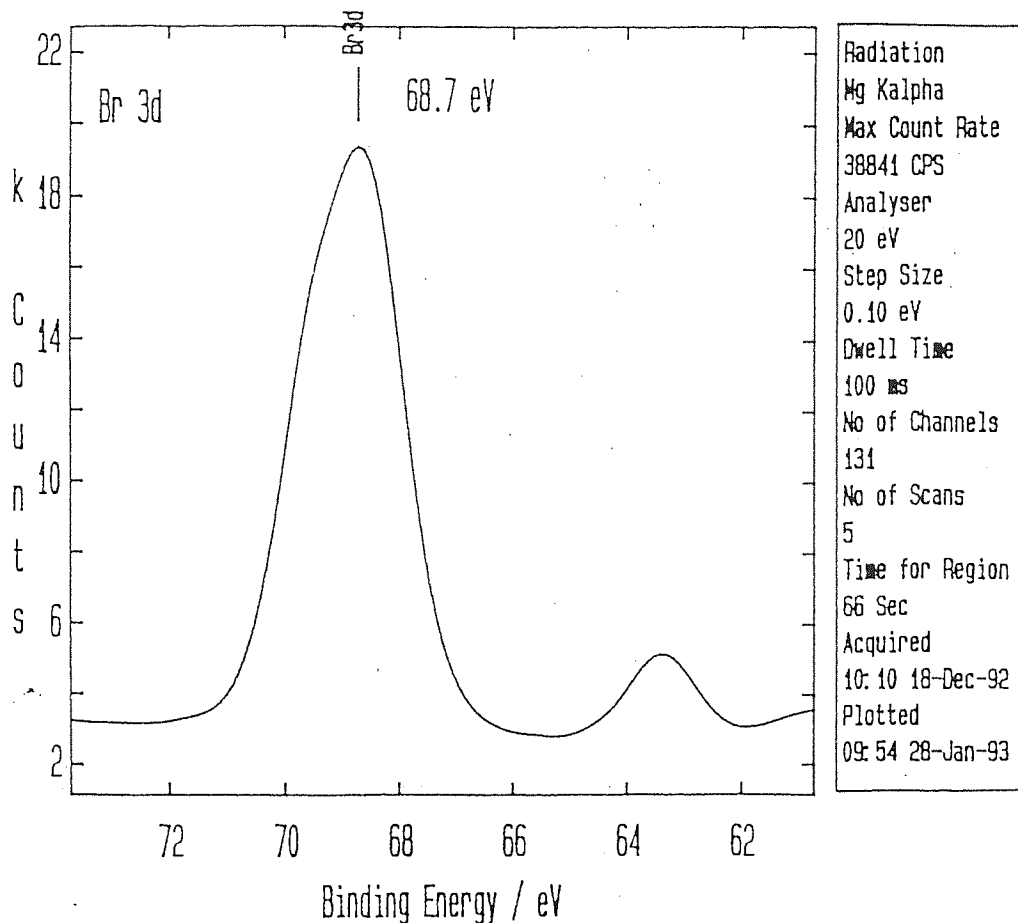


Figure 3.6a Br(3d) XPS spectrum of NaBr

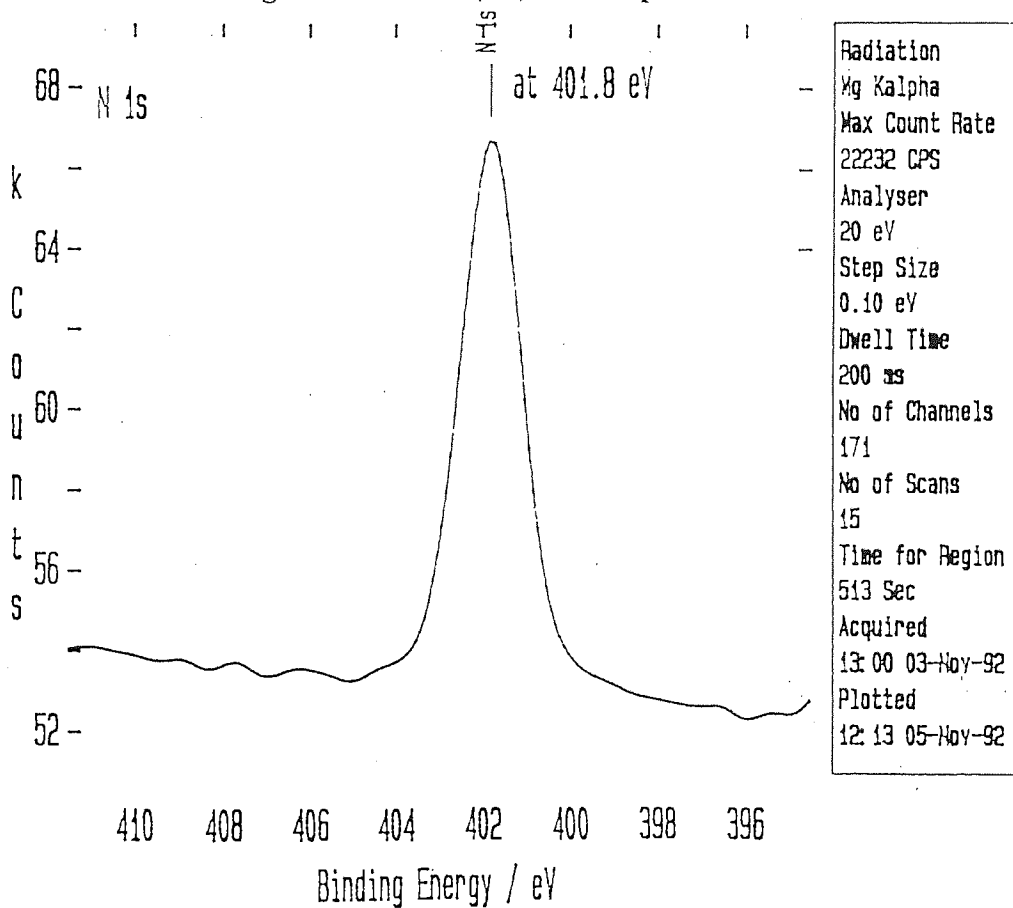


Figure 3.6b XPS spectrum of HDTMA+Br⁻

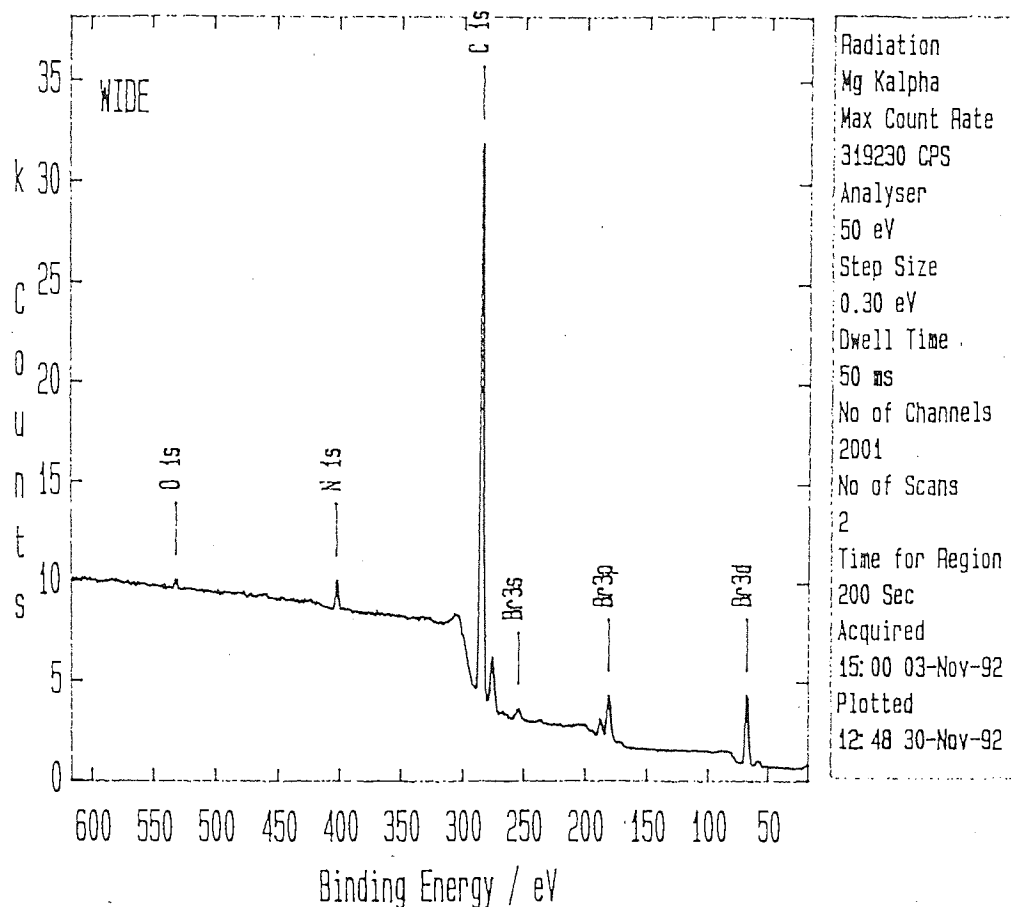


Figure 3.6c XPS spectrum of HDTMA-laponite

3.3.4 Exchanged Laponites - Conclusions

Fully exchanged HDTMA-, HDPY- and TMPA-laponites were prepared by similar methods as those used for the preparation of fully exchanged montmorillonites. The basal spacings of the products are typical of Quat-smectites in which the quaternary ammonium cations are arranged in a monolayer in the interlayer region. As for the montmorillonite clay, the quantity of sodium ions released on exchange depended on the Quat. Exchange with the HDTMA cation resulted in the highest sodium ion release, followed by the TMPA cation. The HDPY cation displaced significantly less sodium ions than the two former Quats.

^{29}Si MASNMR spectrum of montmorillonite and the exchanged montmorillonites show the Si atom to be sensitive to the presence of the Quats in the interlayer region. Shifts of 0.1 - 0.3 ppm were observed for the Q^3 resonance when spectra of laponite and HDTMA-laponite materials are compared. Characterisation of HDTMA-laponite by XPS Br(3d) showed that no Br^- ions were detected in the sample. This suggests

that washing removes the unexchanged HDTMA⁺Br⁻ and a large concentration of the NaBr ion pairs from the exchanged laponite product. As observed for the HDTMA-montmorillonite, results from the N(1s) XPS analysis show that there is a change in the environment of the nitrogen atom on exchange. This is attributed to the interaction of the nitrogen in the exchanged clay, with the oxygen of the silicate layer. The oxygen atom is more electronegative than bromine atom, resulting in the higher binding energies of the core electrons of the nitrogen atoms. This may lead to an increase in the N-C bond strengths within the Quat.

3.4 Adsorption Isotherms

Section 3.1 briefly outlined the adsorption studies of Mortland et al.⁵⁶. The phenols studied by Mortland were phenol, 3-chlorophenol, 3,5-dichlorophenol, 3,4,5-trichlorophenol, 2,4,6-trichlorophenol. Detailed studies of 2,4,6-trichlorophenol were not carried out. The findings of Mortland et al. are summarised in Table 3.18.

Table 3.18 Summary of adsorption of phenol and chlorinated phenols by Quat-montmorillonites, after Mortland et al.⁵⁶

	Adsorbent		
	HDTMA-mont	HDPY-mont	TMPA-mont
Adsorbate			
phenol	na	na	V
3-chlorophenol	V	V	III
3,5-dichlorophenol	V	V	III
3,4,5-trichlorophenol	I	I	III
2,4,6-trichlorophenol	V	ni	ni

na - no adsorption

ni - no isotherm studied.

Quat-montmorillonites with relatively high hydrophobicities, HDTMA-montmorillonite and HDPY-montmorillonite, adsorbed the phenols from water in proportion to their solubilities. The hydrophobic adsorbents, adsorbed the hydrophobic adsorbates. Thus adsorption capacity and/or strength of interaction increased in the order phenol < chlorophenol < dichlorophenol < trichlorophenol. For

TMPA-montmorillonite, only phenol was adsorbed. This was explained as being due to the partially hydrophobic and partially hydrophilic adsorbent only being able to adsorb compounds with similar properties.

In this study, the choice of phenols was guided by those which appear in the list of priority pollutants⁸¹. Phenol, 2-chlorophenol, and 2,4,6-trichlorophenol are detected in water or sediment, they are persistent but non-accumulative and are toxic on direct exposure⁸¹. The two phenol groups - that studied by Mortland et al.⁵⁶ and that to be studied here - possess parallel solubility properties, thus similarities should be observed in adsorption interactions and capacities.

The UV absorption spectrum of the phenols to be studied - phenol, 2-chlorophenol, and 2,4,6-trichlorophenol in aqueous solutions - were obtained as described in Section 2.3. λ_{\max} was found to be at 268 nm, 274 nm and 293 nm respectively. It was found that the Beer-Lambert law was obeyed by phenol at 268 nm and 2-chlorophenol at 274 nm in the concentration range 8×10^{-4} - 8×10^{-3} M and 2,4,6-trichlorophenol at 293 nm in the range 1×10^{-3} - 1×10^{-2} M.

Adsorption isotherms were obtained by weighing 100 mg quantities of the Quat-clay into 250 cm³ conical flasks containing 1.0, 0.8, 0.6, 0.5, 0.4, 0.2 and 0.1 mmole/g 2,4,6-trichlorophenol, and between 0.8, 0.6, 0.5, 0.4, 0.2, 0.1 and 0.08 mmole/g phenol or 2-chlorophenol in distilled water. The total volume of solution was 100 cm³. The flasks were shaken over two nights in a temperature-controlled shaking water bath at 20 °C, filtered and the solution analysis carried out by UV. All the glassware used in this experiment was degreased periodically. The concentration at which the phenols were studied facilitated UV studies as further dilutions were not required before analysis could take place. All isotherms were measured in duplicate.

Control experiments were carried out for all Quat-clay systems investigated for adsorption. The experimental procedure outlined above was followed omitting the addition of the phenolic compound. That is, the Quat-clay is shaken at 20 °C in 100 cm³ distilled water. Results show that for each Quat-clay system at the appropriate UV band for detection of the phenols, no absorption arises due to the presence of the Quat. This is reassuring as the Quats do not interfere with the UV absorption studies and perhaps more importantly, there is no desorption of the Quats from the clay minerals.

Figures 3.7 - 3.9 show the adsorption isotherms of the adsorption of phenol, 2-chlorophenol, 2,4,6-trichlorophenol onto:

HDTMA-montmorillonite - Figure 3.7a,
HDTMA-laponite - Figure 3.7b,
HDPY-montmorillonite - Figure 3.8a,
HDPY-laponite - Figure 3.8b,
TMPA-montmorillonite - Figure 3.9a,
TMPA-laponite - Figure 3.9b,

Tables 3.18 - 3.20 summarise the results

Table 3.18 Summary of adsorption of phenols and chlorinated phenols by Quat-montmorillonites, after Mortland et al.⁵⁶

	Adsorbent		
	HDTMA-mont	HDPY-mont	TMPA-mont
Adsorbate			
phenol	na	na	V
3-chlorophenol	V	V	III
3,5-dichlorophenol	V	V	III
3,4,5-trichlorophenol	I	I	III
(2,4,6-trichlorophenol	V	ni	ni

na - no adsorption

ni - no isotherm studied.

Table 3.19 Adsorption of phenol and chlorinated phenols by Quat-montmorillonites - results obtained in this study

	Adsorbent		
	HDTMA-mont	HDPY-mont	TMPA-mont
Adsorbate			
phenol	na	na	V
2-chlorophenol	V/C	V	na
2,4,6-trichlorophenol	C	C	na

na - no adsorption

Table 3.20 Adsorption of phenol and chlorinated phenols by Quat-laponites

	Adsorbent		
	HDTMA-lap	HDPY-lap	TMPA-lap
Adsorbate			
phenol	na	na	III
2-chlorophenol	I	C	na
2,4,6-trichlorophenol	I	I	na

na - no adsorption

3.4.1 The nature of adsorption

The choice of method employed to obtain adsorption isotherms was guided very much by the work of Mortland⁵⁶. Isotherms, obtained by reaction at constant temperature, were measured at 20 °C. Figures 3.7 - 3.9 show isotherms of the adsorption of phenol, 2-chlorophenol, and 2,4,6-trichlorophenol from water onto HDTMA-, HDPY-, and TMPA-montmorillonites and laponites. It can be seen that the overall pattern observed by Mortland et al. for adsorption of phenols by exchanged montmorillonites, was as observed here with the new group of phenols under investigation. That is, adsorption of the chlorinated phenols was enhanced by using exchanged clays with long alkyl groups present and adsorption of phenol was enhanced by use of adsorbents with more compact Quats present. Interactions between the chlorinated phenols and the long alkyl chain containing adsorbents were generally greater both in capacity and interaction than that observed between the phenol and the compact adsorbents. In the group of phenols investigated here, all interactions were characteristic of weak adsorbate-adsorbent interactions, no Langmuir or Type I interactions being observed.

As an aside it seems that adsorption capacities have not been significantly reduced by the use of a montmorillonite not fully converted to the sodium form, and subsequently undergoing reduced exchange compared to the Quat clays of Mortland et al.⁵⁶.

The isotherms in Figures 3.7a and 3.8a represent adsorption of the phenols by HDTMA-montmorillonite and HDPY-montmorillonite. These isotherms exhibit

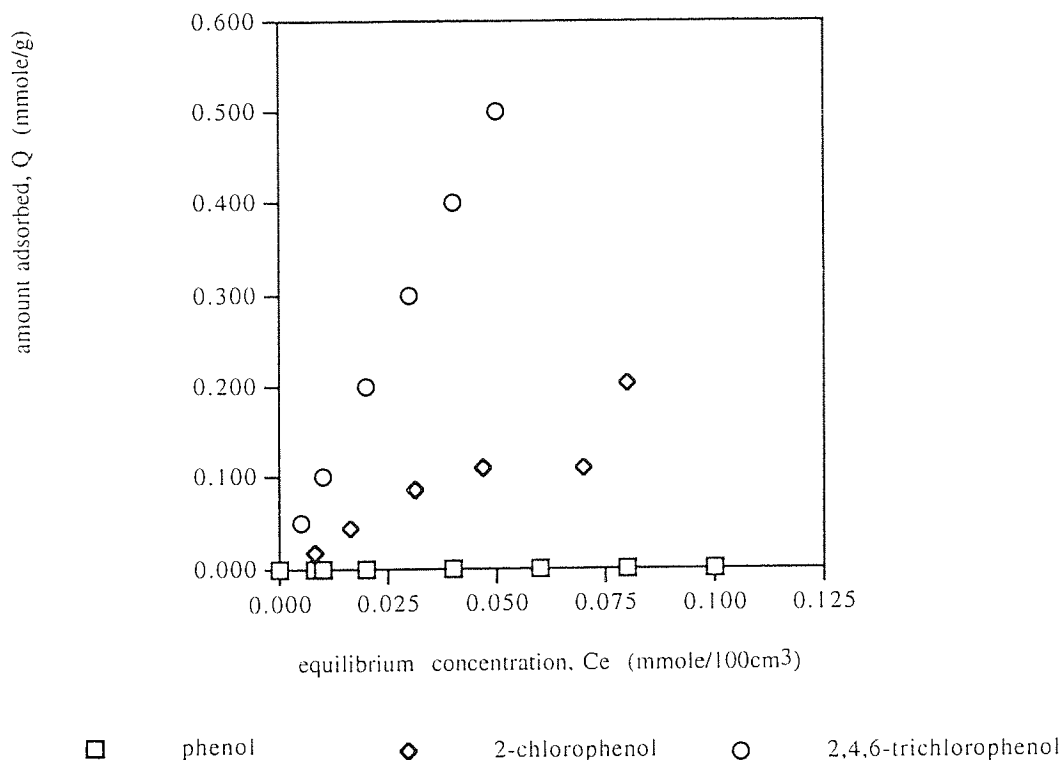


Figure 3.7a Adsorption of phenols from water on HDTMA-montmorillonite

marked differences for the various phenols. As the number of chlorine atoms on the phenol structure was increased, the greater was the adsorption, in terms of capacity and interaction, on the Quat-montmorillonite. Phenol, the most hydrophilic of the phenolic molecules, was not adsorbed at all by these Quat-montmorillonites. One index of the hydrophilic properties of these molecules is their solubility in water (phenol > 2-chlorophenol > 2,4,6-trichlorophenol). An inverse relationship is demonstrated between hydrophilicity of the adsorbate and the adsorption on the hydrophobic surface, thus suggesting that as the hydrophilic properties of molecules decrease, adsorption increases via hydrophobic interaction. All isotherms obtained were typical of weak adsorbate-adsorbent interactions, phenol was not adsorbed and both chlorinated phenols gave Type C isotherms, indicative of a partitioning process, or Type V isotherms. Type C isotherms occur due to the partitioning of the chlorinated phenols between the water solvent and the organophilic Quat-smectite, and Type V isotherms are indicative of a weak adsorbate-adsorbate interactions particularly at low equilibrium concentrations. In the case of interactions via partitioning processes, this suggests that the two chlorinated phenols view the Quat-

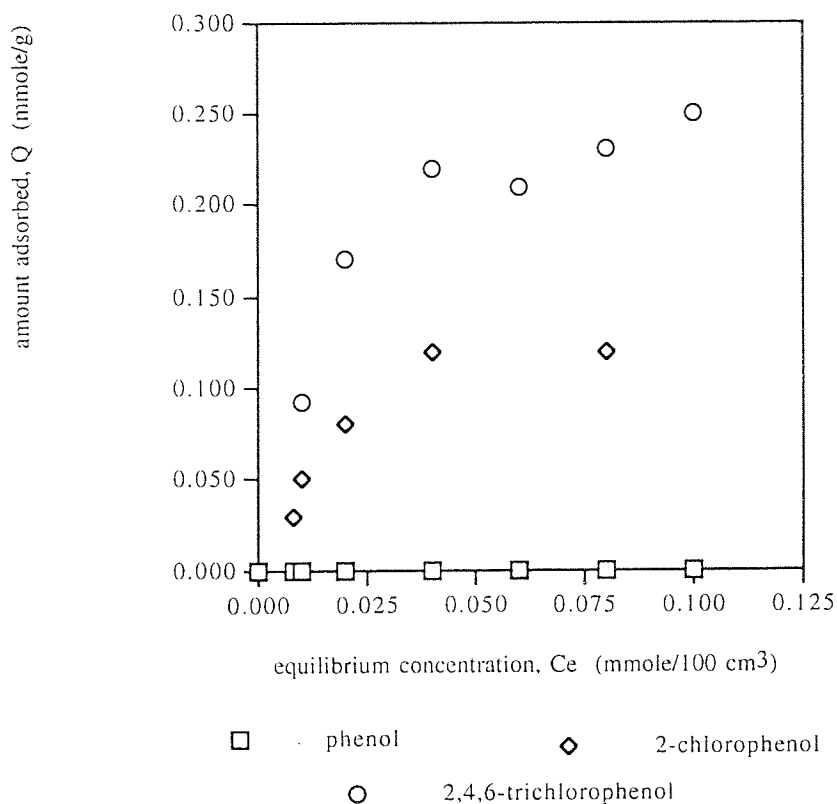


Figure 3.7b Adsorption of phenols from water on HDTMA-laponite

montmorillonite as a type of "organic solvent" and they preferentially interact with the "organic solvent". The phenol being more hydrophilic is not attracted to the "organic solvent". In the partitioning process, the availability of adsorption sites remains constant at all concentrations up to saturation. Linearity suggests that as more adsorbate is adsorbed, more sites must be created. The adsorbate may be able to penetrate into the structure of the adsorbent in regions not already penetrated by the solvent. Partitioning is favoured by the adsorbate having a higher affinity for the adsorbent than for the solvent. As in the work of Mortland⁵⁶, isotherms for the HDPY-montmorillonite adsorbent were the same as those for HDTMA-montmorillonite.

Comparison of adsorption with the HDTMA- and HDPY-laponite adsorbents with the HDTMA- and HDPY-montmorillonite adsorbents shows that both sets of adsorbents exhibit some similar adsorption characteristics. That is the same adsorbates are adsorbed by the same Quat constituent of the adsorbents regardless of the clay. However, where adsorption occurs it does so with a stronger interaction for the

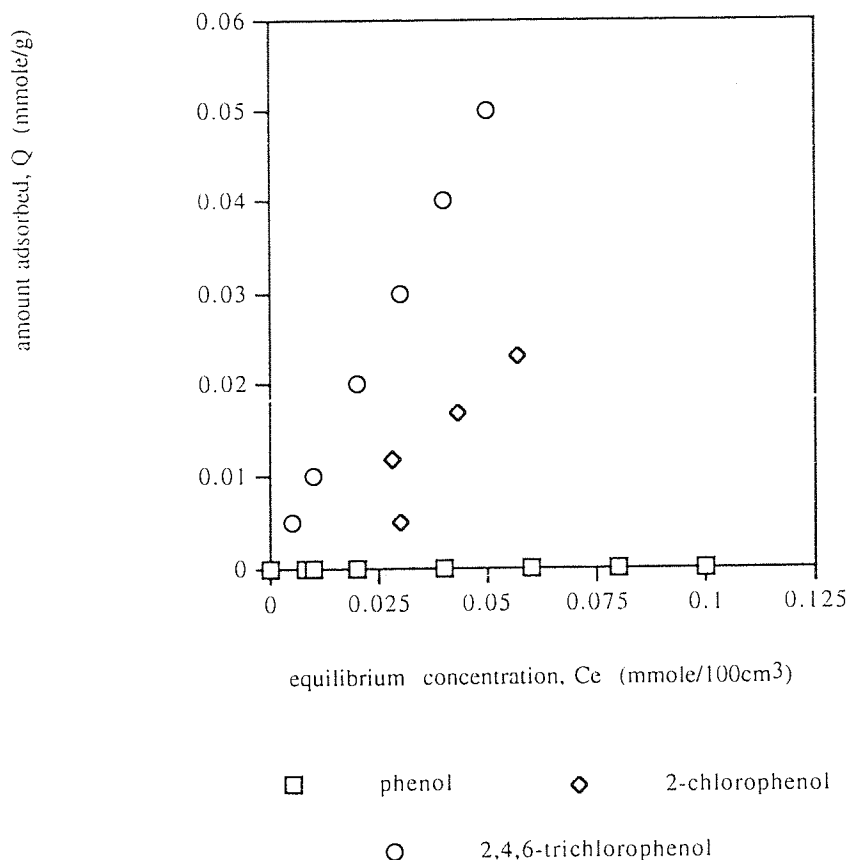


Figure 3.8a Adsorption of phenols from water on HDPY-montmorillonite

laponite based adsorbents than for the montmorillonite based adsorbents. The HDTMA-laponite demonstrates this well. The adsorption capacity is still observed to occur in the order phenol < 2-chlorophenol < 2,4,6-trichlorophenol as is observed for HDTMA-montmorillonite. However, adsorption of the chlorinated phenols yields Type I isotherms for the HDTMA-laponite adsorbent, characteristic of strong adsorbate-adsorbent interactions at all equilibrium concentrations. The initial slope of the isotherm results from the presence of a solute which has such an affinity for the adsorbent that it is completely or almost completely adsorbed.

Jaynes and Boyd⁶¹ studied the adsorption of benzenes and alkyl benzenes by various HDTMA exchanged clays, for example, vermiculites, illites, smectites and kaolinite. The study was directed at the effect of layer charge on adsorption of alkylbenzene compounds. Complete exchange occurred for all the clays, but only the smectites and vermiculites showed an increase in basal spacing. Where interlayer expansion

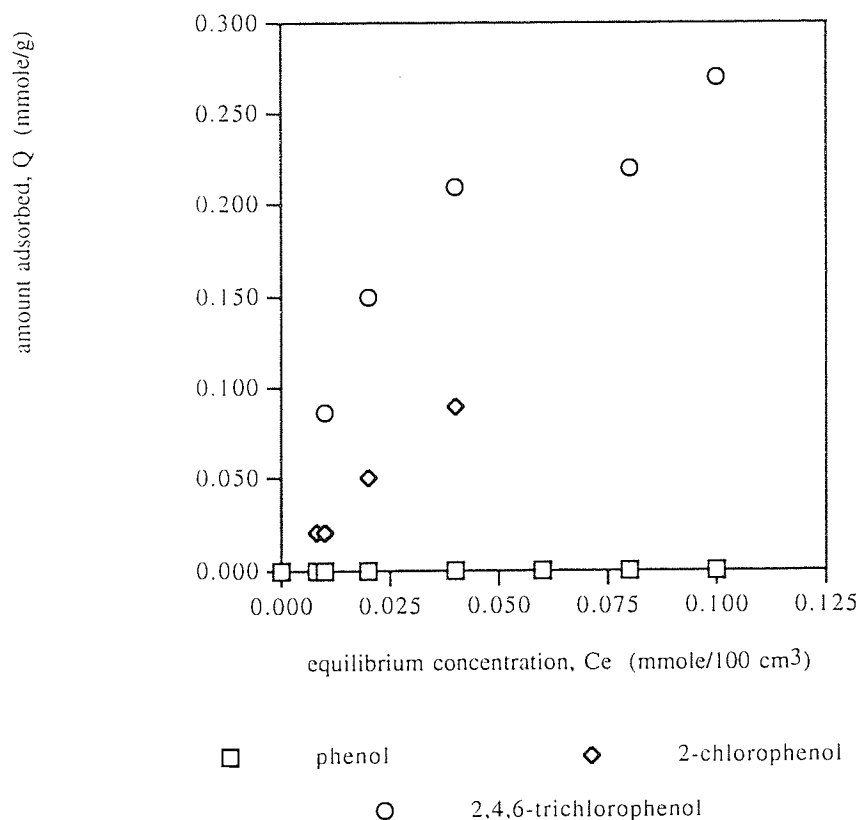


Figure 3.8b Adsorption of phenols from water on HDPY-laponite

occurred, the basal spacings were attributed to formations of bilayers, pseudotrimolecular layers and paraffin complex layer formation⁶². No basal spacing measurements attributable to monolayer arrangements were observed. Adsorption isotherms of alkylbenzene compounds onto a high charge HDTMA-clay and low charge HDTMA-clay were measured in detail. The HDTMA content of both was comparable. All isotherms were linear, the adsorption capacity was higher for the high charged clay than the low charge clay. It was suggested that the difference in adsorption characteristics was due to the greater basal spacing for the high charge clay which was able to accommodate the alkylbenzene compounds to a greater extent than the low charge clay. The high charge clay had a paraffin complex layer formation and the low charge clay a bilayer formation. The arrangement in the interlayer region was thought to influence adsorption. The amount of HDTMA present in the clay interlayer region was also observed to influence adsorption. The greater the HDTMA content, the greater the adsorption observed.

From Sections 3.2.3 and 3.3.3 it can be seen that the two HDTMA exchanged clays studied have different interlayer arrangements. HDTMA-laponite is thought to have a monolayer arrangement and HDTMA-montmorillonite, bilayer. The HDTMA contents

of the clays differ, the montmorillonite having the higher HDTMA concentration. It is seen then, in the case of these two adsorbents, a monolayer arrangement favours adsorption of the chlorinated phenols in terms of strength of interaction, but in terms of capacity either a bilayer arrangement or high HDTMA content is favoured. The reason for greater interaction when a monolayer arrangement occurs is not yet clear, but it is possible that the bilayer arrangement though creating more space for adsorption, also leads to greater van der Waals interactions between alkyl chains on opposite surfaces of the interlayer region, thus possibly reducing the interactions between the HDTMA and the adsorbates. The monolayer arrangements of the HDTMA cations in the laponite effectively frees the cations to interact with incoming adsorbate molecules only.

HDPY-laponite again shows a similar pattern of adsorption capacity to HDTMA-laponite, but unlike the HDTMA-laponite, distinguishes between the chlorinated phenols adsorbing the 2,4,6-trichlorophenol with a Type I isotherm and the 2-chlorophenol with a Type C isotherm. Here it appears that the pyridinium group affects the interaction taking place between the alkyl chain and the chlorinated phenol adsorbates. Adsorbate-solvent interactions may also be effectively competing with adsorbate-adsorbent interactions in the case of 2-chlorophenol and HDPY-laponite.

The adsorption of phenols from water onto TMPA-montmorillonite was quite different (Figure 3.9a), phenol was adsorbed whereas the chlorinated phenols were not, this was also the case for TMPA-laponite. The phenol isotherm was a typical Type V isotherm for TMPA-montmorillonite which indicates weak adsorbate-adsorbent interactions, causing adsorption at low equilibrium concentrations to be low. Once a molecule is adsorbed, however, adsorbate-adsorbate interactions promote the adsorption of more molecules in a co-operative fashion. The same pattern was observed for TMPA-laponite but a Type III isotherm resulted. This isotherm results from low adsorptions throughout the concentration range. Mortland et al.⁵⁶ suggested that adsorption was probably via the interactions of phenol with the silicate layer, however, if this was the case, adsorbate-adsorbent interaction should have increased with the TMPA-laponite due to the increased ratio of silicate layer to quaternary ammonium cations. The adsorption capacity was also significantly decreased for the TMPA-laponite.

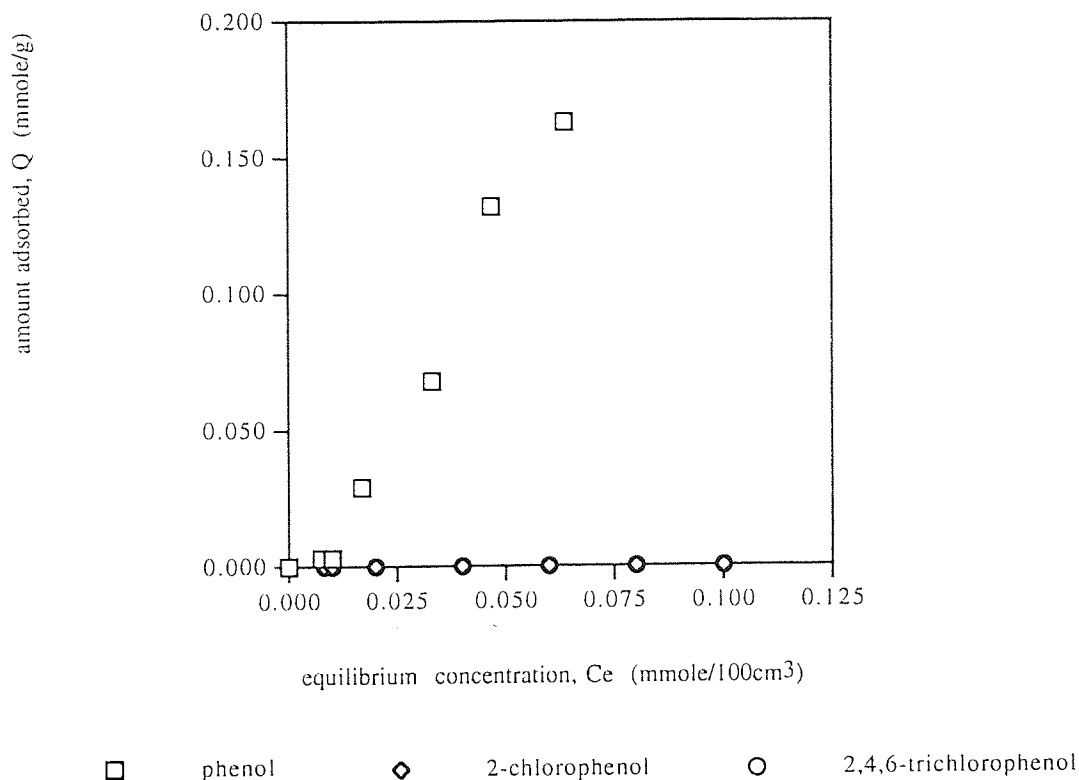


Figure 3.9a Adsorption of phenols from water by TMPA-montmorillonite

In the adsorption of alkylbenzenes by TMPA exchanged clays of various types it was observed that adsorption was inversely proportional to TMPA cation content. This suggested that the alkylbenzenes interact with the silicate layer and the TMPA cations simply act as pillars. Alkylbenzenes appear to be able to interact with the silicate layers with strong adsorbate-adsorbent interactions as evidenced by Type I isotherms. Phenol adsorption by the TMPA-smectites does not appear to follow the same pattern as the alkylbenzenes. From the two smectites studied, phenol adsorption increases with TMPA content and decreases with exposure to the silicate layers. This would suggest that the TMPA cations are the adsorption sites.

The nature of the Quat and the smectite is important in determining the adsorption of the phenols. The adsorption observed results from the nature of the smectite clay, the adsorbate-adsorbent and the adsorbate-solvent interactions. Phenol interacted strongly with water and was not strongly attracted to the HDTMA-montmorillonite or HDTMA-laponite. The addition of chlorine to the phenol structure reduces the interaction with water and thus allows a more significant hydrophobic interaction with HDTMA-montmorillonite and HDTMA-laponite and HDPY-laponite.

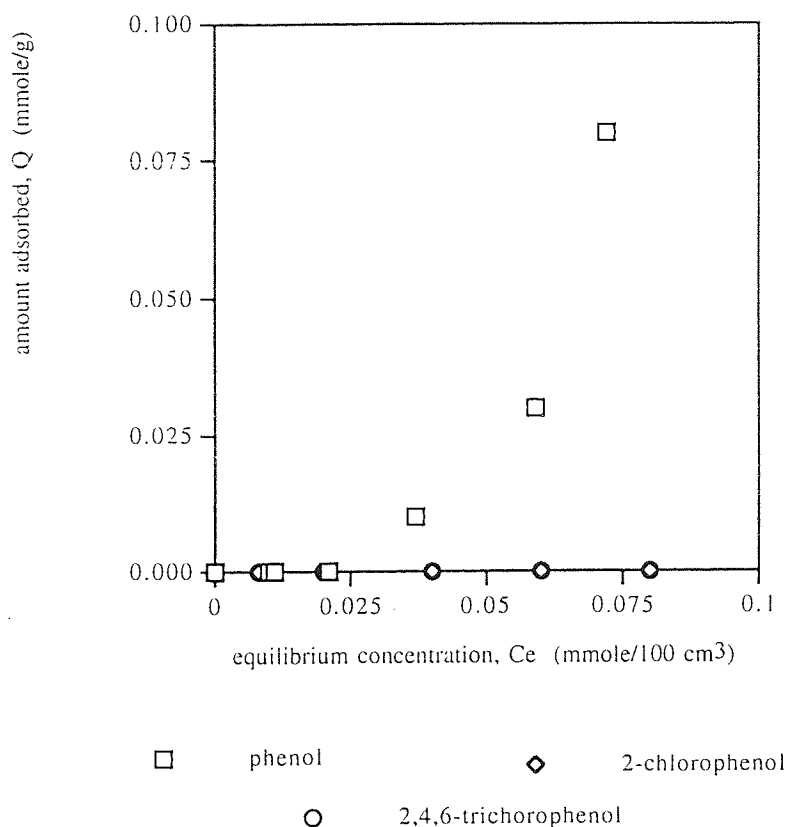


Figure 3.9b Adsorption of phenols from water by TMPA-laponite

Mortland suggests that for TMPA-montmorillonite, some surface oxygens of the silicate structure were exposed. Consequently, such a surface may have both hydrophobic properties bestowed by the Quat and more hydrophilic properties from the areas of exposed silicate oxygens. This slight hydrophilic content may have enhanced adsorption of phenol and decreased adsorption of the chlorinated phenols. Studies here confirm that it appears that some hydrophilic character in the adsorbent must be present to facilitate phenol adsorption, but suggest that the adsorption sites are the TMPA cations.

3.4.2 Adsorption isotherms - Conclusions

For adsorption by Quat-montmorillonites, phenolic compound adsorption was found to be Quat specific. The chlorinated phenols were adsorbed by the Quats containing long alkyl chains, and phenol was adsorbed by Quats containing aromatic groups. All the adsorption isotherms were typical of weak adsorbate-adsorbent interactions. These results show that the observations made by Mortland et al.⁵⁶ for a different group of chlorinated phenols also apply to the group of phenols studied in this work.

Adsorption by the HDTMA-montmorillonite and the HDPY-montmorillonite is dependant on the hydrophobicity of the adsorbate. The mechanism for phenolic compound adsorption is not clearly understood but the balance between adsorbate-solvent interactions and adsorbate-adsorbent interactions plays a part.

In adsorption by Quat-laponites, phenolic compound adsorption was again observed to be Quat specific. The same pattern of chlorinated phenols being adsorbed by the Quats composed of long alkyl chains and phenol being adsorbed by Quats without long alkyl chains was observed. The use of the laponite clay as a basis for the HDTMA and HDPY Quat-clays resulted in greater interaction between the chlorinated phenols and these Quat-laponites. Type I isotherms result from the adsorption of 2,4,6-trichlorophenol and 2-chlorophenol by HDTMA-laponite. The monolayer arrangement of HDTMA and HDPY cations in the interlayer region of the laponite clay leads to greater strength of adsorbate-adsorbent interaction, when the adsorbates are chlorinated phenols, when compared to HDTMA-montmorillonite. However, the adsorption capacities of the two HDTMA smectites are such that the adsorption capacity of HDTMA-montmorillonite is approximately twice that of the HDTMA-laponite. The strength of interaction between the HDTMA-montmorillonite and the 2,4,6-trichlorophenol may be reduced due to van der Waals interactions occurring between the HDTMA cations on opposite sides of the montmorillonite surfaces. The monolayer arrangement in the HDTMA-laponite affords greater interactions with the chlorinated phenols, but with only half of the adsorption capacity.

TMPA-laponite adsorbed phenol in a slightly different manner to the TMPA-montmorillonite. With both the TMPA-smectites, adsorptions were low initially but the TMPA-montmorillonite promoted adsorption via adsorbate-adsorbate interactions (Type V) whereas the TMPA-laponite did not (Type III). Phenol adsorption is proposed to be via interactions with the silicate layer. The results obtained in this study call this theory into question as adsorption by the lower charged TMPA-laponite was of a weaker interaction and lower capacity than the TMPA-montmorillonite. It is proposed that though exposure to the silicate surface is required for phenol adsorption, the TMPA cations may be the phenol adsorption sites.

3.5 Adsorption of 2-chlorophenol by HDTMA-montmorillonite.

3.5.1 Preparation of 2-chlorophenol-HDTMA-montmorillonite

The quantities of Quat-montmorillonite used for the adsorption isotherm experiments discussed above were 0.1 g. This quantity proved too small for analysis of 2-chlorophenol-HDTMA-montmorillonite clay material by spectroscopic methods which may confirm the presence of the 2-chlorophenol in the 2-chlorophenol-HDTMA-montmorillonite clay material, and the mechanism of adsorption. Thus a further, perhaps more crude, adsorption experiment was carried out. 100 cm³ of 1M aqueous solution of 2-chlorophenol was added to 1 g of HDTMA-montmorillonite in a 250 cm³ conical flask. This suspension was shaken as for the adsorption isotherm experiments at 20 °C for 2 nights, filtered and dried. The experiment was carried out in duplicate. After shaking for 2 nights, two different observations were made. In reaction vessel (a) the 2-chlorophenol separated from the solution onto the Quat-clay. The phase separation was distinct. In reaction vessel (b) the 2-chlorophenol solution remained unchanged throughout the reaction, that is, an opaque solution with some organic/water separation onto the Quat-clay occurring. It should be noted that in a 1M solution the 2-chlorophenol does separate from the water phase after approximately one week. In both cases the final solid product had the odour of 2-chlorophenol and was an extremely hard material (harder than the Quat-clay precursor).

The HDTMA-montmorillonite was exposed to a quantity of 2-chlorophenol greatly in excess of the expected adsorption, to ensure that the presence of the 2-chlorophenol, in the 2-chlorophenol-HDTMA-montmorillonite clay material, would be detected by X-ray Photoelectron Spectroscopy (XPS), Secondary Ion Mass Spectrometry (SIMS), and Fourier Transformed Infra-Red Spectroscopy (FTIR). Being the only phenolic compound of the three phenolic compounds consisting of a chlorine atom and being in the liquid state at room temperature made 2-chlorophenol a good model, as this meant a large amount could be exposed to the clay without needing large volumes of water for dilution purposes.

3.5.2 Characterisation of the 2-chlorophenol-HDTMA-montmorillonite material

3.5.2.1 XRD

Table 3.21 shows the basal spacing of the 2-chlorophenol-HDTMA-montmorillonite adsorption product. The high value obtained for the HDTMA-montmorillonite is probably due to the increased relative humidity at the site of analysis. The basal spacing of the 2-chlorophenol product is approximately 1.5 Å different from the HDTMA-montmorillonite precursor. This would suggest monolayer adsorption of the 2-chlorophenol in the interlayer region, though adsorption may occur at accessible sites between HDTMA molecules.

Table 3.21 Basal spacings of 2-chlorophenol-HDTMA-montmorillonite adsorption product

material	d(001) Å
montmorillonite	12.62
HDTMA-montmorillonite	20.07
2-chlorophenol-HDTMA-montmorillonite	21.53

3.5.2.2 XPS

The product from reaction vessel (a), see Section 3.5.1, was submitted for XPS analysis. The XPS results of interest are tabulated below (Table 3.22) and examples of the spectra are shown in Figure 3.10.

Br was detected at binding energy 68.2 eV, typical for NaBr (Table 3.9), and at concentrations too low to allow for the deconvolution of peaks. Initially, no Cl was detected. However, on scanning several times Cl was detected in small concentrations, the Cl concentration was also too low to allow for the deconvolution of peaks. Thus an accurate quantitative analysis of Cl content and thus 2-chlorophenol content could not be undertaken. The low 2-chlorophenol content is initially surprising. However, when one considers that XPS is a surface technique, the results suggest that 2-chlorophenol is not present on the surface of the montmorillonite and is therefore present in the interlayer region as suggested by XRD.

Table 3.22 XPS results of 2-chlorophenol-HDTMA-montmorillonite adsorption products

Element	Binding energies eV (± 0.2 eV)	Peak ratio	Peak centre eV (± 0.2 eV)
N(1s)	399.4	20	402.8
	402.7	80	
Cl(2p)	198.9	/	198.9
Br(3d)	68.2	/	68.2

A small amount of Cl was detected at 198.9 eV. The Cl⁻ ions of CdCl₂ and FeCl₃ have binding energies in this region, whereas those of chlorinated benzenes and phenols have binding energies in the region of 200.8 - 201 eV⁹⁴. The fact that the Cl⁻ ion can be detected is promising and subsequent work must include obtaining the XPS of 2-chlorophenol for use as a reference. This is difficult in practice, as analysis of the 2-chlorophenol by XPS can contaminate the equipment for sometime after the analysis is complete. It is possible that the inability to deconvolute the Cl peak and repeated bombardments to facilitate detection has lead to the decomposition or reaction of the chlorophenol to give a product of Cl(2p) with a lower binding energy than that given in the literature.

An interesting observation of the N(1s) XPS results is that the peak at 402.8 eV is asymmetric and can be deconvoluted into two peaks as shown in Table 3.22. The peaks are also present in the spectra of the Quat-clay before the 2-chlorophenol is added (Table 3.10). The peak in the region of 399.4 eV probably arises due to the presence of amine (RN(CH₃)₂). This initially suggests that exchange and thorough washing of the Quat-clay is accompanied by a dissociation of the Quat to an amine and that addition of the 2-chlorophenol induces no further reactions that involve the N atom. However, as mentioned above the solid material was subjected to high levels of X-ray bombardment to detect Cl and Br. This may have contributed to the decomposition of the Quat in the Quat-montmorillonite.

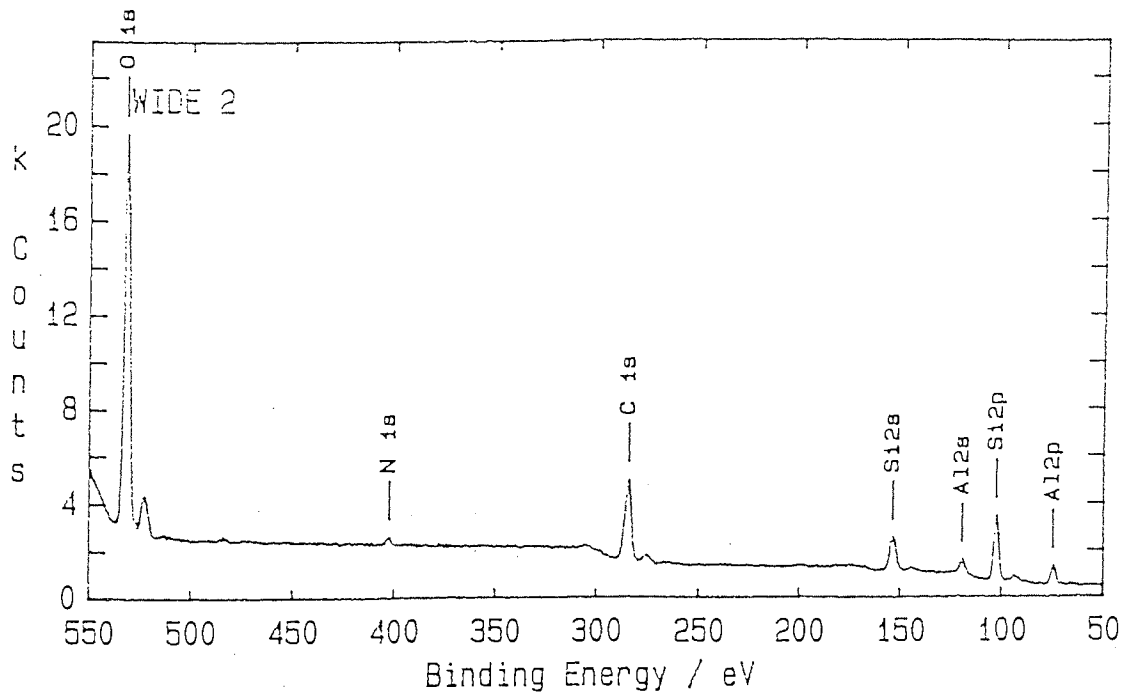


Figure 3.10a XPS wide scan of 2-chlorophenol-HDTMA-montmorillonite

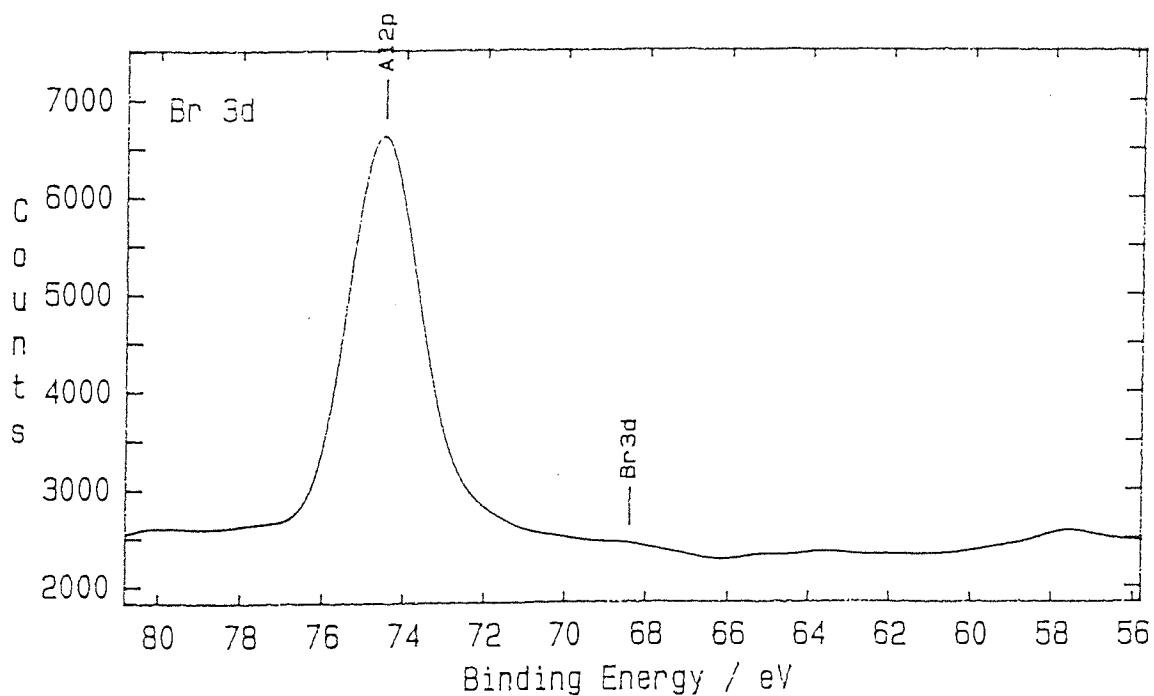


Figure 3.10b XPS scan in the 55-80 eV binding energy region, of 2-chlorophenol-HDTMA-montmorillonite

Peak	Centre (eV)	FWHM (eV)	Hght %	G/L %	Area %
N 1s1	399.4	2.20	24	15	20
N 1s2	402.7	2.15	100	15	60

100% Height (Counts) : 2824
 100% Area (kceV/sec) : 3.76
 Reduced Chi Squared : 0.07

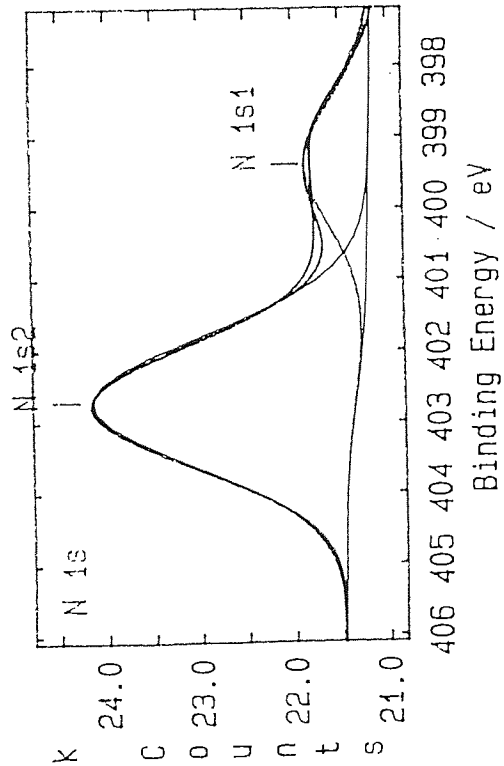


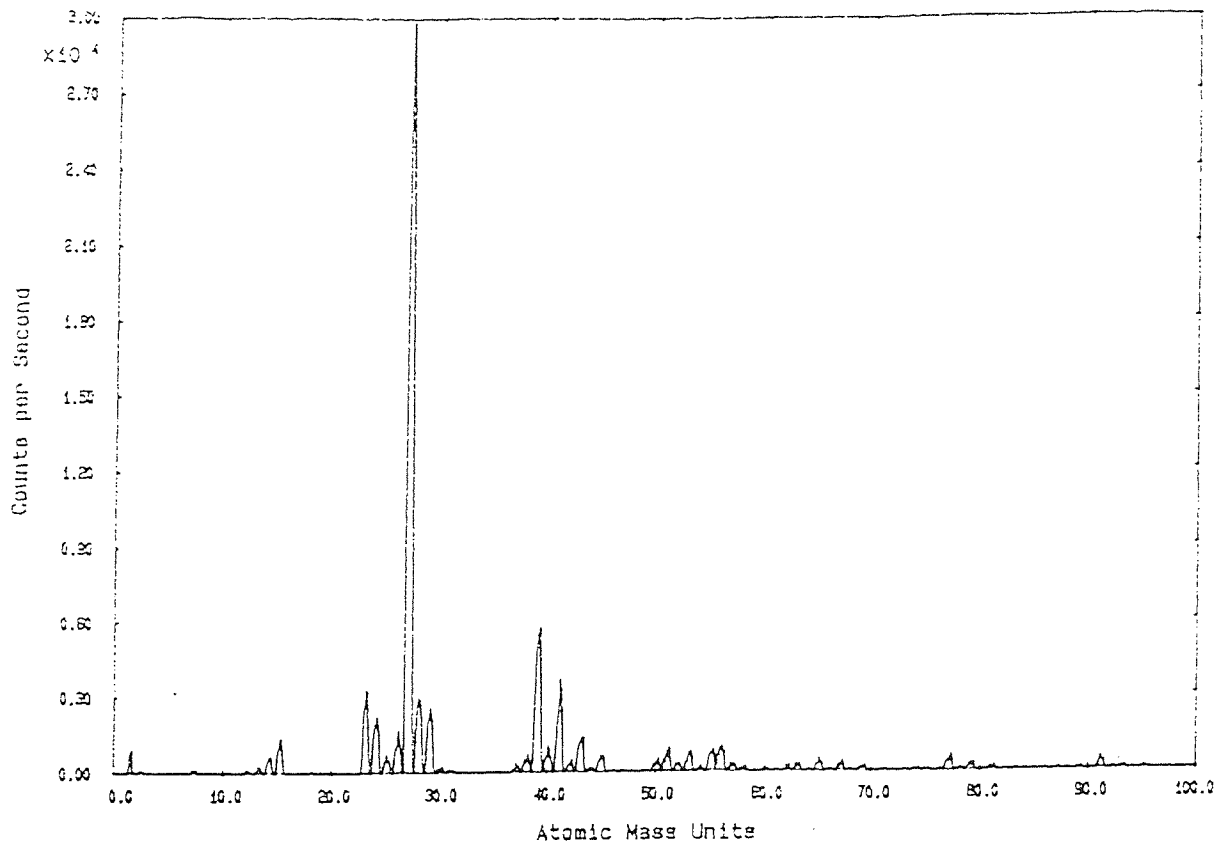
Figure 3.10c XPS N(1s) analysis of 2-chlorophenol-HDTMA-montmorillonite

3.5.2.3 FTNIR

FTIR of the 2-chlorophenol-HDTMA-montmorillonite is as the FTIR of the HDTMA-montmorillonite as described in Section 3.2.3. Additional peaks occur as one might expect due to the presence of 2-chlorophenol without strong interaction with the adsorbent.

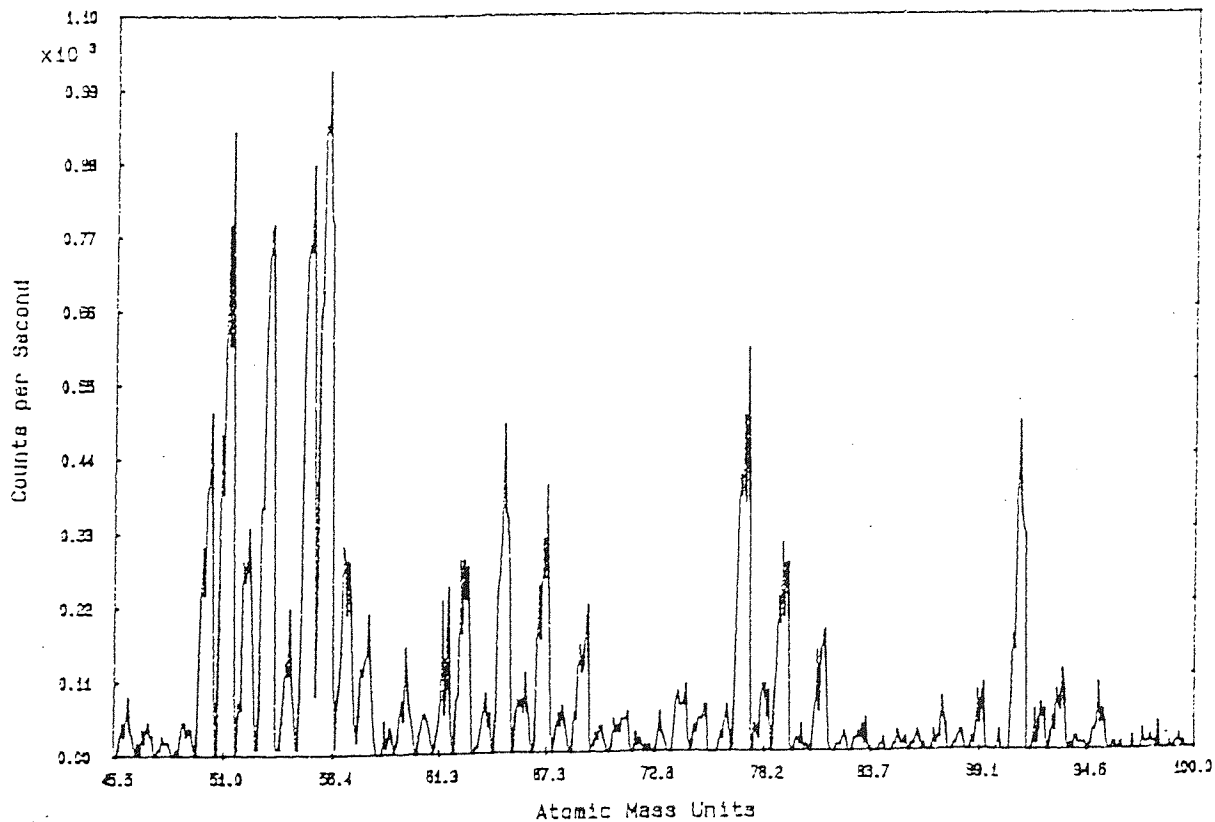
3.5.2.4 Secondary Ion Mass Spectrometry (SIMS)

SIMS affords the mass spectroscopy of solid surfaces. Characterisation of the 2-chlorophenol-HDTMA-montmorillonite material was attempted using this analytical technique. Both negative and positive SIMS were employed and both proved useful for detection of different constituents of the material. The major peaks arising from fragmentation of the quaternary ammonium cation and the 2-chlorophenol are detected. The spectra are shown in Figure 3.11. Overall, positive SIMS was the most informative and negative SIMS filled in gaps of information, for example missing alkyl fragments, especially those of higher molecular weight, and the peaks at 37 amu and 35 amu typical of those due to the presence of the chlorine fragment. From the figures it can be seen that the SIMS spectra are very complex especially between 100 and 200 amu this is due to the presence of the clay mineral. Peaks due to the clay mineral include those at 28 amu due to Si, 16 amu due to O, 27 amu - Al, 24.3 amu - Mg, 17 amu - OH, 23 amu - Na, 40 amu - Ca, 39 amu - K.



AR Primary Beam 3keV 0.20nA

Figure 3.11a SIMS spectrum of 2-chlorophenol-HDTMA-montmorillonite (0 - 100 amu)



AR Primary Beam 3keV 0.20nA

Figure 3.11b SIMS spectrum of 2-chlorophenol-HDTMA-montmorillonite (45.5 - 100 amu)

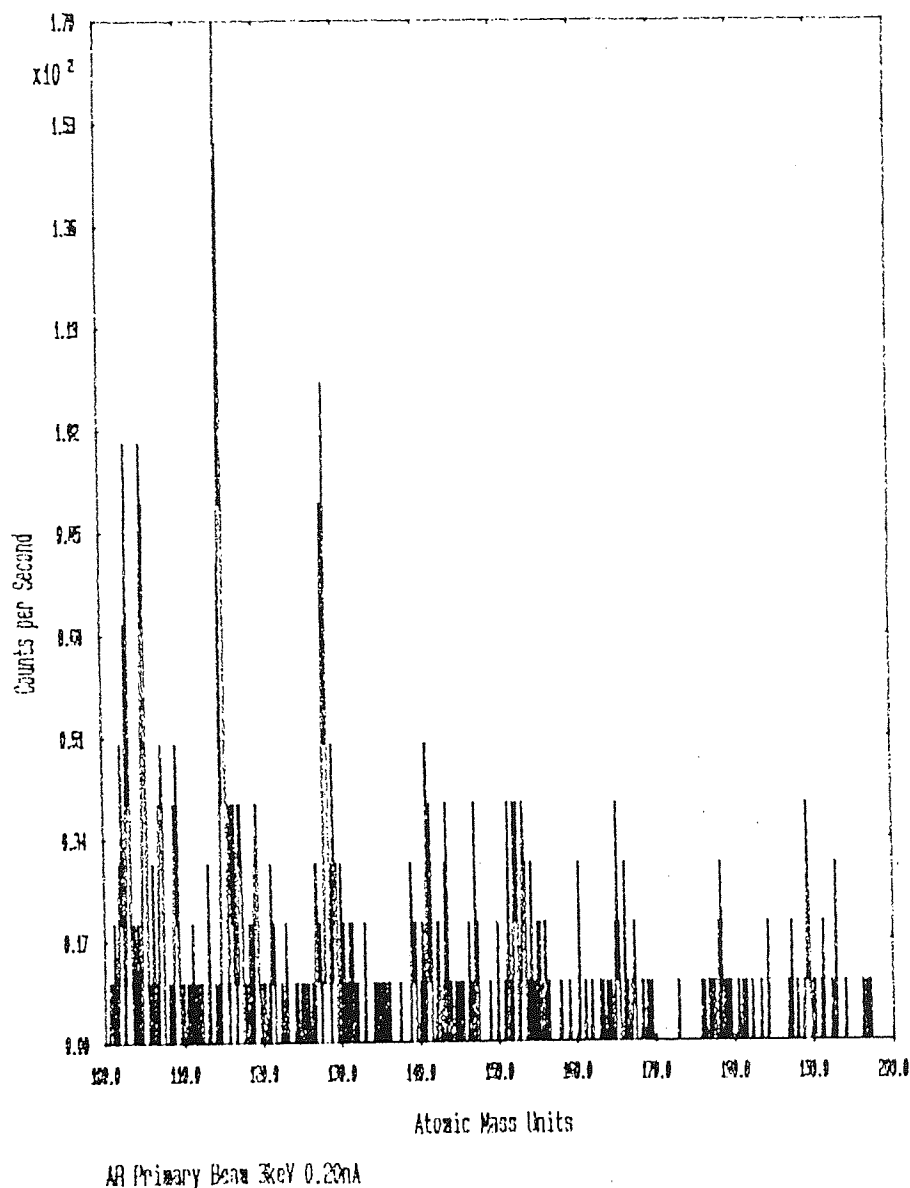


Figure 3.11c SIMS spectrum of 2-chlorophenol-HDTMA-montmorillonite (100 - 200 amu)

3.5.3 2-chlorophenol-HDTMA-montmorillonite - Conclusions

On adsorption of 2-chlorophenol the basal spacing of the HDTMA-montmorillonite increases by 1.5 Å. This suggests monolayer adsorption of the 2-chlorophenol in the interlayer region of the exchanged clay. The presence of 2-chlorophenol in the material was confirmed by SIMS and FTIR. XPS results show that low concentrations of 2-chlorophenol are present on the surface of the HDTMA-montmorillonite, supporting results which suggest that 2-chlorophenol adsorption takes place in the interlayer region.

3.6 Bi Quat-smectites

Having reproduced Mortland's observations on the adsorption of phenols and chlorinated phenols by Quat-smectites, the adsorption study was extended by examining the adsorption of the same organics by what will be termed Bi Quat-smectites.

This direction was taken because an industrial stream or contaminated water will inevitably contain a number of organic compounds. The results of adsorption onto the conventional single Quat-clays suggest there is selectivity towards the phenols studied. It would be useful if more than one contaminant could be adsorbed at the same time. However, before modelling a waste stream or contaminated water with a number of phenols in the laboratory, it was decided to examine whether the adsorption of one phenolic compound was affected by the presence of another Quat-clay in the system.

Two different types of Bi Quat-smectites, which differ in their method of preparation, were studied. It will be seen that the first type of Bi Quat-smectite, a mixture of Quat-smectites, is prepared by mixing equal masses of two previously prepared conventional single Quat-smectites, for example HDTMA-montmorillonite with TMPA-montmorillonite. The second type of Bi Quat-smectite is prepared by using the same exchange reaction as described previously in this chapter (Section 3.2.2), but adding two different Quats to the reaction mixture, adding each at half the c.e.c. of the smectite clay. The Quats chosen for the preparation of the Bi Quat-smectites were HDTMA+Br⁻ and TMPA+Cl⁻. These two Quats were chosen because HDTMA-montmorillonite and HDTMA-laponite show maximum adsorption (interaction and capacity) towards 2-chlorophenol and 2,4,6-trichlorophenol, and TMPA-montmorillonite and TMPA-laponite show maximum adsorption towards phenol. Thus, the adsorption characteristics of the following four Bi Quat-smectites were studied:

mixtures of Quat-smectites: HDTMA-montmorillonite + TMPA-montmorillonite,
HDTMA-laponite + TMPA-laponite,
double-Quat-smectites: HDTMA-TMPA-montmorillonite, and
HDTMA-TMPA-laponite.

3.6.1 Preparation of Bi Quat-smectites

3.6.1.1 Preparation of a mixture of Quat-smectites

The mixture of Quat-smectites were prepared by adding 1 g of HDTMA-smectite and 1 g TMPA-smectite (both thoroughly washed) to 100 cm³ water in a conical flask, stoppering and shaking for about 45 minutes on the mechanical shaker. The product was filtered and air dried.

3.6.1.2 Preparation of Double-Quat-smectites

For the preparation of double-Quat-smectites two methods were attempted. Both methods were based on those described in Section 3.2.2.

Using the montmorillonite clay for preliminary studies:

Method (a) involved the use of the method described in Section 3.2.2 except two ammonium compounds are added each satisfying half the c.e.c. of the clay. The two Quats were mixed together and then added to the montmorillonite slurry. The AA results which measure the extent of exchange are shown in Table 3.23 and they show that fully exchanged clays resulted from this reaction.

Method (b) involved the synthesis of the double-Quat-montmorillonite in a stepwise fashion. To the montmorillonite slurry was added HDTMA⁺Br⁻ to satisfy 0.5 c.e.c. of montmorillonite. The exchange reaction was completed as for conventional preparations, dried and ground. The product of the reaction was then added to 350 cm³ distilled water. At this point TMPA⁺Cl⁻ was added in sufficient quantities to satisfy 0.5 c.e.c. of the montmorillonite. The 0.5 c.e.c. HDTMA-montmorillonite does not disperse readily in the distilled water and it was not apparent that a further exchange reaction had occurred on adding the TMPA⁺Cl⁻. Analysis of the filtrates after each reaction step suggest that on exchange of the HDTMA cations for Na⁺ cations, approximately half of the sodium ions known to be present were released as expected. However, only 16% of the Na⁺ cations expected to be released on the second step of the exchange involving the TMPA cations were detected by AA.

In the preparation of double-Quat-smectites, modifications of the exchange reactions described in Sections 3.2.2 for montmorillonite and 3.3.2 for laponite, were as method (a).

3.6.2 Characterisation of double-Quat-montmorillonites and laponites

The double-Quat-smectites were characterised using Atomic absorption (AA), X-ray diffraction (XRD), silicon-29 magic angle spinning nuclear magnetic resonance (^{29}Si MASNMR) and Secondary Ion Mass Spectrometry (SIMS).

3.6.2.1 AA

The percentage exchange observed in both cases Table 3.23 are encouraging showing high percentage exchange has taken place in both cases.

Table 3.23 Percentage exchange for the double-Quat-smectites

material	sodium release % ($\pm 8\%$)
HDTMA-TMPA-montmorillonite	80%
HDTMA-TMPA-laponite	91%

3.6.2.2 XRD

The $d(001)$ for the HDTMA-TMPA-montmorillonite product was found to be 14.2 Å. That for HDTMA-TMPA-laponite was found to be 14.7 Å. These are the same as the basal spacings observed for TMPA-montmorillonite and TMPA-laponite respectively. Both products have the cations arranged in a monolayer in the interlayer region. In the case of the HDTMA-TMPA-laponite, the results are as expected, as the conventional Quat-laponites as studied in Section 3.3, have a monolayer arrangement. However, the HDTMA-TMPA-montmorillonite results suggest that the HDTMA cations are now arranged in a monolayer rather than the bilayer arrangement observed for the conventional HDTMA-montmorillonite. The HDTMA cations take up a monolayer arrangement when TMPA cations are also present in the interlayer region.

3.6.2.3 ^{29}Si MASNMR

Samples of laponite and exchanged HDTMA-TMPA-laponite were submitted for ^{29}Si MASNMR. The results are presented below - Table 3.24 and examples of the spectra can be found in Figures 3.12a and 3.12b.

Table 3.24 Summary of ^{29}Si MASNMR analysis double-Quat-laponite

Sample	Q ² ± 0.4 ppm	Q ³ ± 0.3 ppm
Laponite	-85.3	-94.8
HDTMA-TMPA-laponite washed	-84.5	-95.3

For laponite the Q² peak results from the presence of silicon atoms at edge sites and Q³ from a silicon atoms within the silicate layer (see Section 3.3.1 for detailed explanation). As can be seen from the MASNMR results in Table 3.24, the Q³ peak shifts upfield. Such a shift is normally indicative of the change of the initial environment for one in which less deshielding of the silicon nucleus occurs. This is consistent with the replacement of sodium cations by Quat cations and consistent with the basal spacing results which suggest an exchange reaction, and would suggest interactions between the silicate layer and the Quats in the interlayer region.

3.6.2.4 SIMS

The HDTMA-TMPA-montmorillonite material was submitted for SIMS analysis. Positive SIMS proved the most useful of the SIMS techniques for the detection of different constituents. Major peaks due to fragmentation of both the quaternary ammonium cations are detected.

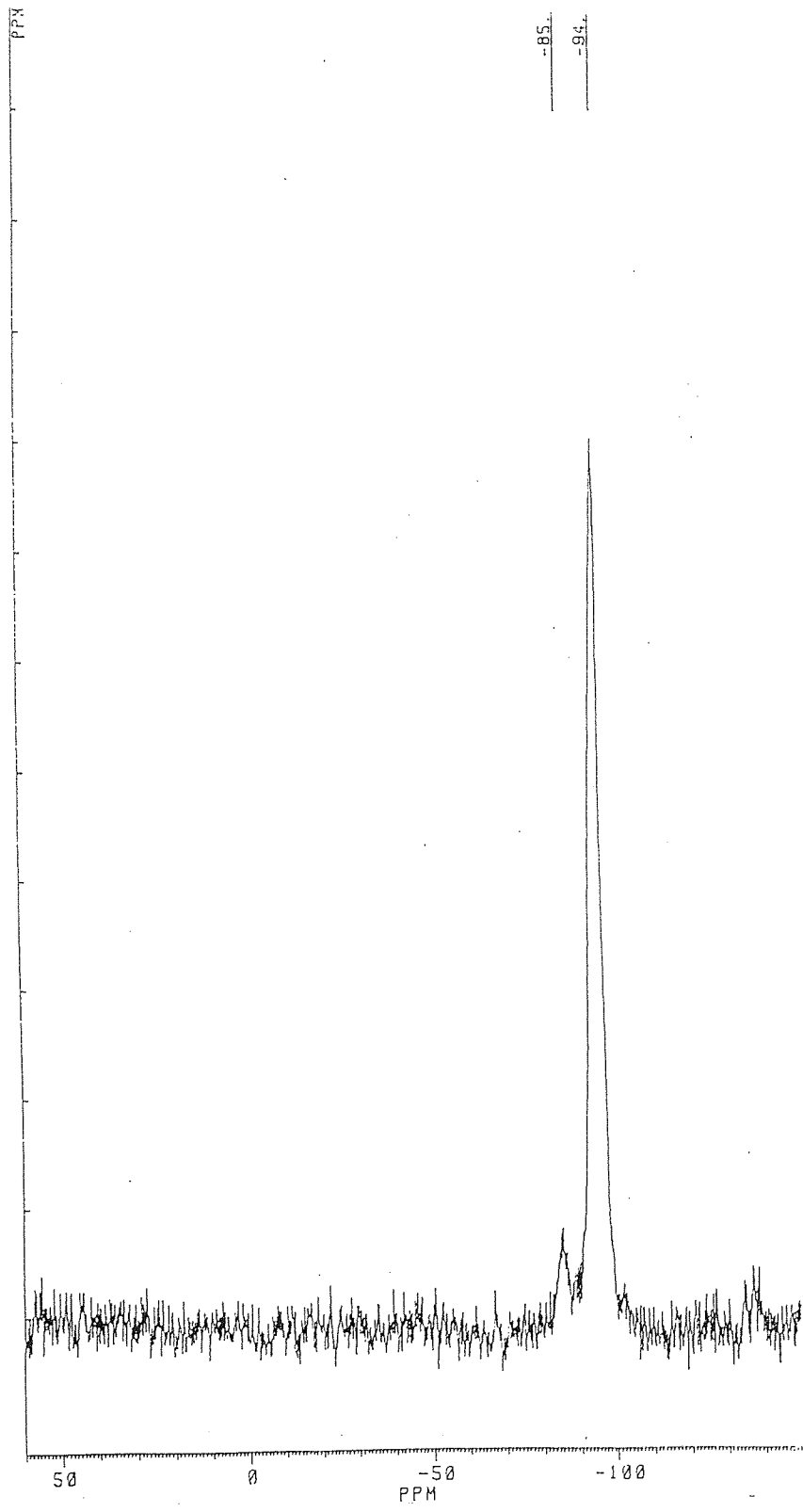


Figure 3.12a ^{29}Si MASNMR spectrum of laponite

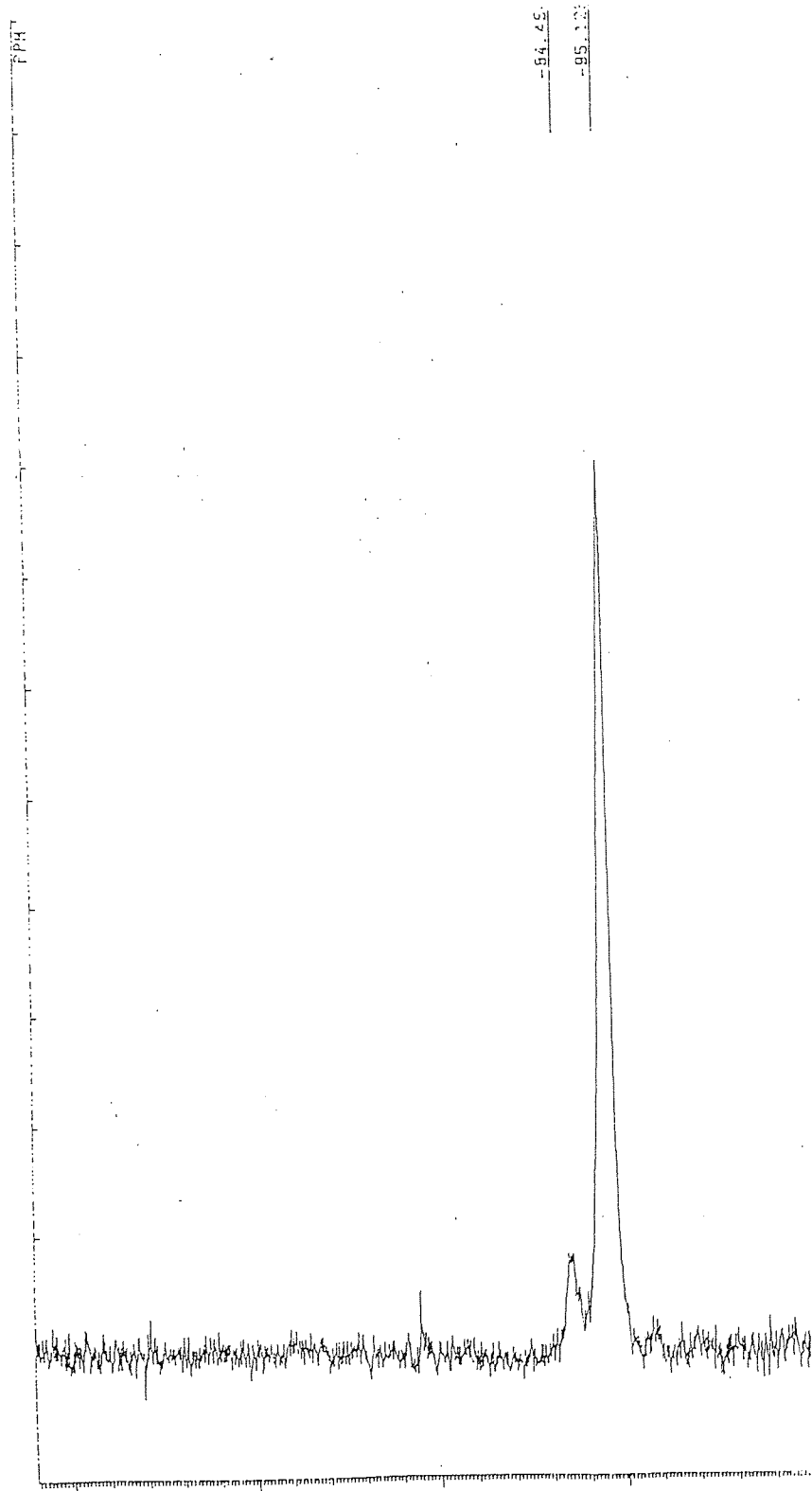


Figure 3.12b ^{29}Si MASNMR spectrum of HDTMA-TMPA-laponite

3.6.3 Adsorption of phenols by Bi Quat-smectites

Adsorption isotherms were obtained for the adsorption of phenols by the four Bi Quat-smectites. These experiments were conducted to study the effect of the presence of a

second Quat, in the case of the double-Quat-smectite, HDTMA-TMPA-smectite, on phenol adsorption as compared to adsorption of phenol by conventional single Quat-smectites; and the effect of the presence of the second Quat-smectite, in the case of the mixture of Quat-smectites, HDTMA-smectite + TMPA-smectite, on phenol adsorption as compared to adsorption of phenol by conventional single Quat-smectites. The adsorption isotherm experiment was carried out as the modified experiment in Section 3.4, except 0.2 g of the mixture of Quat-smectites, HDTMA-smectite + TMPA-smectite, or the double-Quat-smectite, HDTMA-TMPA-smectite, was added to each solution of phenol or chlorinated phenol. 0.2 g of the adsorbent was added to ensure that it was theoretically possible for comparable amounts of phenol or chlorinated phenol to be adsorbed as that observed when 0.1 g of the conventional single Quat-smectite, for example HDTMA-smectite, was used in the adsorption experiments described in Section 3.4.

Figures 3.13 - 3.15 show the effect of the second Quat or second Quat-clay on adsorption of each of the phenols studied thus far. The double-Quat-smectite is compared to the mixture of Quat-smectites and the best conventional single Quat-smectite for both the montmorillonite and laponite materials; (a) where the smectite is montmorillonite and (b) where the smectite is laponite. Figure 3.13 shows 2,4,6-trichlorophenol adsorption by the single Quat-smectite, the mixture of Quat-smectites, and the double-Quat-smectite; Figure 3.14 shows 2-chlorophenol adsorption by the single Quat-smectite, the mixture of Quat-smectites, and the double-Quat-smectite and Figure 3.15 shows phenol adsorption by the single Quat-smectite, the mixture of Quat-smectites, and the double-Quat-smectite.

For both montmorillonite and laponite single Quat-smectite, mixture of Quat-smectites, and double-Quat-smectite series, the results show that all the phenols are adsorbed by one or more of the adsorbents. In each case, the amount of phenolic compound adsorbed is reduced as the series is progressed, and the strength of interaction decreases as the series is progressed (Figures 3.13 - 3.15). For adsorption of the phenols, the use of the conventional single Quat-montmorillonite resulted in the highest adsorption capacity and the highest strength of interaction. Tables 3.25 and 3.26 summarise the results.

In the case of the montmorillonite adsorbents (Table 3.25), partitioning (Type C isotherm) is the strongest adsorbate-adsorbent interaction observed. Partitioning results from the adsorbate having greater affinity for the adsorbent than the solvent and the linearity of the isotherm suggests that the number of adsorption sites remains constant. At low equilibrium concentrations, partitioning results from a greater

strength of interaction and a greater adsorption capacity than that observed for the Type V isotherms, and Type V isotherms result from a greater adsorption strength and capacity of interaction than Type III isotherms. It is the order of Type C, Type V, Type III that is observed for each phenolic compound as we progress through the single Quat-montmorillonite, mixture of Quat-montmorillonite, and double-Quat-

Table 3.25 Summary of adsorption of phenols by single and bi Quat-montmorillonite adsorbents

Adsorption isotherms - montmorillonite clays			
Adsorbate	Adsorbent		
	single Quat	mixed Quat	double Quat
phenol	V	V	III
2-chlorophenol	V	V	V
2,4,6-trichlorophenol	C	III	III

Table 3.26 Summary of adsorption of phenols by single and bi Quat-laponite adsorbents

Adsorption isotherms - laponite clays			
Adsorbate	Adsorbent		
	single Quat	mixed Quat	double Quat
phenol	III	na	na
2-chlorophenol	I	V	na
2,4,6-trichlorophenol	I	na	na

na - no adsorption

montmorillonite adsorbent series. That is, as we progress through the single Quat-montmorillonite, mixture of Quat-montmorillonite, and double-Quat-montmorillonite

adsorbent series the strength of the adsorbate-adsorbent interaction decreases for all adsorbates.

For the laponite adsorbents (Table 3.26), such progressive decreases in adsorbate-adsorbent interactions are not always observed in the adsorption of a particular adsorbate. Such results suggest that it is not simply the case that the chlorinated phenols adsorb onto the HDTMA-laponite portions of the mixture of Quat-laponites, and phenol onto the TMPA portions, but that some other interaction within the mixture of Quat-laponites and double-Quat-laponite occurs. Such interactions may be adsorbent-adsorbent interactions, restricting the adsorption processes which occurred in the single Quat-laponite system. The adsorbent-adsorbent interactions seem much more pronounced in the double-Quat-smectites, and where the smectite is laponite. The adsorbent-adsorbent interactions may result from a significant proportion of the HDTMA-clay interacting with a significant proportion of TMPA-clay leaving less of the HDTMA exposed to the chlorinated phenols and less of the TMPA exposed to adsorb the phenol.

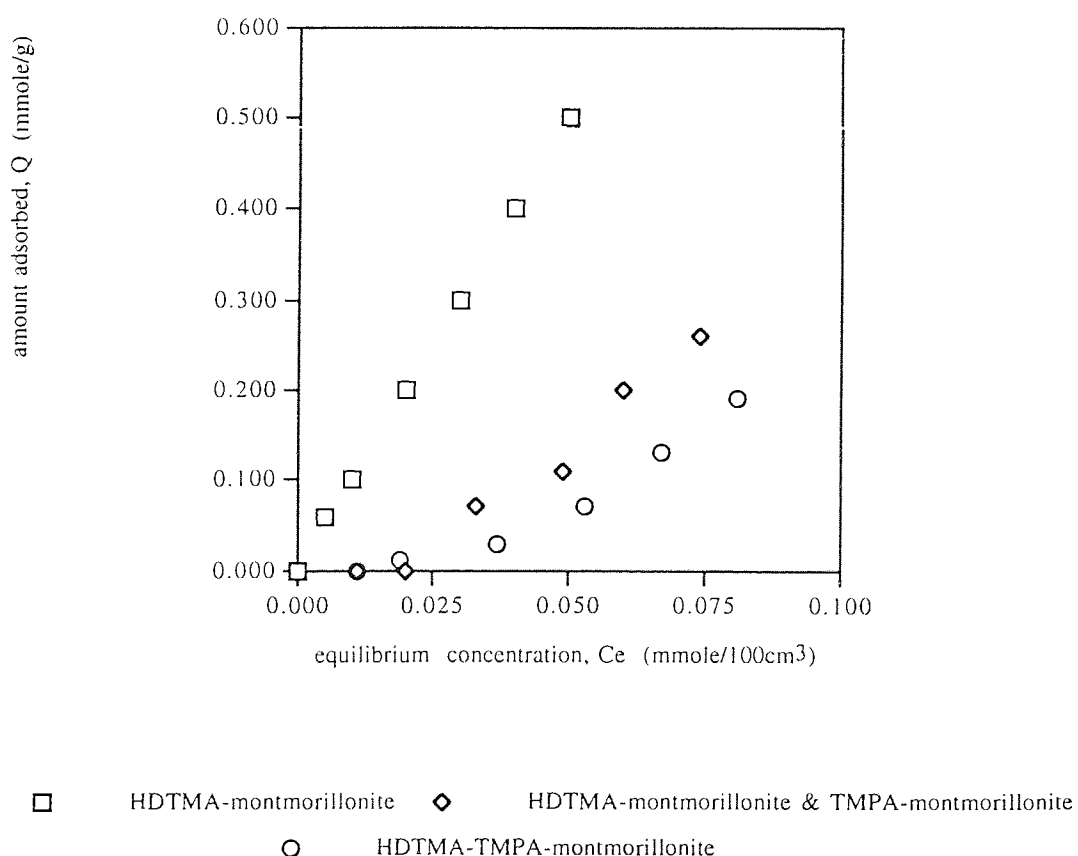


Figure 3.13(a) Adsorption of 2,4,6-trichlorophenol by the single Quat-montmorillonite, the mixture of Quat-montmorillonites, and the double-Quat-montmorillonite

For the mixture of Quat-montmorillonites, the adsorption capacity and the strength of interaction observed in the adsorption of phenol and 2-chlorophenol, is not significantly reduced compared to the best single Quat-montmorillonite. This suggests that the types of adsorbate-adsorbent interactions, that is, the phenol single Quat-smectite interaction and the phenol mixture of Quat-smectites interactions, are not significantly different especially at the lower concentrations, Figures 3.14a and 3.15a.

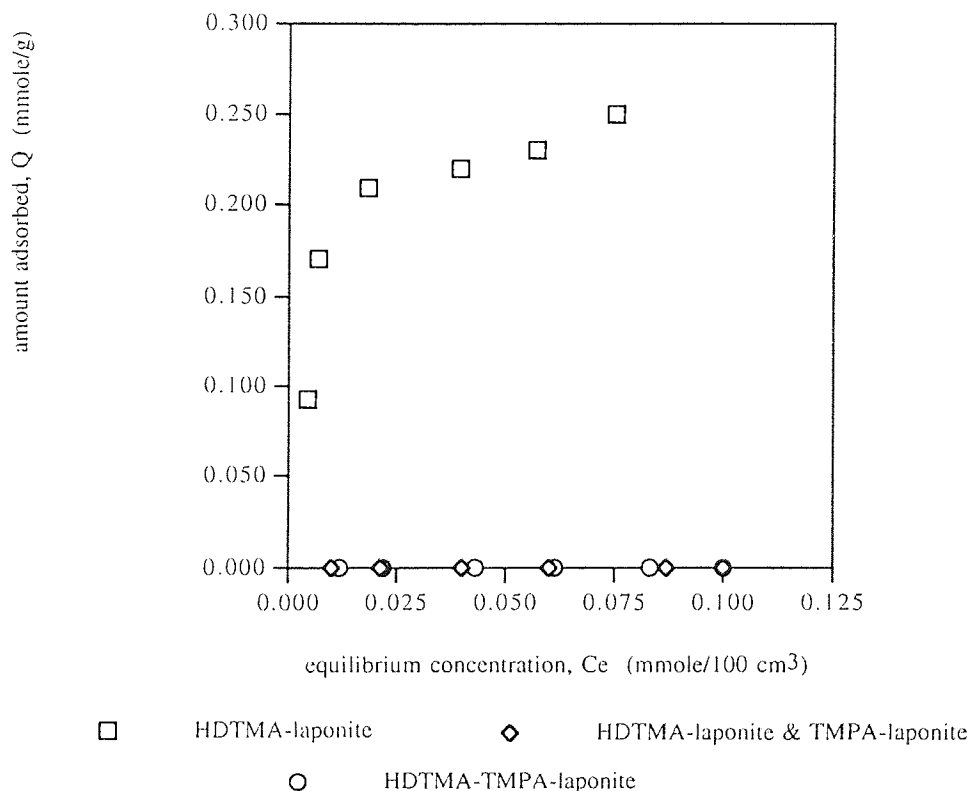


Figure 3.13(b) Adsorption of 2,4,6-trichlorophenol by the single Quat-laponite, the mixture of Quat-laponites, and the double-Quat-laponite

When the adsorptions of 2,4,6-trichlorophenol by HDTMA-montmorillonite and HDTMA-montmorillonite + TMPA-montmorillonite are compared, however, the adsorption capacity of the latter is half of the former, Figure 3.13a. It is not clear why adsorption of 2-chlorophenol is barely affected but that of 2,4,6-trichlorophenol is halved. On preparation of the mixture of Quat-montmorillonites, the silicate layers are dispersed and this may allow for interactions between the silicate layers exchanged with different Quats. HDTMA-montmorillonite is a bilayer arranged Quat-clay and TMPA-montmorillonite a monolayer arranged Quat-clay. The adsorption of 2,4,6-trichlorophenol by HDTMA-montmorillonite and by HDTMA-montmorillonite + TMPA-montmorillonite suggests that a significant concentration of the HDTMA-

montmorillonite is lost to adsorbent-adsorbent or Quat-Quat interactions Figure 3.13a. The remaining HDTMA-montmorillonite concentration in the HDTMA-montmorillonite + TMPA-montmorillonite, that is, that uninvolved in adsorbent-adsorbent interactions, is sufficient to adsorb 2-chlorophenol to the same capacity as that adsorbed by the single HDTMA-montmorillonite even at high equilibrium concentrations, but is not sufficient to adsorb 2,4,6-trichlorophenol to the same capacity as the HDTMA-montmorillonite, even at the low equilibrium concentrations used in these experiments.

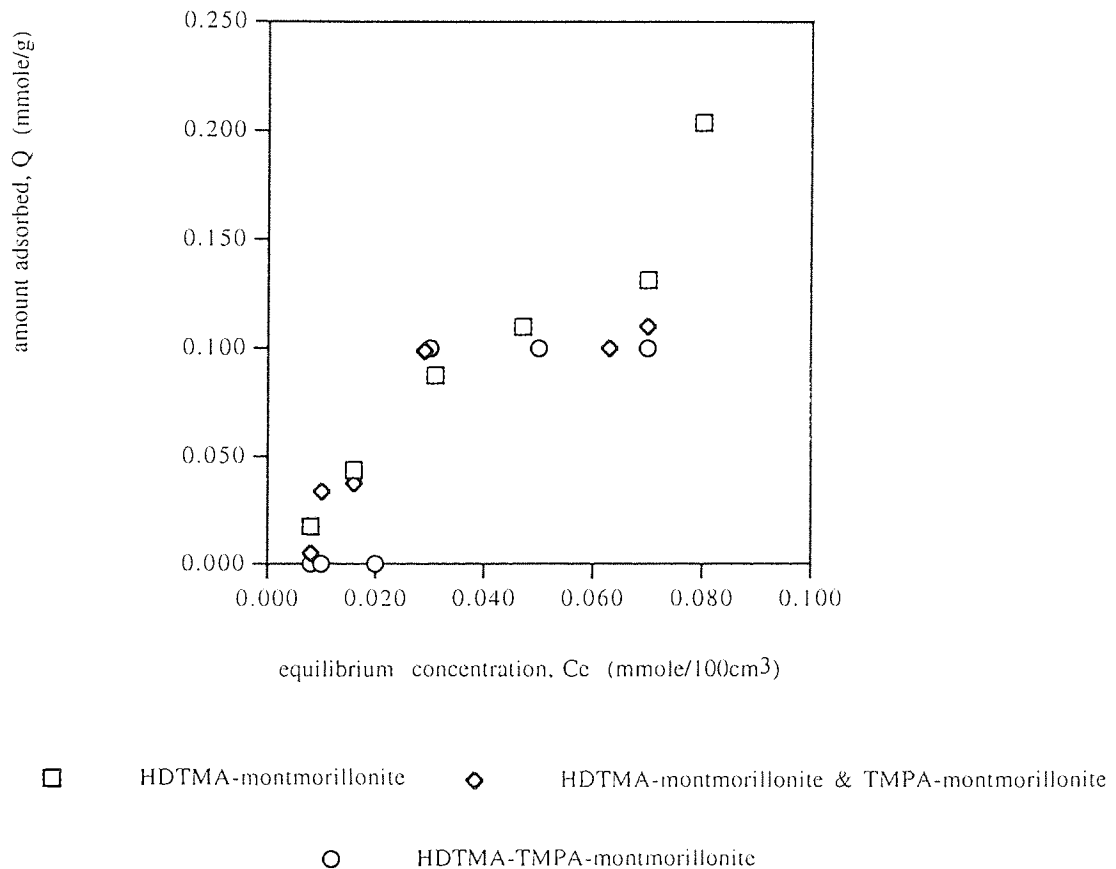


Figure 3.14(a) Adsorption of 2-chlorophenol by the single Quat-montmorillonite, the mixture of Quat-montmorillonites, and the double-Quat-montmorillonite.

A significant proportion of the Quat-montmorillonites present in the mixture of Quat-montmorillonites participate in adsorbent-adsorbent interactions, that is, HDTMA-montmorillonite TMPA-montmorillonite interactions. Either, adsorption of the phenols takes place on the "new" adsorbent fraction formed from adsorbent-adsorbent interactions, or more likely, adsorption takes place on the original Quat-

montmorillonites that have not taken place in the adsorbent-adsorbent interactions. This would explain the similarities in adsorption isotherm types and the decrease in adsorption capacity when the single Quat-montmorillonite is compared with the mixture of Quat-montmorillonites.

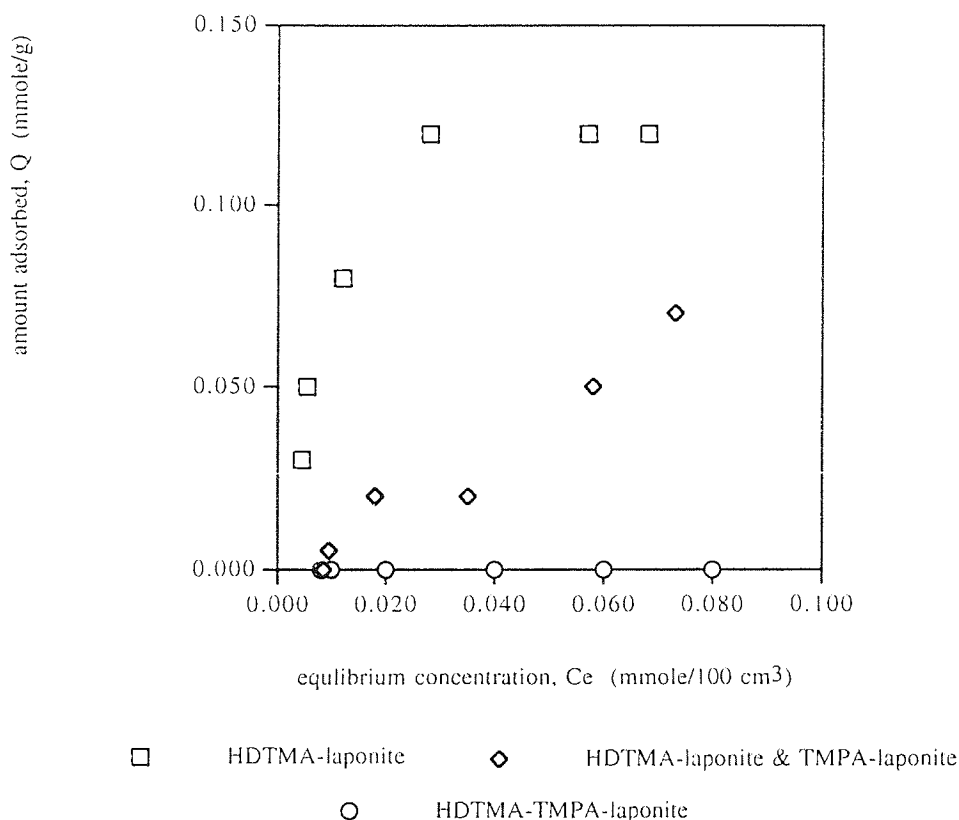


Figure 3.14(b) Adsorption of 2-chlorophenol by the single Quat-laponite, the mixture of Quat-laponites, and the double-Quat-laponite.

The mechanism in the case of the mixture of Quat-laponites appears to be different. In the case of 2,4,6-trichlorophenol adsorption and phenol adsorption, there is no progressive decrease in adsorption as the single Quat-smectite, mixture of Quat-smectites, and double-Quat-smectite series is progressed, Figures 3.13 - 3.15. Adsorption of 2,4,6-trichlorophenol decreases from Type I for HDTMA-laponite to no adsorption for the mixture of Quat-laponites. It would seem that dispersion of the Quat-laponites in water during the preparation of the mixture of Quat-laponites is more pronounced in the case of the Quat-laponites, thus enabling greater interaction between the TMPA-laponite and HDTMA-laponite. Perhaps the fact that for all Quat-laponites studied in this work, the Quats arrange themselves in a monolayer and the Quat-laponites are added in a 1:1 ratio, allows for a significant proportion of the Quat-laponites to interact with each other in the mixture, see Figure 3.16. The significant difference in particle size of the exchanged laponites compared to the exchanged

montmorillonites may influence the dispersion reaction, the exchanged laponites having a much smaller particle size than the exchanged montmorillonites. This would result in a greater degree of dispersion for the exchanged laponites and therefore a greater degree of interaction between the two Quat-laponites than that which appears to occur for the two Quat-montmorillonites.

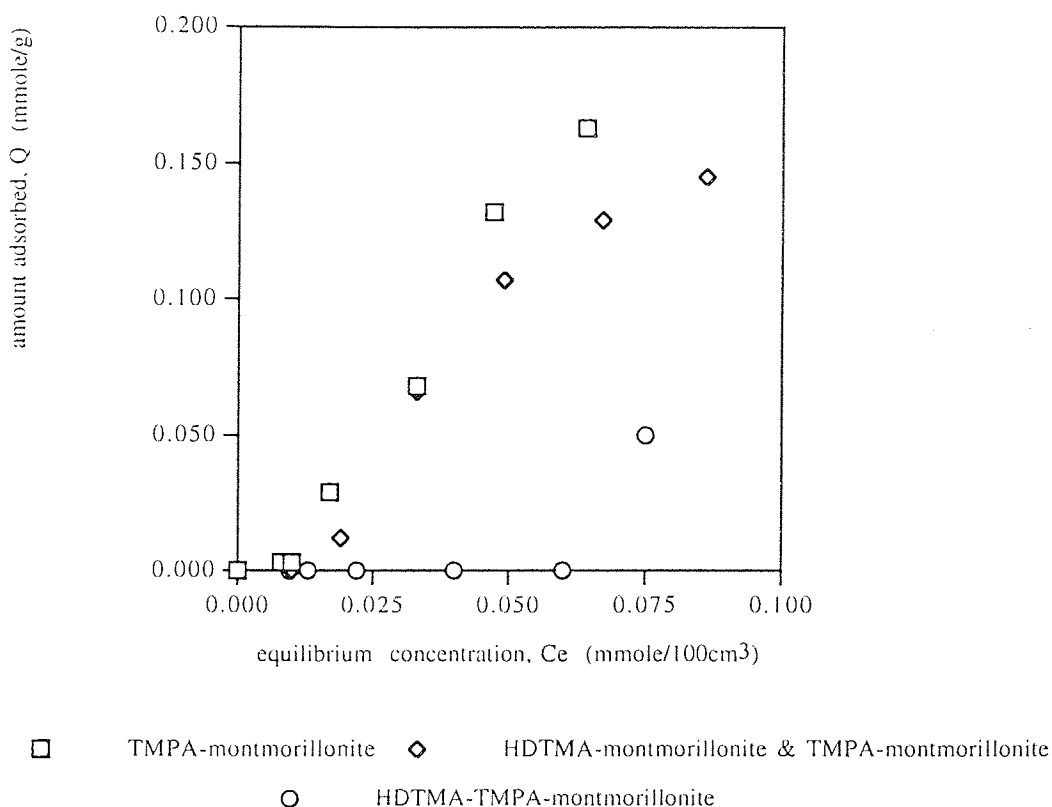


Figure 3.15(a) Adsorption of phenol by the single Quat-montmorillonite, the mixture of Quat-montmorillonites, and the double-Quat-montmorillonite.

For the Bi Quat-laponites, the significant difference in adsorption interactions when 2-chlorophenol is the adsorbate suggests that there is a small concentration of the original Quat-laponites remaining in the reaction mixture. This appears to be too small a concentration to allow for adsorption of phenol or 2,4,6-trichlorophenol. Interestingly, 2-chlorophenol is adsorbed by the mixture of Quat-laponites, the isotherm is Type V compared to Type I for the conventional HDTMA-laponite. This may indicate adsorption of 2-chlorophenol by the "new" adsorbent, if the concentration of the preferred Quat-laponite not involved in the adsorbent-adsorbent interactions is too low.

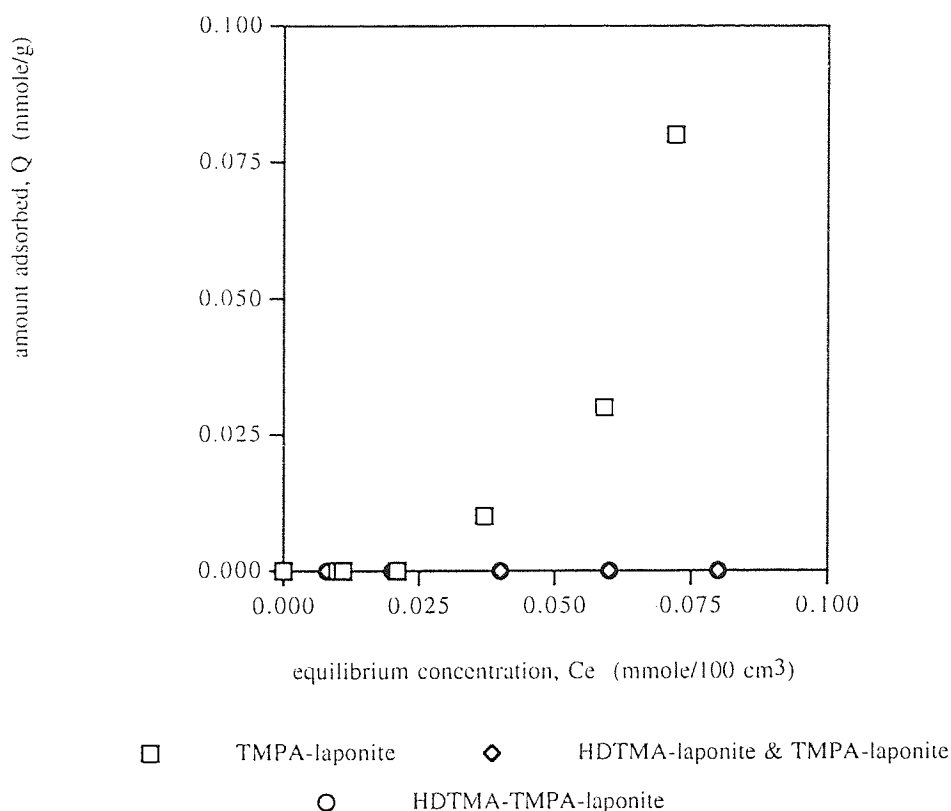
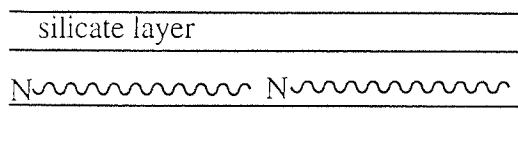


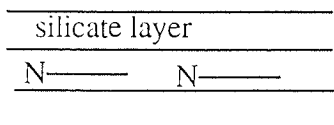
Figure 3.15(b) Adsorption of phenol by the single Quat-laponite, the mixture of Quat-laponites, and the double-Quat-laponite.

The materials resulting from the mixture of Quat-smectites were not analysed by XRD as it was assumed that no change in the arrangement of the Quats would take place. However, it does seem that such an assumption is not correct and that adsorbent-adsorbent interactions have occurred. One can only speculate that on mixing the HDTMA-montmorillonite and the TPA-montmorillonite the silicate layers disperse enough for a significant amount of interaction to occur between the HDTMA-montmorillonite particles and the TPA-montmorillonite particles, Figure 3.16.

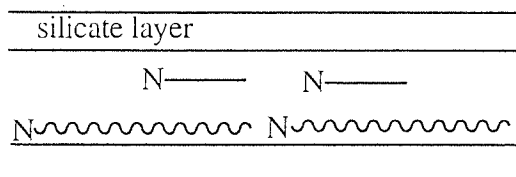
For the double-Quat-montmorillonite the arrangement of the Quats in the montmorillonite is monolayer. The adsorption of the phenol and chlorinated phenols is reduced compared to the conventional single Quat-montmorillonite when the double-Quat-montmorillonite is the adsorbent. This suggests that the adsorbent is made of a mixture of aggregates of HDTMA-montmorillonite and aggregates of TPA-



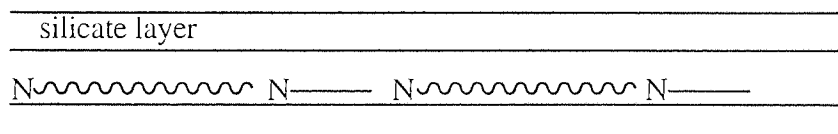
Arrangement of HDTMA cations in HDTMA-laponite



Arrangement of TMPA cations in TMPA-laponite



Arrangement of Quats in both mixture of Quat-smectites and double Quat-smectites



Arrangement of Quats in double Quat-smectites only

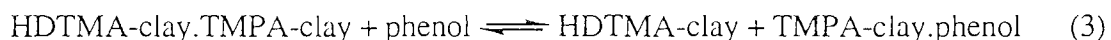
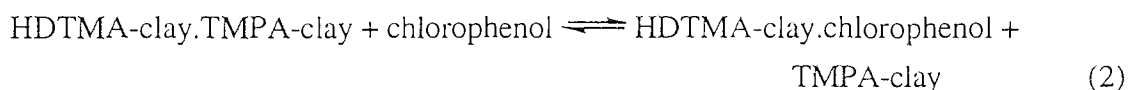
Figure 3.16 Schematic diagram of adsorbent-adsorbent interactions in the Bi Quat-smectites.

montmorillonite and aggregates where HDTMA-montmorillonite and TMPA-montmorillonite are randomly interspersed. For the double-Quat-montmorillonite it seems that the adsorption sites for phenol were significantly reduced but those for the chlorinated phenols were reduced to a lesser extent when compared to adsorption of the same adsorbates by the mixture of Quat-montmorillonites. In the double-Quat-montmorillonite the Quats are arranged in a monolayer. Adsorption capacities of the double-Quat-montmorillonite for 2-chlorophenol and 2,4,6-trichlorophenol are just under half that observed for HDTMA-montmorillonite, the best single Quat-

montmorillonite adsorbent, in which the cations are arranged in a bilayer. It appears therefore, that adsorption at the HDTMA sites occurs readily in the double-Quat-montmorillonite. For adsorption of 2-chlorophenol by double-Quat-montmorillonite adsorption is Type V, indicative of weak interactions at lower concentrations and interactions between the 2-chlorophenol molecules enhancing adsorption at higher concentrations. For both the chlorinated phenols the types of interactions differ at the low concentrations but tend towards those observed for HDTMA-montmorillonite at higher concentrations. This suggests that adsorption sites are relatively more difficult to locate on the double-Quat-montmorillonite for the chlorinated phenols but once located adsorption occurs as for HDTMA-montmorillonite, on the HDTMA-montmorillonite aggregates. The reduction in phenol adsorption by double-Quat-montmorillonite was perhaps the most significant reduction of the three phenols. Here adsorption did not occur except at the highest initial concentration. The reduction may result from the inability of phenol to "locate" the TMPA-montmorillonite adsorption sites. Due to the size of the HDTMA cation, the interlayer region may not appear significantly different to HDTMA-montmorillonite with which phenol did not interact, Figure 3.16.

The adsorptions of phenol and 2,4,6-trichlorophenol by double-Quat-montmorillonite were not significantly different to the adsorptions of the same adsorbates by the single Quat-montmorillonite at high equilibrium concentrations. This suggests that the Quat arrangement in the double-Quat-montmorillonite is predominantly block form. The absence of adsorption of the phenols by the double-Quat-laponite suggests that the monolayer arrangement approaches that of a random arrangement. The phenols are not attracted to this arrangement because it is neither hydrophobic enough for the chlorinated phenols or hydrophilic for the phenol and too much energy may be involved in the search for the "ideal" adsorption site.

The adsorption of phenol and chlorinated phenols, then, can be used as a measure of the adsorbent-adsorbent interaction occurring in the Bi Quat-smectites. Equations (2) and (3) below summarise the adsorption reactions for the phenol and chlorinated phenols by the Bi Quat-clays:



The equilibrium will lie to the left if the adsorbent-adsorbent interaction is high, as little or no phenolic compound will be adsorbed, an example of this is seen in the adsorption of 2,4,6-trichlorophenol and phenol by both Bi Quat-laponites. The equilibrium will lie to the right if the adsorbent-adsorbent interaction is low, as this allow for adsorption of the phenols in a similar manner to that which occurs when single Quat-clays are the adsorbents, examples of this reaction are the adsorption of 2-chlorophenol by both Bi Quat-montmorillonites and the adsorption of phenol by the mixture of Quat-montmorillonites.

3.6.4 Bi Quat-smectites - Conclusions

Four Bi Quat-smectites were prepared:

mixtures of Quat-smectites: HDTMA-montmorillonite + TMPA-montmorillonite,
HDTMA-laponite + TMPA-laponite,
double-Quat-smectites: HDTMA-TMPA-montmorillonite, and
HDTMA-TMPA-laponite.

The mixtures of Quat-smectites were prepared by mixing equal weights of previously prepared HDTMA-smectite and TMPA-smectite. Double-Quat-smectites were prepared by modification of the method for the synthesis for conventional single Quat clays. The modification simply involved the addition of the two Quats, at half the c.e.c., to the reaction mixture simultaneously. A high degree of exchange was observed.

The double-Quat-montmorillonite, HDTMA-TMPA-montmorillonite, had a basal spacing of 14.24 Å. This is the same as that for the TMPA-montmorillonite suggesting the HDTMA cations take up a monolayer arrangement in the interlayer region, as opposed to the bilayer arrangement taken up in the HDTMA-montmorillonite. The double-Quat-laponite, HDTMA-TMPA-laponite, has a basal spacing of 14.71 Å which is the same basal spacing as the TMPA-laponite and greater than that of the HDTMA-laponite. Thus, the cations are arranged as in the conventional single Quat-laponites with regards to interlayer d(001) space.

In the study of adsorption of 2,4,6-trichlorophenol, 2-chlorophenol and phenol by double-Quat-smectite, mixture of Quat-smectites and the best single Quat-smectite, adsorption of each adsorbate is generally seen to decrease in terms of adsorption capacity and/or interaction in the order :

single Quat-smectite > mixture of Quat-smectites > double-Quat-smectite.

Thus adsorption of all phenols decreased with apparent increased adsorbent-adsorbent or Quat-Quat interaction within the Bi Quat-smectites. This adsorbent-adsorbent interaction occurs to a greater extent in the double-Quat-smectite than in the mixture of Quat-smectites.

The adsorption isotherm results suggest that for the HDTMA-TMPA-montmorillonite the cations are arranged predominantly in block form and for the HDTMA-TMPA-laponite the cations are arranged in random form.

3.7 The use of commercial Quats for adsorption: Preparation and adsorption studies of ARQUAD 218,178G-montmorillonite.

The project is sponsored by Akzo Chemicals Limited and, as mentioned in Section 3.1, they manufacture Quats and Quat-bentonites for which they seek new applications. Having established that pure Quat-montmorillonites adsorb phenols and chlorinated phenols to varying degrees, adsorption isotherms were obtained for the same phenolic compounds with the Akzo Quat-bentonite system. The Quat used is a ditallowdimethylammonium chloride, trade name ARQUAD 218,178G.

3.7.1 Preparation of ARQUAD 218,178G-montmorillonite

The preparation of the ARQUAD 218,178G-montmorillonite, ditallowdimethylammonium-montmorillonite, was attempted at room temperature as described in Section 3.2.2. The reaction did not start, remaining as a suspension of montmorillonite and ARQUAD 218,178G throughout. When the reaction was carried out in a 2:3, water:iso-propanol solvent and heated to 60 °C as described in Section 3.2.2 the product obtained had the beige appearance typical of Quat-montmorillonites. Analysis of the filtrates and washings by AA suggest that only 55% exchange occurred. Repeating the experiment yielded similar results. The ditallowdimethylammonium cation is larger than the HDTMA cation used in previous studies. Consequently, the molecule may take up more silicate surface in the interlayer region but displace only one sodium cation for every 1.5 - 2 cation exchange sites present. Thus, full exchange may have taken place with respect to interlayer space but not with respect to sodium cation displacement. Industrially manufactured Quats are known to contain impurities including unreacted amines and unremoved solvent. Such impurities are

allowed for in the preparation of the Quat-montmorillonites but what may not be considered is the possible preferential exchange or adsorption of the impurities in the interlayer region. The impurities may solvate sodium cations excluding them from the displacement reaction with the quaternary ammonium cations. These factors may result in the low percentage of exchange observed for this reaction.

3.7.2 Adsorption of phenols by ARQUAD 218,178G-montmorillonite

Adsorption studies of 2,4,6-trichlorophenol resulted in an isotherm of Type C, which is indicative of adsorption by a partitioning process. In fact the isotherm obtained here and that obtained for HDTMA-montmorillonite are comparable both in the type of adsorption isotherm obtained and adsorption capacity. The presence of two alkyl chains does not result in more 2,4,6-trichlorophenol being taken up. As for HDTMA-montmorillonite, ARQUAD 218,178G-montmorillonite does not adsorb phenol.

3.7.3 ARQUAD 218,178G-montmorillonite - Conclusions

Only 55% sodium cations in the montmorillonite interlayer region are displaced on reaction with ARQUAD 218,178G. The resulting ARQUAD 218,178G-montmorillonite adsorbed 2,4,6-trichlorophenol via a partitioning process, but did not adsorb phenol. Thus adsorption characteristics of this adsorbent are similar to those of HDTMA-montmorillonite.

3.8 The Langmuir model - an alternative measure of adsorbate-adsorbent interactions

3.8.1 Background

Section 1.5.1.2 described the classification of adsorption isotherms as summarised by Sing et al.⁴⁶ and Giles et al.⁴⁸. The Type I isotherm is often called the Langmuir isotherm which, as explained in Section 1.5.1.2, is indicative of strong adsorbate-adsorbent interactions. The Langmuir equation is derived from the model of a dilute solution in which both the solute and the solvent molecules occupy the same area when they are adsorbed onto a surface. The adsorption of the solute may be schematically represented by the equation:

adsorbed solvent + solute in solution ----> adsorbed solute + solvent in solution...(1)

The equilibrium constant for this reaction may be written as:

$$K' = \frac{a_2^s a_1^b}{a_1^s a_2^b} \quad \dots(2)$$

where a stands for the activity of the species; s and b signify surface and bulk values respectively and 1 and 2 represent the solvent and solute respectively. By assuming the two dimensional surface solution is ideal, the activity at the surface can be replaced by the mole fraction at the surface. Mathematical derivation leads to one form of the Langmuir equation:

$$x_2^s = \frac{K_{a_2^b}}{K_{a_2^b} + 1} \quad \dots(3)$$

An alternative form of the Langmuir equation can be derived which shows how the fraction of the surface occupied, θ , by the solute varies with solute activity.

$$\theta_2 = \frac{K_{a_2^b}}{K_{a_2^b} + 1} \quad \dots(4)$$

This relationship and subsequent derivations which can be found in Heimenz⁹⁸ can be used for the calculations of specific surface area of the adsorbent or the area occupied per molecule. Unfortunately surface area studies were not able to be conducted and therefore detailed explanation of the Langmuir equation and surface area studies shall not be expanded upon.

Experimentally, the number of moles of solute adsorbed per unit weight of adsorbent, n/w , and the equilibrium concentration of the solute, c , are measured. The Langmuir equation is often written in a form which connects these two parameters,

$$m \left(\frac{n_2^s}{w} \right) = \frac{\left(\frac{m}{b} \right) c}{\left(\frac{m}{b} \right) c + 1} \quad \dots(5)$$

where m and m/b are regarded as empirical constants. A method for obtaining the numerical values for these constants from experimental data is easily seen by rearranging the previous equation to the form

$$\frac{c}{\left(\frac{n_s}{w}\right)} = mc + b \quad \dots(6)$$

This latter form suggests that a plot of $c/(n/w)$ versus c will be a straight line of slope m and intercept b . Which suggests that if the experimentally determined adsorption is Type I, Langmuir, plots as described above should yield a straight line plot.

3.8.2 Data Analysis

Adsorption data obtained in Sections 3.4 and 3.6.3 can be fitted to the Langmuir equation, $C_e/Q = mC_e + b$, by plotting C_e/Q against C_e . Adsorptions consistent with the Langmuir model yield a straight line (Hiemenz 1986⁹⁸). Linear regression analysis of the data was carried out. Adsorptions which fully conform with the Langmuir model, yield r^2 values in the range of $r^2 > 0.90$.

When the Langmuir equation was fitted to adsorption data displayed in this chapter it was found that some correlation between Type I curves and the Langmuir model was achieved. Below (Table 3.27) are listed the adsorbent and adsorbates having sufficiently strong interactions to yield a Type I isotherm and/or the adsorbate/adsorbents shown to interact sufficiently to yield r^2 values of greater than 0.90 and therefore conform to the Langmuir model.

Table 3.27 Adsorption isotherms and Langmuir model data for adsorbate-adsorbent interactions

Adsorbate	Adsorbent	Adsorption Isotherm	r^2 value
2,4,6-trichlorophenol	HDTMA-lap	I	0.991
2-chlorophenol	HDTMA-lap	I	0.817
2,4,6-trichlorophenol	HDPY-lap	I	0.916
2,4,6-trichlorophenol	HDTMA-mont	C	0.936

Table 3.27 shows that of all the Type I isotherms obtained. Where the adsorbate is 2,4,6-trichlorophenol, the data for adsorption are empirically consistent with the Langmuir model. It also shows that where the isotherm was consistent with Type C

adsorption, the data appeared to be consistent with the Langmuir model. In the case of 2-chlorophenol the isotherm was consistent with Type I whereas the data was not consistent with the Langmuir model.

It is not unusual to find that adsorption isotherms display curves that are Langmuir in nature but do not fit with the model of the Langmuir equation. To understand why the Langmuir model does not hold for all the Type I isotherms and may hold for a Type C isotherm, the assumptions made to create the model must be discussed. Real systems may deviate from the theoretical model for the following reasons:

- (i) the adsorption process described in eqn 1 is a complex one involving several kinds of interactions: solvent-solute, solvent-adsorbent, solute-adsorbent.
- (ii) few solid surfaces are homogeneous at the molecular level
- (iii) few monolayers are ideal.

In the case of the various interactions nothing can be done, except to avoid systems in which the multiplicity of interactions are to be expected.

The assumption of surface homogeneity is one that was not explicitly stated in deriving the Langmuir equation. However, it is essential otherwise a different value of K would apply to equation 1 at various places on the surface.

In the Langmuir derivation no account was taken of adsorbate-adsorbate interactions. The adsorbed layer is assumed to be ideal, which limits the adsorption to a monolayer. It is a fact that adsorption often exceeds that of monolayer capacity of the surface.

In the case of adsorption of 2,4,6-trichlorophenol onto HDTMA-montmorillonite and 2-chlorophenol adsorption onto HDTMA-laponite the solute-solvent interactions unaccounted for in the Langmuir model may have affected the degree of fit of the adsorption data to the Langmuir equation. Adsorption of 2-chlorophenol was Type I in nature and the degree of fit was $r^2 = 0.817$, adsorption of 2,4,6-trichlorophenol was Type C, $r^2 = 0.937$. Clearly, adsorption via a partitioning process is not as great an interaction as Langmuir (Type I) adsorption and yet the data, when applied to the Langmuir equation, suggests that the 2,4,6-trichlorophenol has interacted with its adsorbent to a greater extent than the 2-chlorophenol. This shows the Langmuir model must be modified to allow for the influence of solute-solvent interactions in adsorption reactions before it can be used as an accurate determinant of adsorbate-adsorbent interactions.

3.8.3 The Langmuir model - Conclusions

The Langmuir equation may be used as a guide or to establish the strength of adsorbate-adsorbent interactions. Where the adsorbate is 2,4,6-trichlorophenol. However, the Langmuir equation cannot be used in isolation to study the adsorption characteristics of all the adsorbents studied in this chapter.

3.9 Solidification/stabilisation as a method of landfill pre treatment

To find adequate disposal methods for phenols is a challenge. They are present in wastewaters from plants used for the thermal processing of coal and the manufacture of a variety of chemicals, plastics and dyes. Phenols not only render water toxic even at low concentrations, but are converted into chlorophenols during the chlorination process. Adsorption of phenol by granulated activated carbon, a common method used in the treatment of waste, is Type I in nature representing a strong adsorbate-adsorbent interaction. In the presence of benzene, phenol is preferentially adsorbed⁹⁹. However, the activated carbon has been shown to be difficult to regenerate after adsorption¹⁰⁰, and the activated carbon process is expensive. Thus, an adsorbent or treatment that is considerably less expensive is sought. The use of Quat-smectites has shown the HDTMA- and HDPY- exchanged laponites were effective adsorbents, the isotherms being Type I in nature. The HDTMA- and HDPY- exchanged montmorillonites adsorbed by a partitioning process (Section 3.4). Though the laponite results are encouraging, the economic feasibility of their use is low because they are synthetic clays. Thus, as yet, an economically viable method of disposing of phenols using exchanged clays remains to be established.

Solidification/stabilisation technology has been described in Section 1.7.2.3. Here it will be investigated for the ability to immobilise 2-chlorophenol. It has been shown that Quat-clays are needed to immobilise organic compounds in cement matrices as the presence of the organic compound alone in the cement matrix retards hydration of the cement. The Quat-clay appears to act as an interface preventing the organic compound from interacting with the cement to a large degree. Thus, the Quat-clays are often called stabilising agents and the cement, the solidification agent. Here, preliminary studies of the use of OPC (Ordinary Portland Cement) and a previously uninvestigated OPC/GGBS blend (OPC blended with ground granulated blast furnace slag) in the solidification/stabilisation of 2-chlorophenol are detailed.

The presence of 2-chlorophenol in the HDTMA-montmorillonite interlayer region has been confirmed by XRD, SIMS and XPS (Section 3.5.2). Having obtained an Quat-clay capable of adsorbing chlorophenols, this work describes the study of the attenuation of 2-chlorophenol using HDTMA-montmorillonite and solidification/stabilisation technology. Leaching of 2-chlorophenol is tested in two ways: diffusion from the bulk material and diffusion from the pulverised material.

3.9.1 Preparation of 2-chlorophenol-HDTMA-montmorillonite stabilised materials

The adsorption experiments described in Section 3.4 and 3.5 showed that adsorption of 2-chlorophenol occurred by a partitioning process, 20% adsorption occurring. The preparation of the 2-chlorophenol-HDTMA-montmorillonite was as described in Section 3.5. 200 g of 2-chlorophenol-HDTMA-montmorillonite were prepared in 10 g batches. 5 of the 20 batches were analysed for percentage 2-chlorophenol adsorption and an average of $60\% \pm 7\%$ adsorption was observed to occur, as shown by UV. After drying in a desiccator the 2-chlorophenol-HDTMA-montmorillonite was ground to fine powder using a pestle and mortar.

3.9.2 Preparation of solidified/stabilised 2-chlorophenol materials

The resulting 2-chlorophenol-HDTMA-montmorillonite material was mixed with OPC alone and with an OPC/GGBS mix (ratio 1:3). The water/cement ratio used was 0.5. The 2-chlorophenol-HDTMA-montmorillonite was added at 7.5 wt% solids for both experiments. The experimental conditions, that is, 2-chlorophenol ratios and mix ratios to be used in this preliminary study were determined from the work of Montgomery et. al.^{72,73} and from informative discussions with members of the Civil Engineering department. 2-Chlorophenol contents were restricted somewhat by the maximum 2-chlorophenol adsorbed by HDTMA-montmorillonite. In the work of Montgomery et al. satisfactory unconfined compressive strength (UCS) measurements were achieved when the concentration of Quat-clay used was between 8 and 25 wt% and a water:cement ratio of 0.35-0.45 was applied. Conversations with Civil Engineers¹⁰¹ suggested that a low Quat-clay concentration be investigated initially, this would guarantee solidification materials that would set yielding high compressive strengths. A low Quat-clay concentration would also reduce the water absorption which is normally observed when clays are added to cement mixtures, affecting diffusion due to permeability of the final material. A high water content leads to high permeability. The age time of cements effects the UCS of the products. UCS increases with age time. GGBS/OPC cements are known to reach equivalent strengths

later than OPC when age time lies between 1 and 90 days, but from 90 days onwards the strengths are comparable and the GGBS/OPC may have superior strength⁷⁹.

The experimental mix details are given below. These were mixed thoroughly for five minutes and cast into cylindrical PVC moulds. These were then compacted by vibration and sealed, taking care not to trap the air. To minimise segregation, the specimens were rotated for 24 hours end-over-end. They were then stored at 20 °C for 90 days.

Table 3.28 Experimental mix details for attenuation studies

	Experiment	
	1	2
	OPC/GGBS	OPC alone
Components(weights added in grams)		
2-chlorophenol-HDTMA-mont	60	60
OPC	185	740
GGBS	555	/
distilled water	370	370

3.9.3 Leach testing

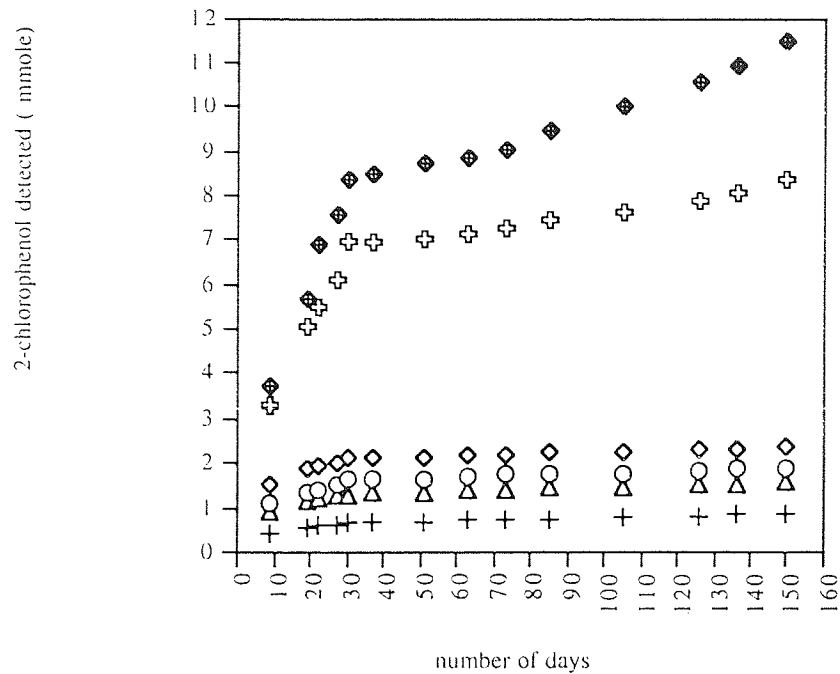
3.9.3.1 Diffusion of 2-chlorophenol from the solidification/stabilisation material

The solidification/stabilisation specimens prepared as described in Section 3.9.2 above were demoulded after the curing period and approximately 1 cm was sliced off the cast end of each cylinder using a diamond saw, the blade of which was lubricated with distilled water. The fresh surface was lightly ground on 600 grade carbide paper, and the remaining surfaces were masked with paraffin wax. Each cylinder was then placed with their axes horizontal in 1 dm³ beakers containing 500 cm³ distilled water. The containers were finally placed in a water bath maintained at 20 °C. The concentrations of the 2-chlorophenol were determined by stirring the solution to ensure equal distribution of any phenol present and then withdrawing 25 cm³ aliquots of the solutions and analysing them by UV. Fresh water was then placed in the

beakers. This analysis was repeated every 7-10 days. Samples were tested in this way over a period of four months. Figure 3.17 shows the results. The graph is presented as cumulative amount of 2-chlorophenol leached in the designated number of days. The reactions were carried out in triplicate.

Generally it can be seen that when the OPC/GGBS is used as the solidification agent it reduces 2-chlorophenol diffusion into the water media. The plot resulting from experiment 4 is the exception and it is likely that GGBS contaminated the OPC cement intended for use in this sample. The OPC/GGBS solidification agent leaches approximately 2 mmole 2-chlorophenol/150 days, compared to the OPC solidification agent which leaches between 8-12 mmole 2-chlorophenol/150 days. This corresponds to the total 2-chlorophenol leached for each solidification material being 17% for the OPC/GGBS solidification material and 75-100% for the OPC solidification material. In slag cements, for example OPC/GGBS, with percentage slag greater than 65%, the pore size distribution differs in that the cement is made up of smaller pores compared to OPC cement⁸⁰. Bakker¹⁰² suggests that the higher permeability of portland cement is due to the precipitation of hydrates close to the reacting grains. The lower permeability of slag is considered as a consequence of hydrate formation between clinker and slag cement grains, filling the space as a semi-permeable membrane.

The attenuation of 2-chlorophenol may not be governed simply by the pore size distribution in cements. Studies of cements with comparable pore size distributions have shown dissimilar diffusion characteristics⁸⁰. It was suggested that another factor affecting diffusion or attenuation may be that of reactions with the hydration products of cement hydration⁸⁰. It has been postulated by Sergi¹⁰³ that diffusion rates are affected by interactions between cement particles and the diffusing ions. The composition of OPC is similar to that of clays in that it contains silicon, aluminium and iron oxides. Under highly dilute conditions 2-chlorophenol is not adsorbed by unmodified smectite clays. It is possible that 2-chlorophenol reacts with any of the metal oxides in the cements, probably by adsorption, before or during hydration, or with the resulting tobermorite, tricalcium disilicate hydrate, after hydration has occurred. However, both the cements contain the metal oxides and tobermorite hydration products, the difference in composition is not known. There are significant differences in the concentration of calcium hydroxide present after the hydration process. Calcium hydroxide was observed at the sides of the reaction vessels containing the OPC solidified material during the leach tests. This leaching of calcium hydroxide may also influence diffusion in that the loss of calcium hydroxide may create holes in the structure for the OPC. However, Sergi¹⁰³ suggested that diffusion of ions was not directly related to calcium hydroxide diffusion. To confirm such



- | | | | |
|---|------------------------------------|---|-----------------------------|
| + | 1 - organo-clay / OPC / GGBS blend | △ | 4 - organo-clay / OPC blend |
| ◇ | 2 - organo-clay / OPC / GGBS blend | ⊕ | 5 - organo-clay / OPC blend |
| ○ | 3 - organo-clay / OPC / GGBS blend | ◆ | 6 - organo-clay / OPC blend |

Figure 3.17 The leaching of 2-chlorophenol from solidification/stabilisation treated materials

findings detailed studies into the nature of the 2-chlorophenol-HDTMA-montmorillonite-cement materials must be undertaken. Such studies should include pore size distributions, unconfined compressive strengths, scanning electron microscopy and adsorption of 2-chlorophenol by the various composites of the cements to examine the effect of the 2-chlorophenol-HDTMA-montmorillonite on the cement properties.

3.9.3.2 Leaching as observed by water percolation tests

As explained above, Quat-clays act as stabilisers and OPC or OPC/GGBS blends act as solidifiers in the solidification/stabilisation materials. Here, the comparison is made between the attenuant properties of the Quat-clays stabilisers and that of the Quat-clay-cement, stabiliser/solidifier materials.

Results of GGBS/OPC and OPC showed the attenuation of 2-chlorophenol, and HDTMA-montmorillonite to be greater when GGBS/OPC was used as

the solidification agent, Section 3.9.3.1. However, the need for the solidification needs to be established. Thus further leach experiments were carried out to compare the leaching characteristics of the stabilised 2-chlorophenol and the solidified/stabilised 2-chlorophenol. For this experiment, the GGBS/OPC-2-chlorophenol-HDTMA-montmorillonite was pulverised, ground and sieved to pass 210 μm and exposed to 50 cm^3 aliquots of groundwater. Pulverisation was carried out to facilitate equal comparison of the materials with respect to surface area exposed to the water medium. HDTMA-montmorillonite-2-chlorophenol - the stabilised 2-chlorophenol - was prepared as described in Section 3.5 and sieved to pass 210 μm . The leaching, or desorption, of 2-chlorophenol was studied by using the percolation column shown in Figure 3.18. The columns are modified 100 cm^3 dropping columns with extra large ports to facilitate the handling of clay samples. The columns are closed systems to reduce evaporation of the 2-chlorophenol and water. The glass balls and glass wool are present to avoid clogging of the cock with the solid materials. Solid materials (10 g) were added to each column with only slight compaction. Uncontaminated groundwater (50 cm^3) was then added on top of the solid material. The percolation columns were kept in the dark to prevent algae growth. Thus, simulation of groundwater and/or rainwater contact with hazardous waste containing landfills was achieved.

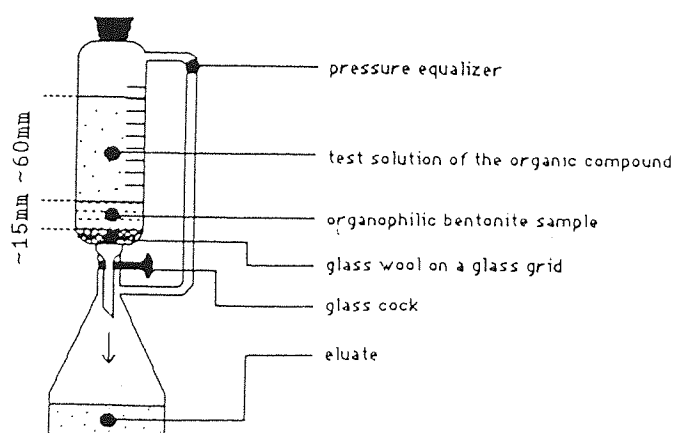


Figure 3.18 The percolation column

The taps were opened weekly, and the liquids percolated the solid materials. The eluate solutions were collected and analysed by UV. The taps were closed and fresh water was added to the columns and left for one week. This was repeated for 10 weeks. The results of the percolation test are shown in Figure 3.19.

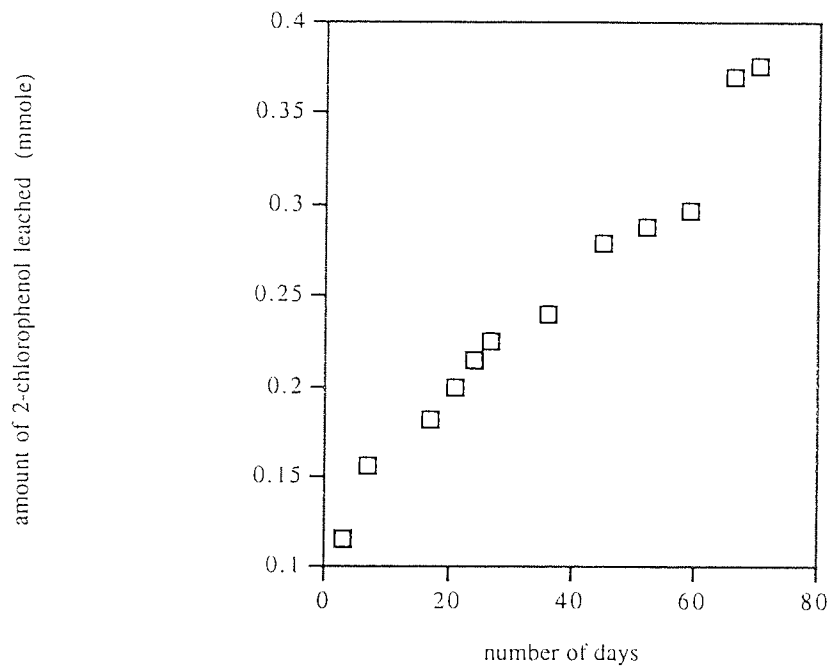


Figure 3.19 (a) The leaching of 2-chlorophenol from solidification/stabilisation treated materials.

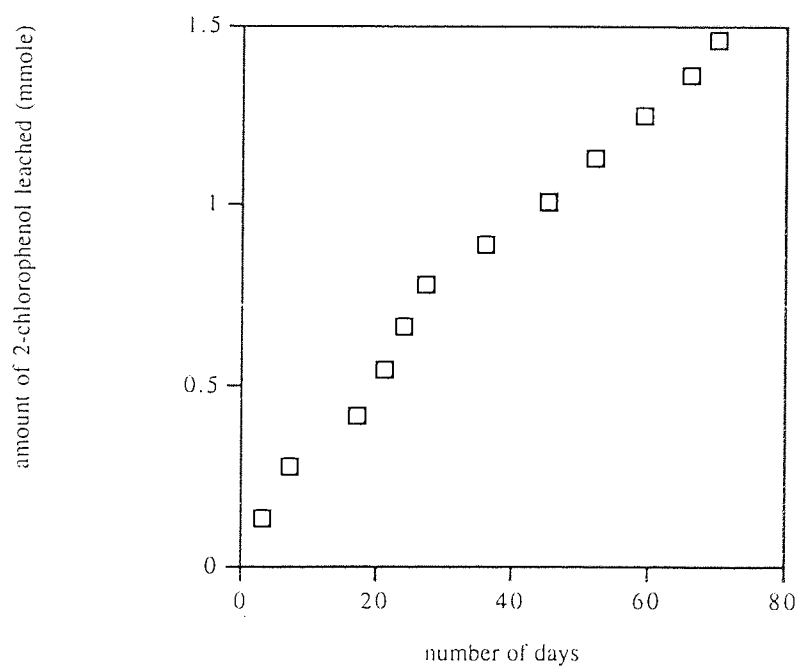


Figure 3.19 (b) The leaching of 2-chlorophenol from stabilisation only treated materials.

The graphs are presented as the cumulative amount of 2-chlorophenol leached in the designated number of days. The data are not directly comparable because 10 g of HDTMA-montmorillonite contains approximately 5 mmoles of 2-chlorophenol in total whereas 10 g OPC/GGBS/HDTMA-montmorillonite contains approximately 0.4 mmoles of 2-chlorophenol. This could not be avoided as scaling one or other of the materials down to allow for equal concentrations of the 2-chlorophenol to be present would mean that either material would be subjected to concentration effects when percolation was carried out, for example, 50 cm³ of water exposed to 0.75 g HDTMA-montmorillonite compared to 50 cm³ of water exposed to 10 g of the solidified material. With these considerations it can be seen that leaching of 2-chlorophenol occurs readily from the pulverised solidified/stabilised system. When the OPC/GGBS is used as the solidification agent and pulverised it increases the rate 2-chlorophenol diffusion into the water medium. The stabilisation agent alone, HDTMA-montmorillonite, turns out to be the better attenuator when the particle size of the solidification and/or stabilisation agent is reduced to 210 µm. The OPC/GGBS solidification agent leaches approximately 0.38 mmole 2-chlorophenol/70 days, compared to the HDTMA-montmorillonite stabilisation agent which leaches 1.5 mmole 2-chlorophenol/70 days. This corresponds to the total 2-chlorophenol leached for each material being 100% and 30% respectively. However, the concentration effects present here cannot be dismissed.

The breaking up of the GGBS/OPC-2-chlorophenol-HDTMA-montmorillonite material resulted in the release of all the 2-chlorophenol present in the material on exposure to ground water. It is probable that fission is along the points where hydration had occurred previously, i.e., between clinker and slag grains. The 2-chlorophenol-HDTMA-montmorillonite is thought to fill in the spaces between these grains where hydration of the cement does not occur. The action of pulverisation and grinding destroys some or all of the small pores which retained the 2-chlorophenol and displaces the trapped 2-chlorophenol from the cement matrix. This action facilitates the release of 2-chlorophenol from the material, the water medium simply displacing the 2-chlorophenol from the materials' surface. However, that comparable diffusion from the HDTMA-montmorillonite does not occur is not readily explainable. The HDTMA-montmorillonite is sieved to pass 210 µm as is the cement stabilisation/solidification product. It is probable that during the mixing process, when the stabilisation product is solidified, the water present during mixing, plays a part in the desorption of the 2-chlorophenol from the HDTMA-montmorillonite material. The results suggest all the 2-chlorophenol is leached from the stabilisation/solidification product. Thus a high concentration of 2-chlorophenol may have been desorbed from the Quat-clay during mixing and adsorbed onto the cement

components of the mixture. On hydration, the 2-chlorophenol may have been trapped at the cement clinker slag grain interface and thus on grinding, the fission of this interface caused desorption of the 2-chlorophenol. The 2-chlorophenol-HDTMA-montmorillonite was not exposed to agitation with water previous to the leach experiments, thus desorption of 2-chlorophenol was significantly less from the stabilised material.

3.9.4 Solidification/stabilisation - Conclusions

In the application of stabilisation/solidification technology to attenuation of 2-chlorophenol, the use of the cement blend OPC/GGBS in a ratio of 1:3 proved to be a more effective attenuator than the established use of OPC alone. This is due to

- (i) the smaller pore sizes present in the OPC/GGBS,
- (ii) interactions between cement particles and the 2-chlorophenol, and may be due to,
- (iii) the creation of holes in the OPC structure resulting from diffusion of calcium hydroxide from the stabilised/solidified 2-chlorophenol material.

However, when the OPC/GGBS stabilised/solidified 2-chlorophenol material was ground to 210 μm and compared to HDTMA-montmorillonite stabilised 2-chlorophenol, the HDTMA-montmorillonite was found to be the better attenuant. This was thought to result from the breaking up of the cementitious material exposing the 2-chlorophenol which may have preferentially adsorbed onto the hydration sites of the cement during the mixing process. Concentration effects may also have influenced desorption. The exposed 2-chlorophenol was easily removed from the exposed surfaces by the ground water used in the leach tests.

3.10 Further work

The high degree of interaction between the chlorinated phenols and HDTMA- and HDPY-laponites marks a step forward in the adsorption of chlorinated phenols by exchanged clays. Laponite is an expensive synthetic clay similar to the hectorites in structure and a similar study should be undertaken with hectorite clays before waste disposal applications can be considered.

Studies, similar to those of Jaynes and Boyd⁵⁹, of the effect of clay layer charge and TMPA cation concentration on phenol adsorption by TMPA exchanged clays may identify the adsorption sites in these exchanged clays.

There is a need for the investigation of phenol adsorption by different quaternary ammonium cations exchanged clays with a view to achieving Type I adsorption.

Further characterisation (X-ray Diffraction, Scanning Electron Microscopy) of the mixture of Quat-smectites and double-Quat-smectites will aid elucidation of the mechanisms of the adsorption of the phenols.

The study of the competition reactions involved during the adsorption of two or more phenols by single, mixed and double Quat clays as well as adsorption from various solvents as a model of industrial waste streams warrants study.

In order to speculate on the orientation of the 2,4,6-trichlorophenol on adsorption by various adsorbents, surface area of the adsorbents must be obtained to allow for use of the Langmuir equation to estimate the surface area occupied by the 2,4,6-trichlorophenol and therefore the orientation.

Though OPC/GGBS is a good attenuator for 2-chlorophenol when stabilised by HDTMA-montmorillonite, the compressive strength of the material will need to be tested. Mix development studies will need to be developed to optimise leach characteristics, strength characteristics and optimum hazardous organic waste concentrations. A more accurate comparison between 2-chlorophenol-HDTMA-montmorillonite stabilised and 2-chlorophenol-HDTMA-montmorillonite-OPC/GGBS stabilised/solidified materials is needed before an informative discussion on the leaching of these two materials can take place.

Detailed studies on the surface area and pore size distributions of the stabilisation and solidification materials would enable the investigation between diffusion and pore size to be more fully investigated.

Chapter 4

Adsorption of phenol and mono-chlorinated phenols from aqueous solutions by tetramethylammonium-, tetramethylphosphonium- and tetraphenylphosphonium-exchanged montmorillonites

4.1 Introduction

The presence of Na^+ cations or Ca^{2+} cations in the interlayer region of natural montmorillonite, renders the clay surface relatively hydrophilic. This makes the natural clay ineffective as an adsorbent for organic contaminants such as chlorinated phenols. Modification of these natural clays with quaternary ammonium cations (Quats), result in a relatively more hydrophobic/organophilic clay compared to the clay precursor. These Quat-clays, have been shown to remove various organic contaminants from water, see Chapter 1.

When the tetramethylammonium cation is used to modify the clay surface, the cations exist as discrete, organic-modified surface adsorption sites on the clay surface^{104,58}. Modification of the clay surface from relatively hydrophilic to relatively hydrophobic, results from the presence of the organic cations reducing the degree of hydration of the clay, and decreasing the aluminosilicate mineral surface area. When tetramethylammonium exchanged montmorillonite, TMA-montmorillonite, is used as an adsorbent to adsorb organic contaminants from water, comparison of the isotherms obtained suggest that adsorption is dependant on the size and shape of the organic contaminant. It has generally been found that Type I isotherms are obtained for the smaller organic contaminants, for example benzene. Such isotherms are characteristic of strong adsorbate-adsorbent interactions. For larger organic contaminants such as the alkyl benzenes, the isotherms obtained are generally Type III or V, characteristic of weak interactions. This is exemplified both in the work of Lee et. al.⁵⁸ and Kukkadapu and Boyd¹⁰⁵.

Work by Mortland et al.⁵⁶ and subsequent studies described in Chapter 3 show that for the uptake of phenol and mono-chlorinated phenols from water, adsorption efficiencies increased when the clays were modified with quaternary alkyl ammonium ions. Adsorption of phenol was maximised when trimethylphenylammonium-smectites (TMPA-montmorillonite and TMPA-laponite) were the adsorbents. Hexadecyltrimethyl ammonium-smectites (HDTMA-montmorillonite and HDTMA-

laponite) proved to be the better adsorbents for the chlorinated phenols. Phenol was not adsorbed by TMA-smectite. In the case of the 3-chlorophenol/HDTMA-montmorillonite system⁵⁶, the Type V isotherm obtained and the observed dependence of adsorption upon solubility, suggested that the mechanism for adsorption was that of a partitioning process due to presence of the long $C_{16}H_{33}$ - chains of the HDTMA cation. The partitioning process, however, could not explain the adsorption characteristics of the TMPA-smectite systems.

The adsorption isotherms observed for the uptake of phenols - phenol and chlorinated phenols - from water when exposed to TMPA-montmorillonite, TMPA-laponite and TMA-montmorillonite were Type V or showed no adsorption. Adsorption by the TMPA-smectite adsorbents was not dependant on the solubility of the phenol. This was suggested to be due to the arrangement of the quaternary ammonium cations in the interlayer region for these Quat-smectites, which leave the aluminosilicate mineral surfaces of the clay exposed. Thus, the Quat-smectites can be described as partially hydrophilic and partially hydrophobic. The phenols and chlorinated phenols were not always able to interact with this type of adsorbent⁵⁶, see also Chapter 3.

Work by Kukkadapu and Boyd¹⁰⁵, described a detailed preliminary study of the adsorption of alkylbenzenes from water by TMA-montmorillonite and the novel tetramethylphosphonium exchanged montmorillonite (TMP-montmorillonite) system. Here it was suggested that the difference in adsorption efficiencies was not due to differences in surface area or interlayer spacings, but due to the fact that the TMA-montmorillonite interlayer surfaces were hydrated to a greater degree than those of tetramethylphosphonium exchanged montmorillonite, TMP-montmorillonite. It was proposed that hydration of TMA-montmorillonite lead to a decrease in the pore size accessible for adsorption.

In this chapter, the hydrophobicity of TMP-montmorillonite relative to TMA-montmorillonite and, the size and shape exclusion phenomena are further explored. The adsorption efficiencies of TMA-montmorillonite and TMP-montmorillonite in the adsorption of phenol, and mono-chlorinated phenols of comparable solubilities, from water are studied. Adsorption characteristics of tetraphenylphosphonium exchanged montmorillonite, TPP-montmorillonite, are also studied. This research was conducted under the supervision of Prof. Stephen Boyd, Department of Crop and Soil Science, Michigan State University, USA.

4.2 Preparation of exchanged montmorillonites

4.2.1 Preparation of sodium saturated montmorillonite

Wyoming montmorillonite clay, was obtained from the American Colloid Company as Wyoming bentonite. This clay is also referred to as SAC. Prior to use the clay was purified and sodium saturated by standard techniques. A $< 2 \mu\text{m}$, sodium saturated homoionic clay fraction was obtained by stirring 10 g of the clay with 1 dm³ of 1M NaCl solution overnight. This was followed by centrifugation at 5000 - 6000 rpm, and replacement of the supernatant, NaCl, with a fresh solution. This sequence was repeated three times after which the clay was washed with distilled water and centrifuged until the supernatant was chloride free as indicated by 0.1M AgNO₃. The sodium saturated clay was then wet sedimented to obtain the $< 2 \mu\text{m}$ fraction. The weight:volume ratio of the suspension was calculated by extracting a 25.0 cm³ portion and leaving to air dry. The dried clay was then weighed. The $< 2 \mu\text{m}$ fraction was stored as ~1 wt.% suspension for further use.

4.2.2 Preparation of exchanged clay

Three exchanged clays were prepared by exchanging the interlayer Na⁺ cations of the purified clay suspension with the cations of (CH₃)₄N⁺Cl⁻ or TMA⁺Cl⁻ (supplied by Kodak), (CH₃)₄P⁺Br⁻ or TMP⁺Br⁻ and (C₆H₅)₄P⁺Br⁻ or TPP⁺Br⁻ (supplied by Aldrich). The exchanged clays were prepared as described by Kukkadapu and Boyd¹⁰⁵. 300 cm³ of TMA⁺Cl⁻, TMP⁺Br⁻ and TPP⁺Br⁻ solutions were added to 700 cm³ of ~1 wt.% sodium saturated montmorillonite suspension. The Quats were added at 5 times the c.e.c of the montmorillonite clay (90 meq/100 g) over a period of 5 - 10 minutes. The mixture was stirred at room temperature overnight, then centrifuged several times with distilled water until the supernatant was chloride or bromide ion free as indicated by 0.1M AgNO₃.

4.3 Characterisation of exchanged clays

Table 4.1 summarises the physical characteristics of the exchanged clays

Table 4.1 Properties of Parent reference smectite and Quat-smectites

Material	Basal spacing Å	Surface Area ¹ (m ² /g)	Organic carbon content (%)
SAC (montmorillonite)	9.40 ¹⁰⁶	—	—
TMA-montmorillonite	14.03	212	3.9
TMP-montmorillonite	14.37	156	3.8
TPP-montmorillonite	18.60	—	21.20

¹ from N₂ BET

4.3.1 X-ray Diffraction (XRD)

X-ray diffraction patterns were obtained for oriented film and powder samples using a Rigaku diffractometer with a rotating anode and CuK_α radiation.

The slight difference in the basal spacings of the two tetramethyl- exchanged clays (0.35 Å) is in good agreement with the difference in the ionic radii of the N(III) and P(III) ions, 0.16 Å and 0.44 Å respectively¹⁰⁷. TPP-montmorillonite was found to have a basal spacing of 18.60 Å. The basal spacings suggest that all cations are arranged in a monolayer in the interlayer region of the montmorillonite clay.

4.3.2 Surface area

Surface area measurements were carried out at liquid nitrogen temperatures (77 K) on a Coulter Omnisorb 360CX sorptometer. For surface area measurements, samples were degassed at 120 °C for approximately 12 hours at 10⁻⁴ Torr. Surface areas were obtained using the BET method.

The high surface areas of the two tetramethyl- exchanged clays combined with the increase in basal spacings from 9.4 Å to 14 Å confirm exchange of the interlayer

sodium cations by the TMA and TMP cations. The TMP cations, being larger than TMA cations, also occupy a greater volume leading to lower N₂ BET surface areas.

4.3.3 Elemental analysis

C, H, N and P elemental analyses were carried out by Microanalysis Laboratory of the School of Chemical Sciences of the University of Illinois, Urbana-Champaign, Illinois.

The organic carbon contents of the two tetramethyl- exchanged clays correspond to 93% of the expected exchange occurring in the interlayer region. Both the TMA and TMP cations are exchanged to similar extents. 95% exchange resulted from the reaction of the TPP cation with montmorillonite clay.

4.4 Adsorption studies

4.4.1 Adsorption isotherms

Phenol, 2-chlorophenol, 3-chlorophenol and 4-chlorophenol were obtained from Sigma Chemical Corporation and were used without further purification.

Table 4.2 Water solubilities and Ultraviolet absorption bands (λ_{\max}) of phenols investigated

Compound	λ_{\max} (nm)	solubility (g/dm ³)
phenol	268	77.5
2-chlorophenol	274	28.5
3-chlorophenol	274	25.0
4-chlorophenol	274	27.1

The adsorption isotherms were measured using the batch equilibration technique. For each isotherm, 100 mg portions of the exchanged clay were weighed onto 250 cm³ Erlenmeyer flasks, to this was added the phenol under investigation in concentrations

of 0.02 - 0.15 mmole/100 cm³ distilled water. The flasks were shaken overnight at 20 °C. The contents of each flask were filtered and the concentration of the supernatant determined from the UV absorbance at λ_{max} of the phenol (Table 4.2). A UV-Hewlett Packard 8452A Diode Array Spectrophotometer with HP 89531A MS-DOS UV/VIS operating software was used for absorbance measurements. The amount of phenol adsorbed was determined by the difference between the initial and final phenol concentrations. All adsorption isotherm experiments were carried out in duplicate.

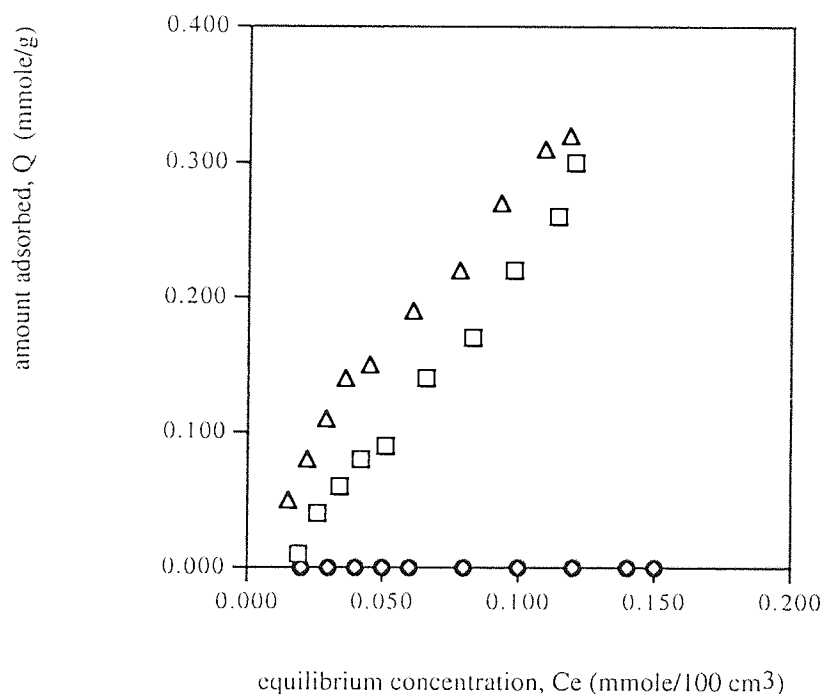


Figure 4.1 Adsorption of phenols from water by TMP-montmorillonite; phenol (squares), 2-chlorophenol (diamonds), 3-chlorophenol (circles) and 4-chlorophenol (triangles).

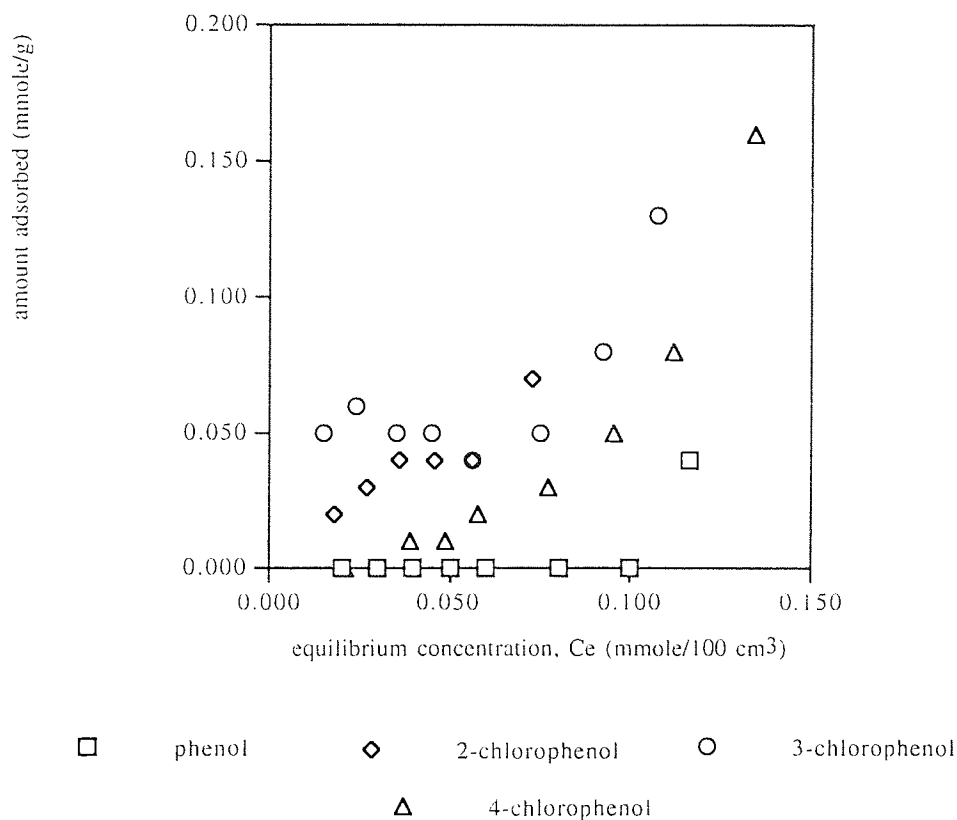


Figure 4.2 Adsorption of phenols from water by TPP-montmorillonite; phenol (squares), 2-chlorophenol (diamonds), 3-chlorophenol (circles) and 4-chlorophenol (triangles).

Figure 4.1 shows adsorption isotherms of the four phenols on TMP-montmorillonite and Figure 4.2 shows adsorption of the phenols by TPP-montmorillonite. TMA-montmorillonite does not adsorb the four phenols.

On comparison of adsorption by TMA- and TMP-montmorillonite, a distinct difference in the adsorption efficiencies of the two Quat-montmorillonites is evident from the isotherms, see Figure 4.1. The TMA-montmorillonite results are similar to those observed by Mortland et. al.⁵⁶ in that a negligible quantity of phenol is adsorbed. The chlorinated phenols show no affinity for this Quat-montmorillonite. This can be juxtaposed with TMP-montmorillonite where adsorption of phenol and 4-chlorophenol occurs, 4-chlorophenol being adsorbed to higher capacity and with greater strength of interaction than phenol. The difference in adsorption persists to a relatively high equilibrium concentration.

It is interesting to observe that only phenol and 4-chlorophenol are adsorbed by the TMP-montmorillonite. The adsorption isotherm of phenol was Type V, typical of

weak adsorbate-adsorbent interactions. 4-chlorophenol exhibited a Type II isotherm which indicates strong adsorbate-adsorbent interactions at low equilibrium concentrations, followed by a slight plateau and then a final upsweep. Adsorption of 2- and 3-chlorophenol was not observed despite the comparable solubilities of 2-, 3-, and 4- chlorophenol in water (Table 4.2). Thus adsorption is not solubility dependant for the TMP-montmorillonite adsorbent.

In the comparison of TMA- and TMP- montmorillonites as adsorbents for the phenols, it must be concluded that neither interlayer spacing, or surface area are responsible for the difference in adsorptive behaviour. TMP-montmorillonite has a lower N₂ BET surface area than TMA-montmorillonite and the interlayer spacings of the two Quat-montmorillonites are comparable.

Adsorption in the interlayer "pores" is apparent from the absence of surface adsorptions. Surface adsorptions are typical of weak adsorbate-adsorbent interactions, normally as a result of using a non-porous adsorbent, and result in Type III isotherms¹⁰⁸. If adsorption is on the surfaces of particles, as opposed to in the "pores", TMA-montmorillonite and TMP-montmorillonite should exhibit adsorption efficiencies proportional to their surface areas¹⁰⁵. The failure to observe Type III isotherms or adsorption proportional to surface area indicates adsorptions are occurring in the interlayer "pores" of the TMP-montmorillonite. TMP-montmorillonite, in spite of it's lower surface area, exhibits higher adsorption due to the larger interlayer "pore" size compared to TMA-montmorillonite. The adsorptions observed for TMP-montmorillonite suggest that interlayer adsorptions are occurring.

The apparent inability of TMA-montmorillonite to adsorb this group of phenols may be due to the fact that the interlayer "pore" sizes are not large enough to accommodate phenol or the chlorinated congeners. Thus, the different adsorption behaviours by TMA- and TMP-montmorillonites in water are due to a difference in interlayer "pore" structure.

In the study of the adsorption of water vapour by TMA-montmorillonite and TMP-montmorillonite in order to ascertain the hydrophobic/hydrophilic nature of the Quat-montmorillonites, it was shown that TMA-montmorillonite adsorbs more water than TMP-montmorillonite and is therefore relatively more hydrophilic than the TMP-montmorillonite¹⁰⁵. The greater hydrophilicity observed for TMA-montmorillonite will result in hydration of the interlayer region of TMA-montmorillonite to a greater extent than that which may occur in the interlayer region of TMP-montmorillonite¹⁰⁵.

This solvation may decrease the "pore" size of the Quat-montmorillonites. Despite this decrease in "pore" size, TMP-montmorillonite is still able to accommodate two of the phenols investigated. However, TMA-montmorillonite undergoes a decrease in "pore" size which results in no adsorption. Thus, the increased phenol adsorption efficiencies observed for TMP-montmorillonite compared to TMA-montmorillonite may be attributable to both the higher hydrophobicity of the TMP-montmorillonite and the subsequent decrease in the pore size of the TMA-montmorillonite resulting from hydration, Figure 4.3.

Similar conclusions were reached by Kukkadapu and Boyd¹⁰⁵, when adsorption of alkylbenzenes by similar Quat-montmorillonites was investigated.

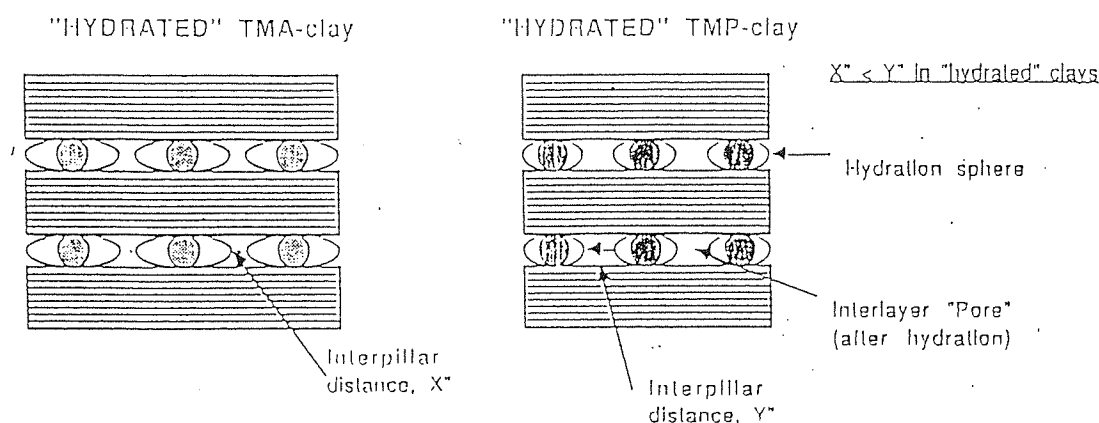


Figure 4.3 Schematic representation of hydration of the TMA and TMP cations in the montmorillonite interlayer region.

For TMP-montmorillonite adsorption of phenols, it may be concluded that adsorption is specific towards certain phenols and mono-chlorinated phenols. This seems apparent due to the adsorption of phenol and 4-chlorophenol and the absence of adsorption of 2- and 3-chlorophenols. Physically, the interlayer "pores" may not be the correct size or shape to accommodate 2- or 3-chlorophenol. Phenol is the smallest molecule of the four, but the adsorption of 4-chlorophenol over 2- and 3-chlorophenol when their solubilities are comparable suggests that the shape of the molecule may effect adsorption. Chemically, the difference in adsorption efficiencies may be affected by the electronic state of the molecules. Dipole moments of the molecules may affect adsorption. Unfortunately, dipole moment data of these compounds in aqueous solution are not documented.

The adsorption characteristics of TPP-montmorillonite observed here are similar to the characteristics of the TMP-montmorillonite adsorbent described above. The interaction between 3-chlorophenol and TPP-montmorillonite is a strong one at low equilibrium concentrations resulting in a Type II isotherm. 2-chlorophenol is adsorbed via a partitioning process. 4-chlorophenol and phenol interact weakly with the adsorbent, the adsorption isotherms being Type III. Thus, as in the case of TMP-montmorillonite, adsorption is not solubility dependant and is phenol specific, but the specificity of the TPP-montmorillonite adsorbent appears to be directly opposite to that of the TMP-montmorillonite adsorbent.

In the case of the 3-chlorophenol, and to a certain extent the 2-chlorophenol, interactions between the adsorbate and the adsorbent may be via the benzene rings of the two aromatic components. The TPP cations are large cations, expected to form a monolayer arrangement in the interlayer region of the montmorillonite clay. The strong adsorbate-adsorbent interaction between the 3-chlorophenol and the TPP-montmorillonite suggests that the 3-chlorophenol is able to adsorb in the interlayer region. Interlayer adsorption may also occur for 2-chlorophenol. Thus, the interlayer region is only able to accommodate a high concentration of 3-chlorophenol and 2-chlorophenol. The Type III isotherms obtained for phenol and 4-chlorophenol suggest adsorption of these two phenols is on the surface of the adsorbent only. Reasons for the specificity shown towards 3- and 2-chlorophenol are not yet clear but possible explanations were discussed above as for TMP-montmorillonite adsorption.

4.4.2 Competitive adsorption studies

The effect of the presence of phenol upon 4-chlorophenol adsorption, and visa versa, was examined by studying the effect of a constant concentration of one solute, A, on a varying concentration of another solute, B. The adsorption of solute B was monitored. To determine the extent of competitive adsorption, the adsorption experiments were conducted as described in Section 4.1 except the second phenolic compound, phenol or 4-chlorophenol, was added to each Erlenmeyer flask at a constant concentration of 0.05 mmole/100 cm³ and 0.1 mmole/100 cm³. The final concentrations of the phenols were determined by HPLC. In this case, NaOH, at a concentration equivalent to the initial concentration of the phenols, was added to the supernatants. The resulting solution was then filtered with 13 mm minispice, 0.45 µm, Acro disc PVDF filters. High Performance Liquid Chromatography was carried out on a Hewlett Packard Series 1050 HPLC. An octadecylsilane phase column and a wavelength of 218 nm was used for separations. Carrier solutions employed were

0.1% phosphoric acid, and methanol at a ratio of 50:50. Chromatography was achieved under conditions of helium and nitrogen. A HP 3396A integrator was employed for peak area calculations and a sample changer was used to automate runs.

Figures 4.4 and 4.5 show the competitive effects in the adsorption of phenol and 4-chlorophenol by TMP-montmorillonite. If the adsorption isotherms of 4-chlorophenol as a single solute and as a binary solute from its mixtures with two different concentrations of phenol are plotted on the same diagram, they are nearly superimposable (Figure 4.4). When the initial phenol concentration was some five times greater than the initial 4-chlorophenol concentration, phenol was unable to compete effectively with 4-chlorophenol and the adsorbate-adsorbent (4-chlorophenol/TMP-montmorillonite) interaction remains unchanged - isotherm Type II. This suggests that at the relative concentrations studied here, phenol was unable to compete effectively with 4-chlorophenol for adsorption sites on the TMP-montmorillonite.

When the adsorption isotherms of phenol as a single solute and as a binary solute from its mixtures with two different concentrations of 4-chlorophenol are plotted on the same diagram, a difference in adsorption capacity is observed (Figure 4.5). Thus, in the binary solute systems, 4-chlorophenol significantly depressed the adsorption capacity of the adsorbent for the phenol, with no effect on the type of adsorbate-adsorbent interaction (phenol/TMP-montmorillonite), that is the isotherm Type remains as Type V. 4-chlorophenol shows that it is able to compete effectively with phenol for adsorption sites on the TMP-montmorillonite and thus the adsorption of phenol is reduced in the presence of 4-chlorophenol.

The 4-chlorophenol adsorption isotherm is unaffected by the presence of phenol, but that of the phenol is affected by 4-chlorophenol. The presence of 4-chlorophenol in a phenol solution noticeably reduces the amount of phenol adsorbed when the two phenols are present at equal concentrations. It is interesting to note that even though phenol uptake is reduced by the 4-chlorophenol, the interaction remains as Type V rather than being "reduced" to Type III.

Both the adsorption capacity and interaction of 4-chlorophenol remains unchanged in the presence of phenol and it is therefore assumed that 4-chlorophenol adsorbs at the same adsorption sites whether in a single or binary system. Phenol adsorption capacity is reduced in the presence of 4-chlorophenol, this suggests that 4-chlorophenol is able to adsorb at some of the phenol adsorption sites. Thus it seems that phenol and 4-chlorophenol have their own adsorption sites. Phenol is able to

adsorb only at specific adsorption sites, whereas 4-chlorophenol can compete and adsorb at phenol adsorption sites.

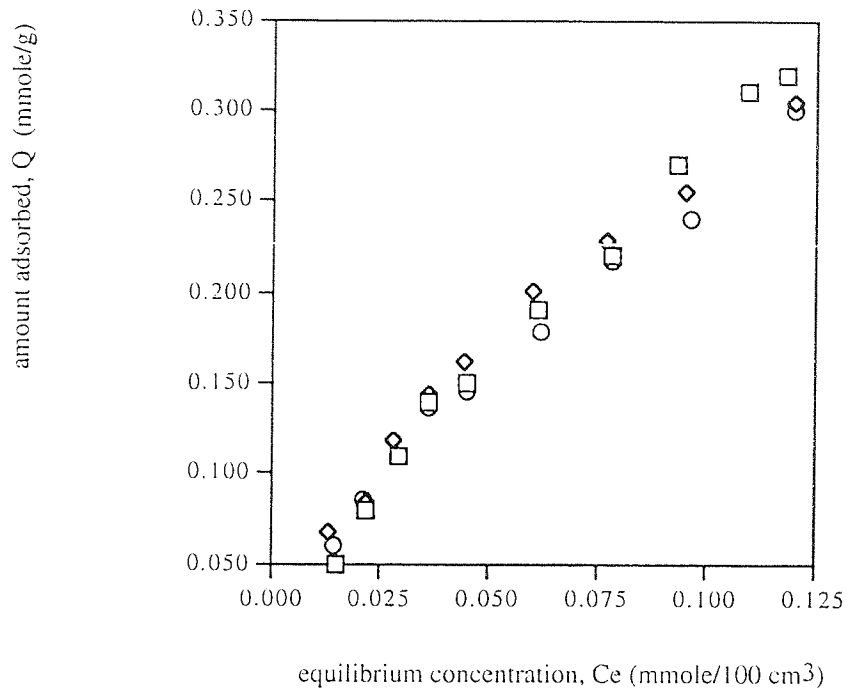


Figure 4.4 Adsorption of 4-chlorophenol from water by TMP-montmorillonite in the presence of phenol; 0.05 mmole/100 cm³ phenol (diamonds), 0.1 mmole/100 cm³ phenol (circles) and in the absence of phenol (squares).

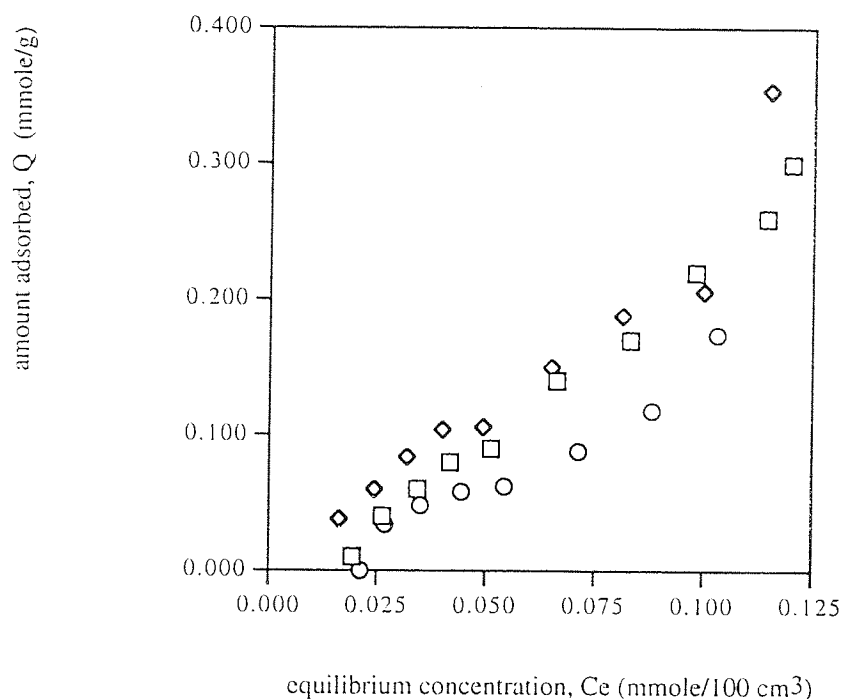


Figure 4.5 Adsorption of phenol from water by TMP-montmorillonite in the presence of 4-chlorophenol; 0.05 mmole/100 cm³ 4-chlorophenol (diamonds), 0.1 mmole/100 cm³ 4-chlorophenol (circles) and in the absence of 4-chlorophenol (squares).

4.5 Conclusions and Further work

TMA-, TMP- and TPP- cations react with montmorillonites yielding high percentage exchange products.

In the comparison of adsorption of phenol and its mono-chlorinated congeners by TMA-montmorillonite, TMP-montmorillonite and TPP-montmorillonite it may be concluded that TMA-montmorillonite is unable to adsorb phenol or mono-chlorinated phenols.

Adsorption in the case of TMP-montmorillonite and TPP-montmorillonite, apparently, occurs on the aluminosilicate mineral surfaces between the organic cations. TMP-montmorillonite was found to be a better adsorbent than TMA-montmorillonite. This disparity in adsorption efficiency is suggested to be due to hydration of the interlayer cations occurring to a greater extent in TMA-montmorillonite than in TMP-montmorillonite. This would result in the interlayer pore size being smaller for TMA-

montmorillonite than for TMP-montmorillonite. TMP-montmorillonite shows selective adsorption within the group of chlorinated phenols, studied here, having comparable solubilities. Phenol and 4-chlorophenol are adsorbed by the TMP-montmorillonite whereas 2- and 3-chlorophenol are not adsorbed.

TPP-montmorillonite also shows selective adsorption within the group of phenols studied here. However, the selectivity is directly opposite to the adsorption characteristics of TMP-montmorillonite showing greater affinity towards 2- and 3-chlorophenol over phenol and 4-chlorophenol.

The selectivity exhibited by TMP-montmorillonite and TPP-montmorillonite for phenol and mono-chlorinated phenols is suggested to be shape or electronic state dependant.

4-chlorophenol is able to compete effectively with phenol for adsorption sites when TMP-montmorillonite is used as the adsorbent.

Further work should include some study of the effect of various adsorbate-adsorbent interactions on the interlayer spacing of the adsorbent. This will support or negate the theory that Type III isotherms are indicative of surface adsorption and the remaining adsorption types are indicative of interlayer adsorption, when solution adsorption is studied.

Chapter 5

Adsorption of organo-tin compounds by exchanged and non-exchanged smectites

5.1 Introduction

Legislation has been set in place and is constantly reviewed to reduce the amount of hazardous organic compounds in industrial waste streams. The impetus for research in the area of adsorption of organic compounds by quaternary ammonium exchanged clays (see Section 1.5.2), has been the need for novel and effective methods for adsorption of problematic organic contaminants, for example phenolic compounds.

Research in the field of adsorption of organo-metallic compounds has not received as much attention as adsorption of organic compounds. It was only in the late 1980s and early 1990s that legislation, reducing pollution of the aquatic environment by hazardous organo-tin compounds, started to take effect (see Section 1.8). As with the organic compounds, legislation has highlighted the need for more effective methods of treatment and/or disposal of organo-metallic compounds.

Meer¹⁰⁹ studied the adsorption of triphenyltin chloride and bis(tributyltin) oxide from ethanol, by quaternary ammonium exchanged montmorillonites. The two organo-tin compounds were found to be only slightly soluble or sparingly soluble in water, their solubility lying below that which would allow for spectroscopic investigations of the aqueous solutions. Thus, adsorption from ethanol was studied. UV studies of bis(tributyltin) oxide in ethanolic solution showed that bis(tributyltin) oxide was found to obey the Beer-Lambert law within the concentration range required for obtaining adsorption isotherms. However studies of triphenyltin chloride in a range of solutions did not obey the Beer-Lambert law. Triphenyltin chloride is susceptible to hydrolysis in polar solvents¹¹⁰ producing triphenyltin hydroxide and subsequently bis(triphenyltin) oxide. This susceptibility to hydrolysis is found to be enhanced on laponite clay surfaces⁹⁵. It is probable that in a waste stream, triphenyltin chloride would be hydrolysed to triphenyltin hydroxide. In the case of direct landfilling, for example, a clay landfill liner designed for the attenuation of triphenyltin chloride would also need to be capable of attenuating the hydroxide. The complex water chemistry of triphenyltin chloride and the high probability of its conversion to the hydroxide lead to research continuing with triphenyltin hydroxide in ethanolic solution, which obeyed the Beer-Lambert law.

Adsorption isotherms were obtained where hexadecyltrimethyl ammonium exchanged montmorillonite (HDTMA-montmorillonite) and trimethylphenyl ammonium exchanged montmorillonite (TMPA-montmorillonite) were the adsorbents, and triphenyltin hydroxide and bis(tributyltin) oxide were the adsorbates. The results are summarised in Table 5.1. Adsorption of bis(tributyltin) oxide by both exchanged clays was found to follow a Type V isotherm, characteristic of weak adsorbate-adsorbent interactions. Adsorption of triphenyltin hydroxide on both exchanged clays followed a Type I isotherm characteristic of strong adsorbate-adsorbent interactions. Adsorption always occurred to a greater extent with HDTMA-montmorillonite. This was suggested to be due to the fact that the long alkyl chains present on the clay surface enhance the adsorbate-adsorbent interactions. Figures 5.1 and 5.2 show the results from these studies.

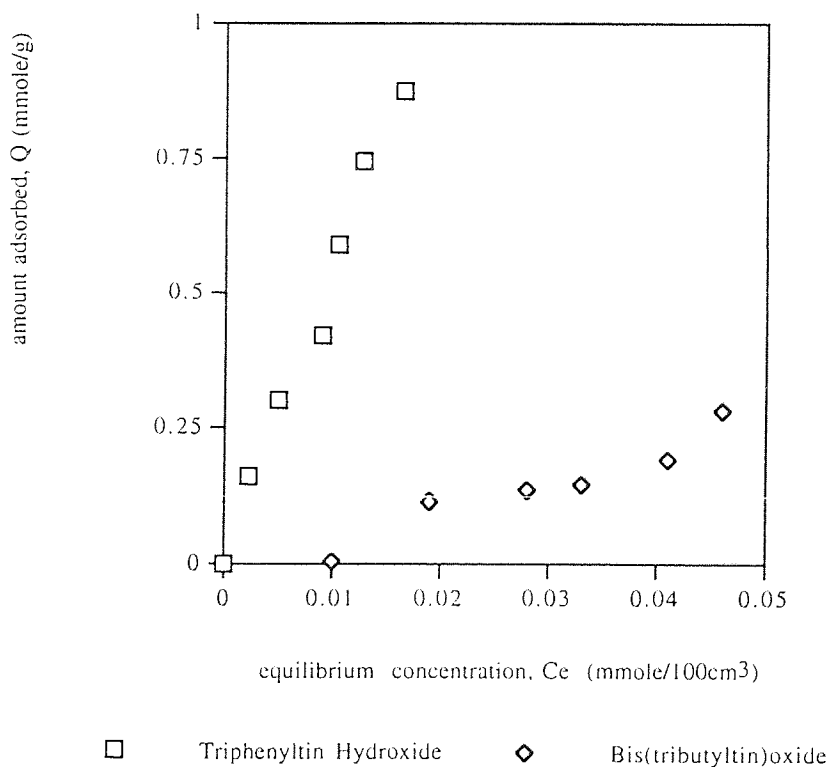


Figure 5.1 Adsorption of organo-tin compounds from ethanol by HDTMA-montmorillonite¹⁰⁹

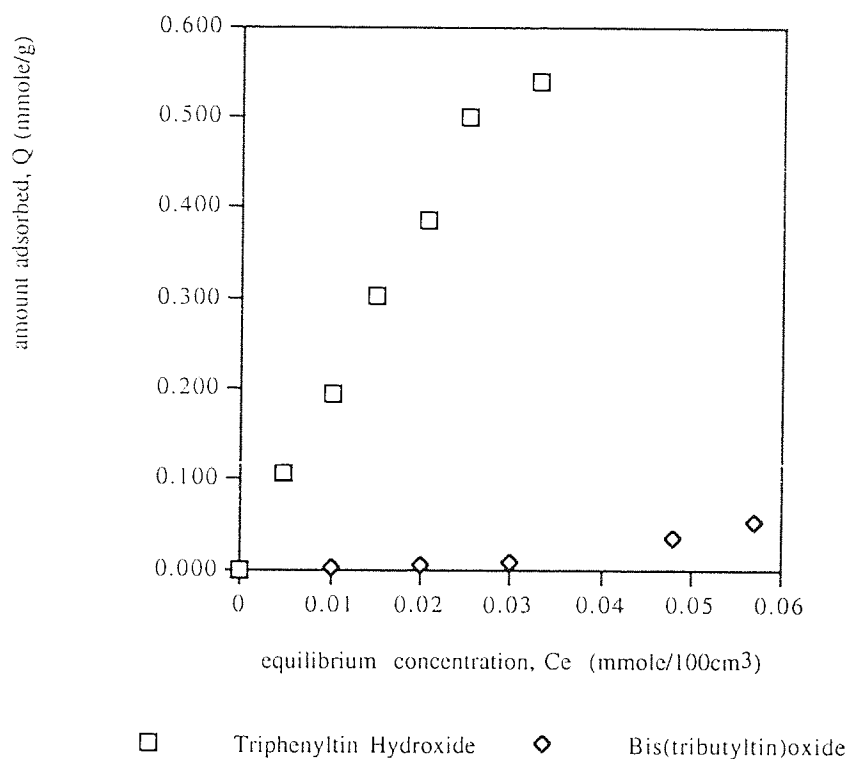


Figure 5.2 Adsorption of organo-tin compounds from ethanol by TMPA-montmorillonite¹⁰⁹

Table 5.1 Summary of adsorption of organo-tin compounds by Quat-clays and percentage adsorption, after Meer¹⁰⁹

Adsorbent	Adsorbate	Isotherm Type	% adsorption
HDTMA-mont	bis(tributyltin) oxide	V	23
	triphenyltin hydroxide	I	73
TMPA-mont	bis(tributyltin) oxide	V	4
	triphenyltin hydroxide	I	45

Both adsorbents had a greater adsorption capacity for the triphenyltin hydroxide than for the bis(tributyltin) oxide. It was suggested that a solubility effect was being observed, in that if one assumes bis(tributyltin) oxide is more soluble than triphenyltin hydroxide, the more hydrophobic triphenyltin hydroxide is adsorbed by the hydrophobic clays. In summary, adsorbate-adsorbent interactions were thought to be in competition with adsorbate-solvent interactions.

5.2 Adsorption of organo-tin compounds by quaternary ammonium exchanged smectites

In the adsorption of organic compounds, quaternary ammonium exchanged clays have proved effective in terms of the strength of interaction, adsorption capacity and selectivity. In investigating new methods for the treatment of organo-tin compounds it seems logical to examine the quaternary ammonium exchanged clays as adsorbents for these compounds. Thus the work of Meer was repeated and extended with a view to characterising the types of interactions that take place.

The organo-tin compounds under investigation in this chapter are triphenyltin hydroxide and bis(tributyltin) oxide. The uses and reasons for environmental concern with regard to these compounds were outlined in Sections 1.8.1 and 5.1

5.2.1 Quaternary ammonium exchanged smectite preparation

For preliminary investigations, the Quat-clays prepared in Chapter 3 were used in the attempted adsorption of organo-tin compounds.

5.2.2 Adsorption Isotherms

For reasons discussed earlier in this chapter, adsorption isotherms were obtained for organo-tin compounds adsorbed from ethanolic solution, dry absolute ethanol was used for all experiments. Absolute ethanol was dried by distillation and storing over molecular sieve. Bis(tributyltin) oxide and triphenyltin hydroxide were used without further purification. In UV studies of bis(tributyltin) oxide in ethanolic solution, the Beer-Lambert law was obeyed in the concentration range 10^{-5} M - 10^{-4} M, equivalent to between 6 ppm (mg dm^{-3}) and 60 ppm, when a wavelength of 218 nm was used for analysis. Triphenyltin hydroxide in ethanolic solution was found to obey the Beer-Lambert law in the concentration range 10^{-4} M - 10^{-3} M, equivalent to between 37 ppm and 370 ppm, when a wavelength of 263 nm was used for analysis. Both concentration ranges are three to four orders of magnitude greater than that regarded as toxic to fish⁸⁴.

Preliminary adsorption experiments were conducted as described in Chapter 3, using ethanol as the solvent, to assess firstly the time taken for the solutions to reach equilibrium concentration and secondly, the degree of ethanol evaporation occurring during the experimental time scale. Ethanol evaporation was significantly reduced by

limiting the headspace in the conical flask, i.e. use of 125 cm³ conical flasks, and using teflon tape as an extra sealant.

Thus the modified adsorption experiment involved the use of the technique described in Section 3.4. 100 mg of the exchanged clay were weighed into 125 cm³ conical flasks. To this was added 0.001 - 0.01 mmoles of bis(tributyltin) oxide or 0.01 - 0.1 mmoles of triphenyltin hydroxide. The total volume of each solution was made up to 100 cm³ with dry ethanol. The flasks were shaken for six hours at 18 °C at which point an equilibrium concentration was reached. Approximately 8 cm³ of the contents of the flask were then filtered and the concentration of the supernatant determined from the UV absorbance at the wavelengths specified above. The amount of organotin adsorbed was determined by the difference between the initial and final organotin concentrations. All adsorption isotherms were measured in duplicate.

Contrary to the results reported by Meer¹⁰⁹ (see Figures 5.1 and 5.2), no adsorption of either of the organotin compounds was observed for the following exchanged clays under the conditions described above: HDTMA-montmorillonite, TMPA-montmorillonite, tetramethyl ammonium exchanged montmorillonite (TMA-montmorillonite), HDTMA-laponite, TMPA-laponite, TMA-laponite. Thus the findings of Meer may be disregarded.

The range of exchanged clays studied encompasses interactions that may occur via partitioning (HDTMA-clays); via benzene ring interactions (TMPA-clays); and to allow for interactions with the silicate layer (TMA-clays). The incorporation of the lower charged laponite clays, allows for a greater combination of mixed interactions and in the case of TMA-laponite greater interaction with the silicate layers. However, the results of these adsorption experiments suggest that no adsorbate-adsorbent interactions occur under the experimental conditions. The low degree of adsorbate-adsorbent interactions may have resulted from the high degree of adsorbate-solvent interactions that occur in the organotin/ethanol mixture.

HDTMA-montmorillonite has a basal spacing of 18.01 Å, opening the silicate layers by 5.4 Å. The organotin molecules are large compared to the phenolic compounds discussed in the previous two chapters and it is possible that a spacing of 5.4 Å is not enough to allow interlayer adsorption of these organotin molecules. The energy needed for further expansion of the exchanged clay layers in order to accommodate the organotin compounds, may be too great and thus adsorption does not occur.

Another factor resulting in the absence of adsorbate-adsorbent interactions, may be that of limited interaction with the silicate surfaces. The TMA-clays examined in this experiment, which display the least silicate surface coverage, may not allow adequate exposure of the silicate surface for interaction between the organo-tin compounds and the adsorbent. That is, the inter (quaternary ammonium) cation distance in the interlayer region of the clay is too small for the organo-tin compounds to interact with the silicate layers, resulting in the screening of the organo-tin compounds from the silicate layers. The latter theory was investigated by carrying out adsorption experiments with the unmodified clays.

5.3 Adsorption of organo-tin compounds by smectite clays at ambient temperatures

In Section 5.2, it was suggested that the lack of interaction between the Quat-clays and the organo-tin compounds may be due to screening of the silicate layer by the quaternary ammonium cations. Interactions of phenyl tin compounds with unmodified clays have been found to result in the decomposition of the phenyl tin compounds to inorganic tin and benzene. Such decomposition was found to occur at ambient temperatures after shaking for seven days, and on exposure to microwave radiation⁹⁵. Under these conditions the tin was found to have intercalated into the clay matrix as SnO₂ and the benzene released, in the case of triphenyltin chloride, found to be trapped in the clay layers.

It is possible that the use of unmodified clays for adsorption of the organo-tin compounds, may enhance adsorption and render the organo-tin non toxic as decomposition occurs on the clay surface. If reactions progressed as explained above the products of reactions with bis(tributyltin) oxide and triphenyltin hydroxide would be SnO₂/butane and SnO₂/benzene respectively.

5.3.1 Clay preparation

The Wyoming bentonite was treated as described in Section 2.2.1. Approximately 50 cm³ of the dispersed montmorillonite was then poured into an evaporating dish and placed in a 80 °C oven for 24 hours. After cooling the dried montmorillonite is removed from the evaporating dish, ground and sieved to pass a 210 μm mesh. The basal spacing of the montmorillonite was found to be 12.65 Å. Laponite was used as supplied and the basal spacing was found to be 12.95 Å

5.3.2 Adsorption isotherms and the nature of the adsorption process

Adsorption isotherms were obtained as described in Section 5.2.2 using montmorillonite (210 μm) and laponite. Figure 5.3 shows the results.

Adsorption of triphenyltin hydroxide was not observed for either of the clays. Adsorption may not have occurred for two reasons: Firstly, though polar molecules have been shown to interact with the silicate layer of clay minerals, it may be that triphenyltin hydroxide is not sufficiently polar to compete with ethanol and interact with the silicate layer. Secondly, the adsorbate-solvent, i.e triphenyltin hydroxide-ethanol, interactions may have been in competition with adsorbate-adsorbent interactions here as triphenyltin hydroxide is readily soluble in ethanol.

Adsorption of bis(tributyltin) oxide by montmorillonite occurred, some 20% of the initial concentration of the bis(tributyltin) oxide was adsorbed at the higher initial concentrations. The isotherm can be seen to be Type V in nature. Such isotherms result from weak adsorbate-adsorbent interactions. Adsorption of bis(tributyltin) oxide by laponite occurred only at the highest concentration used in this experiment. Again 20% adsorption was seen to occur but the type of isotherm is difficult to ascertain from the results obtained, though it is probable that the isotherm will be of Type III or Type V, both typical of weak interactions.

Bis(tributyltin) oxide will readily undergo hydrolysis to tributyltin hydroxide¹¹¹. This hydrolysis may occur due to the presence of water in the solvent, and may be further facilitated by interaction with a clay surface, due to sites of Brønsted acidity providing protons to electrophilically attack the Sn-O-Sn bond. It is also possible that bis(tributyltin) oxide reacts with ethanol to form tributyltin ethoxide. The polarity of the resulting hydroxide or ethoxide may be sufficient to allow for interactions with the exchangeable cations by solvation or with the silicate layer via hydrogen bonding; but the tributyltin compound may also interact more favourably with the solvent than with the clays.

If the adsorption reaction proceeded as described by Ashcroft et al.⁹⁵, there is no reason why proton attack should not lead de-alkylation of bis(tributyltin) oxide or tributyltin hydroxide to produce of SnO_2 pillars and butane.

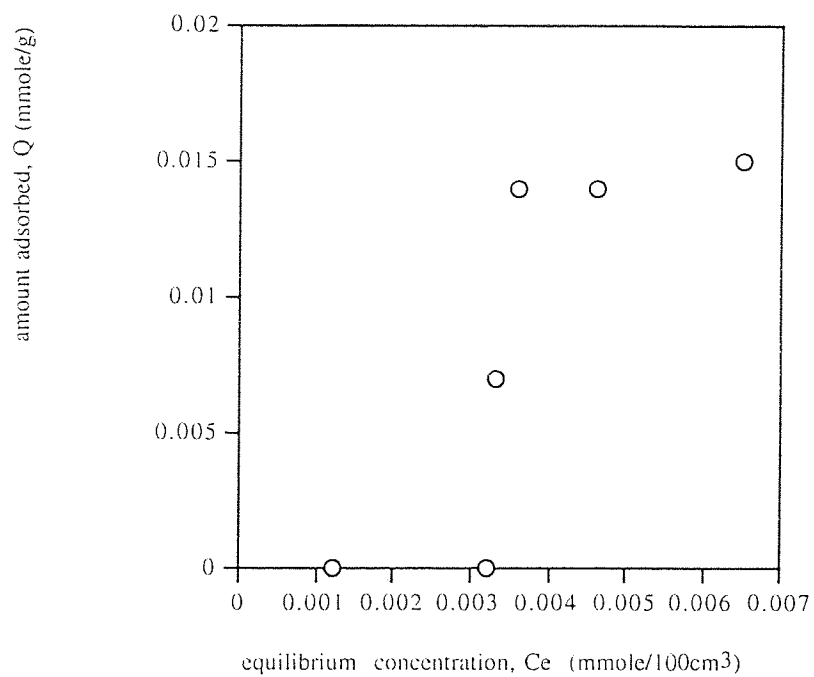


Figure 5.3(a) Adsorption of organo-tin compounds from ethanol by montmorillonite

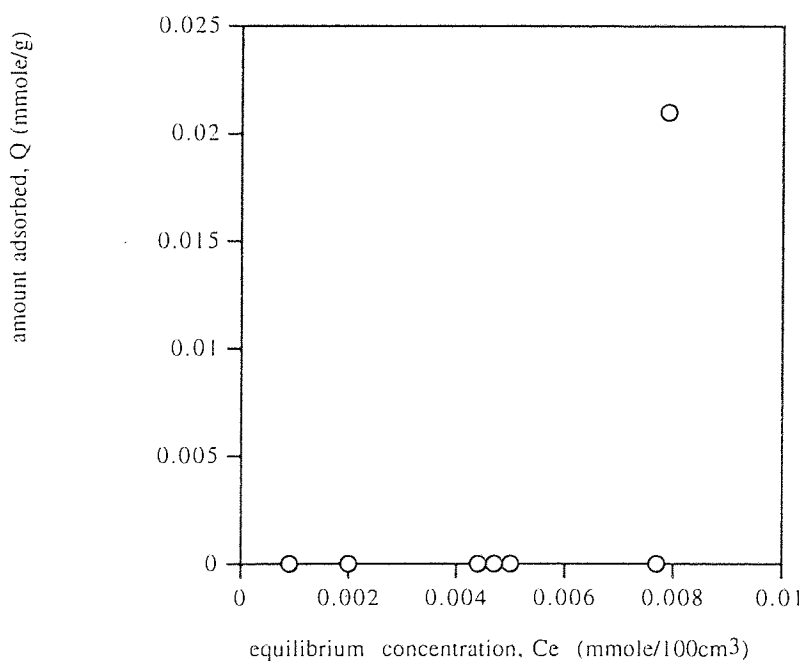


Figure 5.3(b) Adsorption of organo-tin compounds from ethanol by laponite

5.3.3 Characterisation of the tin-smectite materials

To enable analysis of the solid clay-tin products, the highest initial concentration experiment of the adsorption isotherm experiments was scaled up such that 1 g clay was shaken with 0.1 mmole bis(tributyltin) oxide/100 cm³ dry absolute ethanol for 6 hrs at 18 °C. UV results indicated that 20% adsorption resulted from the reaction. The tin-clay material was analysed by X-ray Diffraction (XRD), Diffuse Reflectance Fourier Transformed Infra-red and Near Infra-red (FTIR and FTNIR) and X-ray Photoelectron spectroscopy (XPS).

5.3.3.1 Powder X-ray Diffraction (XRD)

XRD results are summarised below in Table 5.2

Table 5.2 Basal spacing, d(001), results of smectite clays and the organo-tin smectite materials

product	basal spacing, Å
montmorillonite	12.62
montmorillonite-bis(tributyltin) oxide	12.62
laponite	12.95
laponite-bis(tributyltin) oxide	13.47 - 16.04

Interactions between bis(tributyltin) oxide and montmorillonite have little effect on the basal spacing of montmorillonite. Bis(tributyltin) oxide, being a large molecule, will inevitably effect the basal spacing of the clay if it is adsorbed in the interlayer region. However, the basal spacing results suggest that any adsorption occurs at edge and surface sites of the clay.

For the laponite clay an increase in basal spacing ranging from 1.5 to 3.0 Å is observed, perhaps resulting from the adsorption of more than one compound. Such compounds may be one or more of the following: bis(tributyltin) oxide, it's hydration and/or de-alkylation products, or ethanol.

Section 5.4 describes similar reactions carried out using microwave radiation. The results show that ethanol readily adsorbs into the interlayer region of laponite. It is

possible that at ambient temperatures, the adsorption species is primarily ethanol in the interlayer region and bis(tributyltin) oxide on the clay surface. The small increase in basal spacing of the laponite clay on adsorption, suggests that if any adsorption of bis(tributyltin) oxide occurs, the species lie flat in the interlayer region (see Figure 5.4), i.e. with the Sn-O-Sn plane of the molecule lying parallel to the silicate layer.

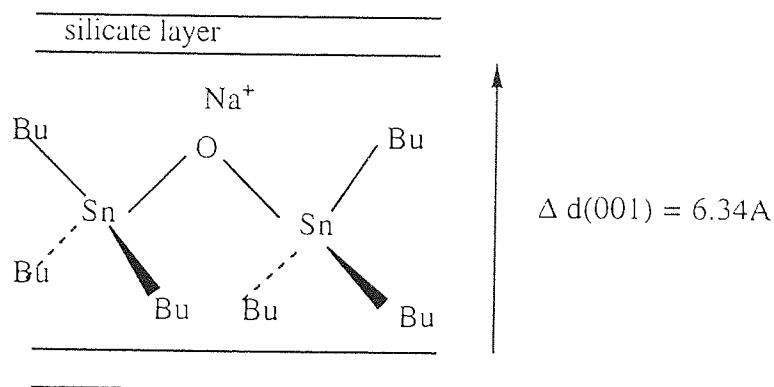


Figure 5.4 Schematic representation of bis(tributyltin) oxide adsorption into the montmorillonite interlayer (ethanol not shown)

5.3.3.2 Diffuse Reflectance Fourier Transformed Infrared (FTIR)

On reaction with the smectite clays, the bis(tributyltin) oxide may have been hydrolysed to tributyltin hydroxide and de-alkylated to form tin(IV) oxide. Due to the adsorption capacity of the smectites, the adsorption of the bis(tributyltin) oxide may not be detectable on the solid, organo-tin clay material by FTIR since the bis(tributyltin) oxide is present at concentrations of 1 wt% when 20% adsorption occurs.

Investigation of the solid, organo-tin clay material by diffuse reflectance FTIR suggested that no alkylated species were present in the materials formed from either the bis(tributyltin) oxide-montmorillonite or bis(tributyltin) oxide-laponite reactions, i.e. no peaks in the region 3000 cm^{-1} - 400 cm^{-1} were observed. The FTIR spectrum of tin oxide is characterised by a broad peak between 570 cm^{-1} - 450 cm^{-1} with a maximum intensity at 490 cm^{-1} - 500 cm^{-1} . The peak will be partially masked by the montmorillonite and laponite spectra and any presence of tin oxide would be evidenced by the broadening of the clay peaks in the 550 cm^{-1} - 450 cm^{-1} region. This broadening is not observed and thus SnO_2 is not present in concentrations detectable by the FTIR experiment. Peaks due to the presence of Si-O bonds are in the 1200 cm^{-1} - 1000 cm^{-1} region, these peaks remain unchanged after interaction with bis(tributyltin) oxide. Figure 5.5 shows the FTNIR spectrum of laponite.

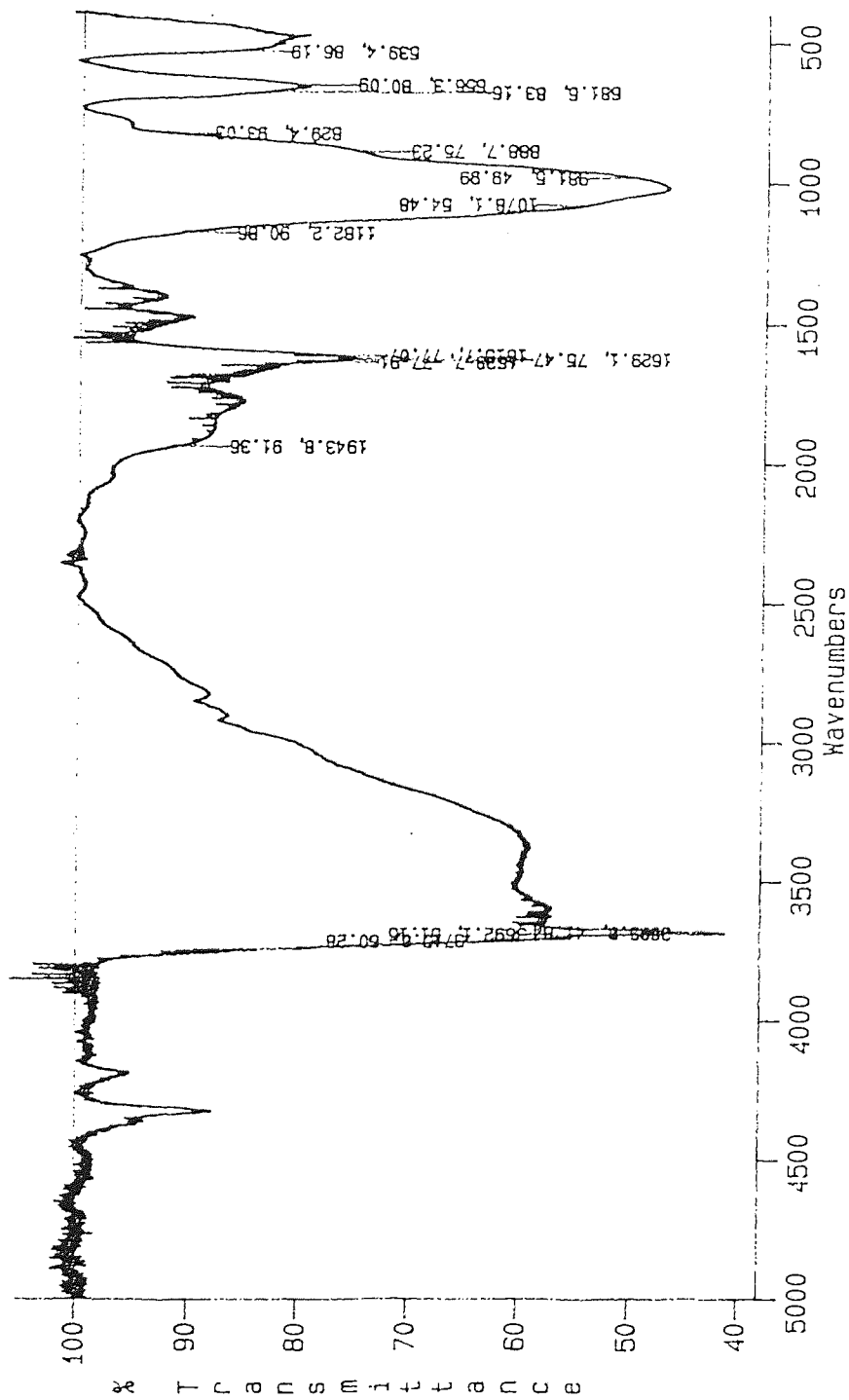


Figure 5.5a FTNIR spectrum of laponite

In the study of the adsorption of organo-tin compounds by silica, Nédez et al.¹¹² suggested that as well as interactions between the Si-O group of the silicate and the Sn in the tin compounds, the alkyl groups of R₄Sn bent back on themselves to form hydrogen bonds with the silicate layer. This was evidenced by IR. No evidence for either of these interactions was obtained in this study.

5.3.3.3 X-ray Photoelectron Spectroscopy (XPS)

Analysis of the bis(tributyltin) oxide precursor and of a sample of tin(IV) oxide by XPS gave the results shown in Table 5.3.

Table 5.3 XPS results of tin compounds used as standards

Binding energy (eV) (± 0.2 eV)	Assignment	Compound
486.6	Sn-O, 3d5	SnO ₂
486.1	Sn-O, 3d5	Bis(tributyltin) oxide

XPS studies of the organo-tin-clay materials yielded interesting results which are summarised in Table 5.4. XPS is a surface sensitive technique enabling detection of elements present down to 0.2% composition. From Table 5.3 the technique should be able to distinguish between the Sn-O bonds in the organo-tin starting material, binding energy 486.1 eV, and the Sn-O bonds in the tin-clay material produced as a result of adsorption, binding energy 486.6 eV. XPS will also yield information on the amount of tin present. The XPS results in Table 5.4 suggested that only a very small percentage of the tin expected to be present, from adsorption isotherm measurements, was present on the clay surface and that a different tin species was formed as a result of the adsorption process.

Figure 5.6 a, b and c show the XPS spectra obtained from analysis of the starting materials and products for the montmorillonite reaction.

The negligible amount of tin found on the surface of the solid tin-clay materials is contrary to the UV results which suggest 20% adsorption occurred. Adsorption of bis(tributyltin) oxide by montmorillonite was not accompanied by an increase in basal spacing. This suggested that adsorption at surface or edge sites occurred. Though

Table 5.4 XPS results of the bis(tributyltin) oxide smectite reaction products

product	% tin expected* 486.1 (eV)	% tin found and binding energy (eV)
bis(tributyltin) oxide-mont	0.5	0.1, 487.1
bis(tributyltin) oxide-laponite	0.5	0.03, 487.1

* Amount expected to be detectable by XPS if 20% of the initial concentration of bis(tributyltin) oxide is adsorbed on the clay surface

adsorption of bis(tributyltin) oxide by laponite was accompanied by an increase in basal spacing, it is suspected that bis(tributyltin) oxide was primarily adsorbed on the clay surface. However, XPS results did not detect a significant concentration of bis(tributyltin) oxide on the clay surfaces. This may be attributed to the time between adsorption reactions and XPS analysis which may have allowed for significant desorption of any tin species present.

For both tin-clay materials, the only tin species present was found to have a binding energy of 487.1 eV. No tin species were detected at 486.1 eV or 486.6 eV, therefore neither SnO₂ pillars or bis(tributyltin) oxide show evidence of being present in the tin clay products. However, it should be noted that at these low concentrations, the XPS results in the Table 5.4 have less accuracy than if the Sn present had been detected at concentrations greater than 0.2%. This considered, the binding energies stated at these low percentages are probably within 0.3 eV - 0.5 eV of the actual binding energy. This being the case, the binding energy at which the tin was detected lies between 486.6 eV and 487.6 eV. This range of binding energies encompasses the possibility of SnO₂ being formed and the formation of various inorganic tin(IV) and organotin(IV) compounds¹¹³. Thus one can only conclude that the adsorption reaction results in a different tin(IV) species being present on the clay surface, but methods of analysis used here could not identify that species. The compound results from the hydration and/or de-alkylation of bis(tributyltin) oxide in ethanolic solution and/or on the clay surface.

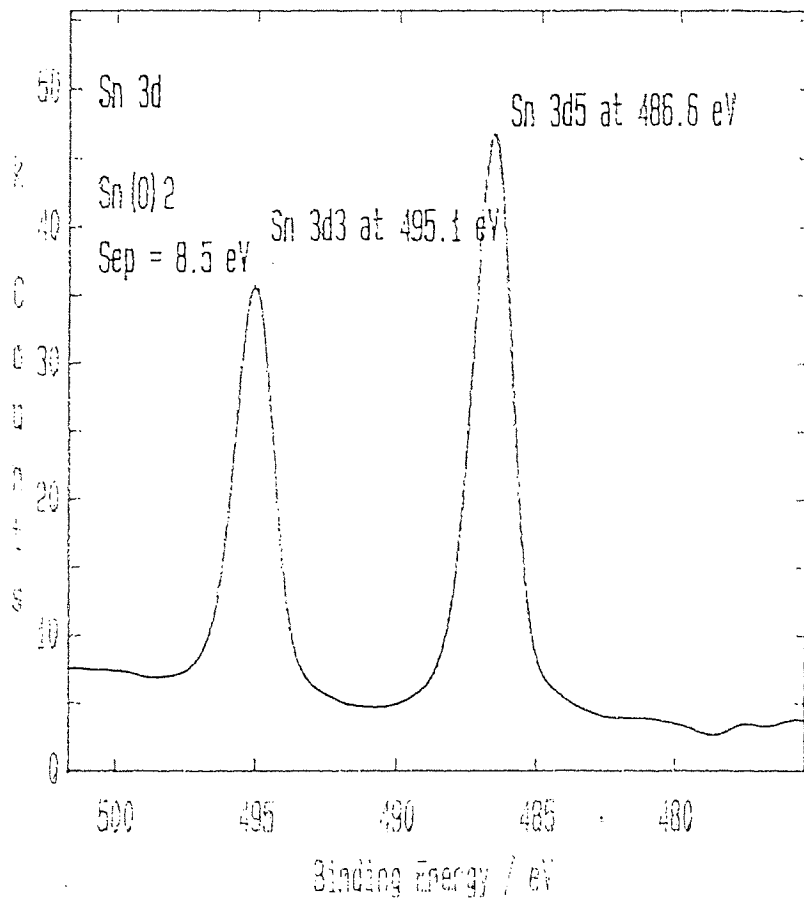


Figure 5.6a Sn(3d5) XPS spectrum of SnO₂, standard

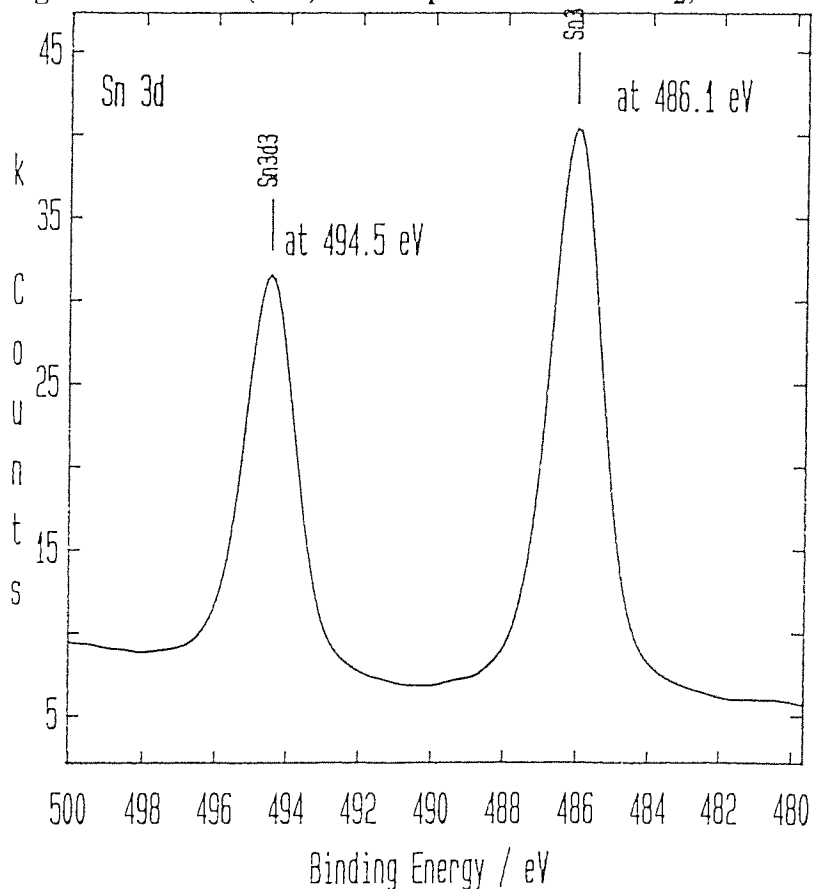


Figure 5.6b Sn(3d5) XPS spectrum of bis(tributyltin) oxide, standard

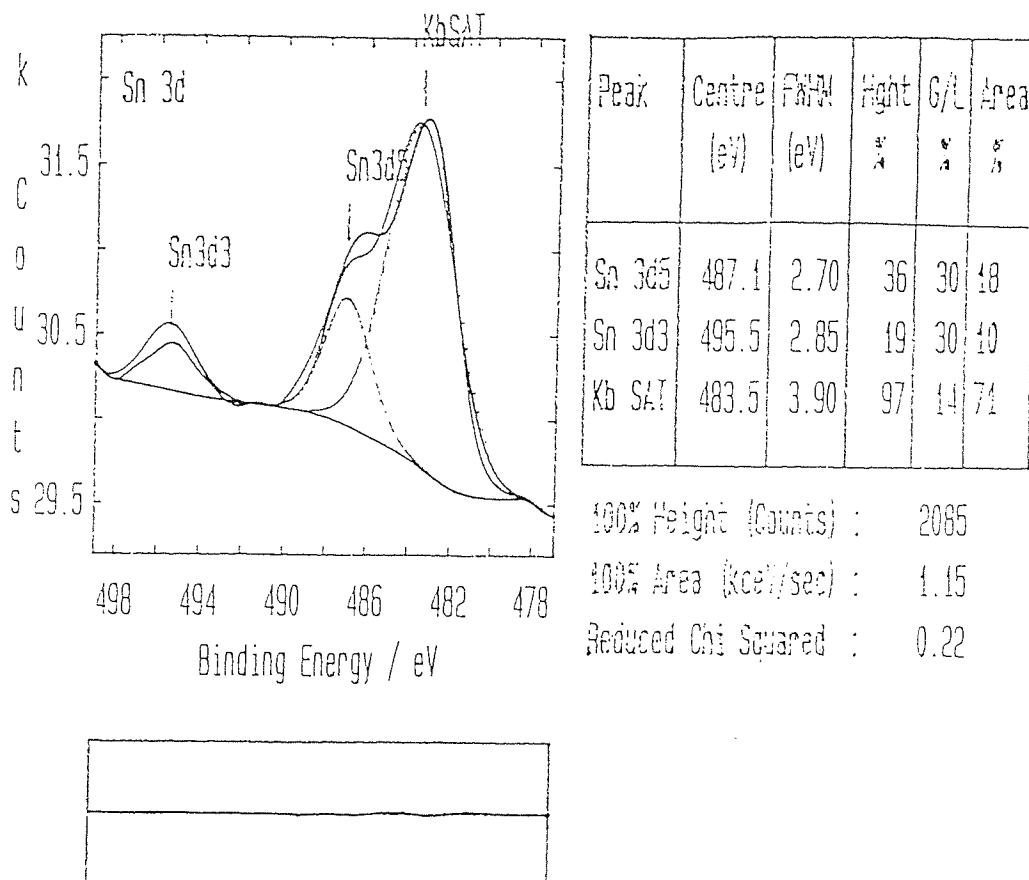


Figure 5.6c Sn(3d5) XPS spectrum of bis(tributyltin) oxide-montmorillonite material

The low concentration of tin present in the reaction products did not allow for analysis by Mössbauer spectroscopy, ^{119}Sn MASNMR or ^{13}C MASNMR.

Adsorption of bis(tributyltin) oxide by montmorillonite and laponite appears to be via weak interactions with the surface of the clay only. The low percentage of tin detected on surface can only result from desorption from the clay surface. It is concluded that the compound present in the interlayer region of laponite is principally ethanol, with perhaps small concentrations of bis(tributyltin) oxide being adsorbed.

5.4 The effect of microwave radiation on organo-tin clay interactions

Microwave heating can greatly increase reaction rates. Organic compounds have been synthesised at 1240 times faster in sealed Teflon vessels (see Figure 5.7) in a microwave oven than by conventional techniques, Gedye et al.¹¹⁴. The increase in reaction rate was found to be dependant on the polarity of the compounds involved in

the reaction, and not wholly dependant on the increased pressure within the sealed vessel. Polar compounds are found to absorb significant amounts of microwave energy. This results in polar compounds with boiling points of less than 100 °C generally reaching their boiling points within 1 minute¹¹⁴. Baghurst and Mingos¹¹⁵ found that organic solvents in a microwave cavity superheat by 13 - 26 °C above their conventional boiling points.

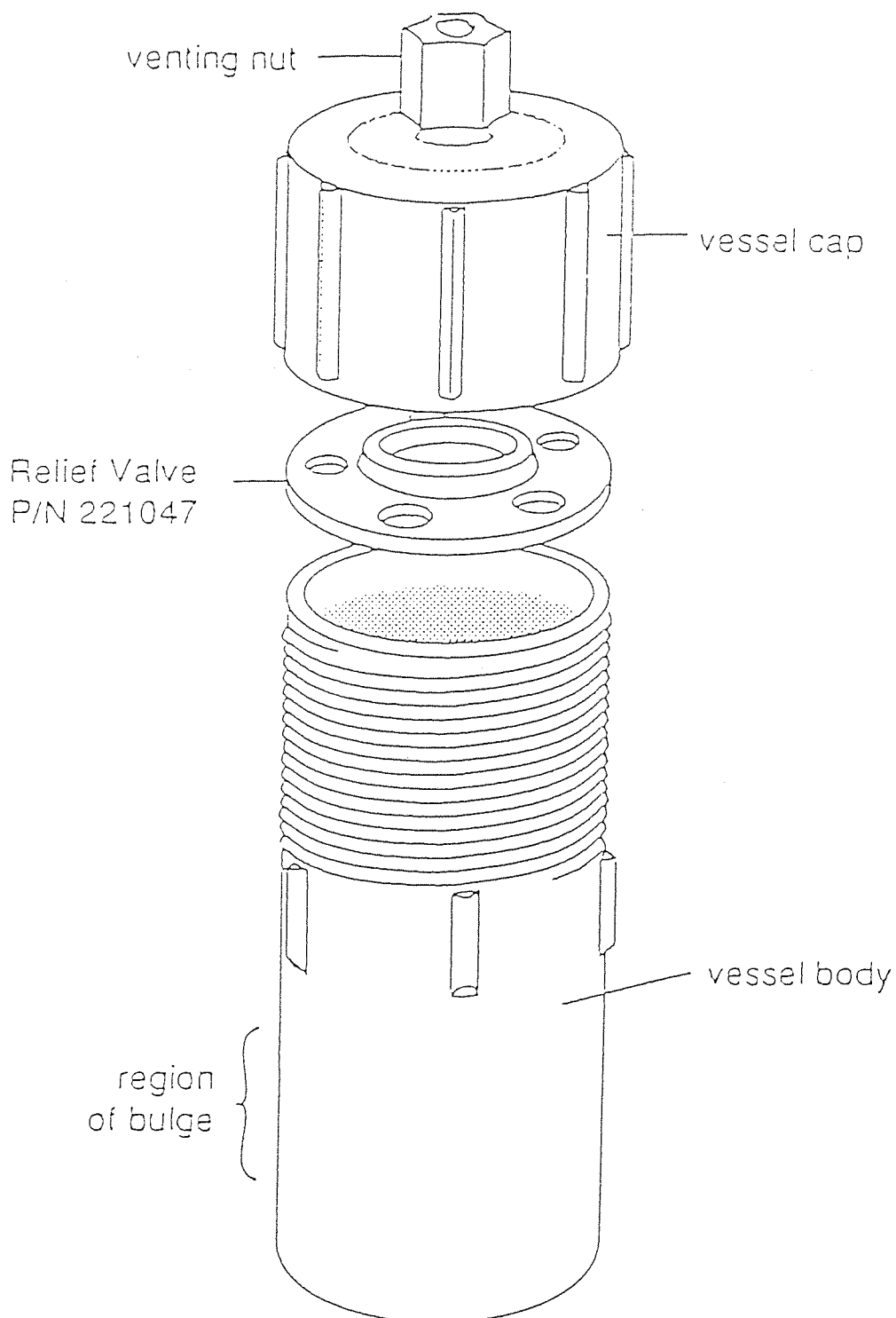


Figure 5.7 Diagram of Teflon container used in microwave reactions

Layered inorganic materials have been shown to intercalate greater quantities of materials at a faster rate when the reaction is conducted in a microwave oven^{92,95,116}. The intercalation of aryltin compounds [Ph_3SnCl , $(\text{Ph}_3\text{Sn})_2\text{O}$, Ph_2SnCl_2]⁹⁵ into laponite, under ambient conditions (7 days, mechanical shaker) results in the formation of tin(IV) oxide pillars. Mössbauer data indicated the presence of tin(IV) oxide. The organic product of the pillaring reaction is benzene, this was detected by ^{13}C MASNMR spectroscopy as trapped within the pillared lattice. The pillaring reaction occurred without the displacement of the exchangeable cation, sodium. When the reaction is conducted in Teflon containers in a domestic microwave oven, the rate of reaction is reported to increase (5 minutes). This method of intercalation was attempted for the adsorption of bis(tributyltin) oxide and triphenyltin hydroxide by the Quat-clays used in Section 5.2.2 and the unmodified clays used in Section 5.3.2.

5.4.1 Adsorption of bis(tributyltin) oxide and triphenyltin hydroxide by various clay materials under microwave conditions

Bis(tributyltin) oxide or triphenyltin hydroxide (0.2 g) was dissolved in dry absolute ethanol (10 cm³). 1 g of the clay or exchanged clay was added to this solution and sealed in a 120 cm³ Teflon container with a screw top (Figure 5.7). The container was placed in a Sharp Carousel 650 W domestic microwave oven. The mixture was subjected 5, 1 minute bursts of microwave radiation on a medium high setting. The container contents were agitated after each one minute burst of radiation to prevent pressure build up. The container was then allowed to cool to room temperature before being carefully opened. The clay was gravity filtered and then washed with four 25 cm³ aliquots of solvent. The combined filtrate and washings were analysed by UV and AA.

As found in the adsorption experiments described in Section 5.2.2 and 5.3.2, triphenyltin hydroxide was not adsorbed by the quaternary ammonium exchanged or non-exchanged clays under microwave conditions.

5.4.2 Adsorption of bis(tributyltin) oxide by non-exchanged clays

UV spectroscopy results showed that bis(tributyltin) oxide was taken up by the non-exchanged clays. Table 5.5 below shows the percentage uptake of bis(tributyltin) oxide by the clays.

Table 5.5 Percentage uptake of bis(tributyltin) oxide by smectite clays

material	percentage uptake of bis(tributyltin) oxide
montmorillonite	15
laponite	15

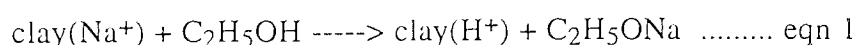
Results suggest that uptake of bis(tributyltin) oxide occurs when an ethanolic solution containing smectite clays and bis(tributyltin) oxide is superheated.

5.4.3 Characterisation of the tin-smectite products

The tin-clay material was analysed by X-ray Diffraction (XRD), Diffuse Reflectance Fourier Transformed Infra-red and Near Infra-red (FTIR and FTNIR) and X-ray Photoelectron spectroscopy (XPS). The filtrate and washings were analysed by Atomic Absorption (AA).

5.4.3.1 AA

Table 5.6 shows that when a mixture of montmorillonite and bis(tributyltin) oxide is exposed to microwave radiation, the sodium ions are released from the interlayer region of the montmorillonite. A subsequent reaction was conducted with montmorillonite and ethanol only, and a similar release of sodium ions was observed. This suggests that ethanol is responsible for the release of sodium ions from the montmorillonite interlayer region. Release of sodium ions must be accompanied by a replacement of these ions. The only cation capable of replacing sodium cations and present in the reaction mixture is the H⁺ ion. Thus, a possible reaction is:



Such a reaction should be accompanied by an increase in pH. Measurement of the pH of the montmorillonite/ethanol reaction mixtures before and after reaction show no change in the H⁺ ion concentration of the solution occurs. The pH being 6.4 pH units for both mixtures. Thus, the mechanism for sodium release from montmorillonite under microwave conditions remains unexplained.

The release of sodium cations is not observed when the laponite/ethanolic bis(tributyltin) oxide mixture is exposed to microwave radiation. Subsequent reactions, under the same conditions, with laponite and ethanol as reactants, also occur without displacement of sodium cations.

Such differences in the reactions of the two smectite clays is difficult to explain, but imply a stronger interaction between the silicate layer and exchangeable cations for laponite than for montmorillonite, under microwave conditions.

Table 5.6 The displacement of sodium cations during the adsorption reaction and the accompanying change in basal spacing.

Material	percentage Na ⁺ ions released during the reaction	XRD
montmorillonite-ethanol alone	88	12.44 (12.65)*
montmorillonite-bis(tributyltin) oxide	72	12.44
laponite-ethanol alone	1	19.79 (12.95)*
laponite-bis(tributyltin) oxide	2	14.69

* figures denote the basal spacing of the parent clays as supplied in the case of laponite and when purified and processed in the case of montmorillonite (see Section 5.3.1 for clay preparation)

5.4.3.2 XRD

German and Harding¹¹⁷ observed that ethanol is adsorbed by sodium montmorillonite. The isotherm is Type I or Langmuir in nature, apparently because the alcohols adsorbed displace the water molecules in the primary hydration shell of the exchangeable cations¹¹⁷. It is probable that the mechanism for the adsorption of ethanol also involves some formation of hydrogen bonds between the ethanol molecules and the Si-O bonds of the clay. After the initial interaction with the clay (via exchangeable cations or silicate layers), subsequent adsorption occurs via extensive hydrogen bonding between ethanol molecules. Swelling of smectite clays in water is well known, a four layer arrangement yielding a basal spacing of 20 Å for montmorillonite clays⁸. It is probable that similar swelling will be seen with organic solvents such as ethanol.

The changes in basal spacing accompanying the smectite/bis(tributyltin) oxide and the smectite/ethanol reactions are interesting. In the case of montmorillonite, the release of sodium ions seems to accompany a slight decrease in basal spacing, 0.2 Å (Table 5.6). This result would tie in with the reaction of the sodium montmorillonite to produce hydrogen montmorillonite, as shown in eqn 1, the hydrogen ion being smaller than the sodium ion. However, pH results suggests that this reaction did not occur. The presence of bis(tributyltin) oxide seems not to significantly effect either the release of sodium ions or increase the basal spacing of the product. This suggests that little adsorbate-adsorbent interaction occurs in the interlayer region of the montmorillonite.

The results obtained for laponite are very different from those obtained for montmorillonite, but parallel previous observations made for adsorption of polar molecules by smectite clays¹¹⁷. On exposure to microwave radiation in the presence of ethanol, no significant loss of sodium ions is observed but the basal spacing of the laponite-ethanol material increases by some 7 Å (Table 5.6) compared to untreated laponite. This is due to the intercalation of the ethanol, in a multilayer fashion, into the laponite interlayer region. The retention of the sodium cations suggests that the clay-ethanol interaction is via solvation of the sodium cation. Interaction may also occur via hydrogen bonding with the silicate layer. It is surprising that swelling in ethanol is only observed for the laponite clay.

When the bis(tributyltin) oxide is added to the laponite/ethanol reaction mixture, an increase in the basal spacing of laponite is still observed but not to the same extent as that observed in the laponite/ethanol reaction (Table 5.6). It is probable that bis(tributyltin) oxide competes with the ethanol for adsorption sites. The fact that the basal spacing increase is not as large as that with the ethanol alone, suggests bis(tributyltin) oxide may be preferentially adsorbed. Alternatively, the ability of ethanol to form an ordered arrangement via hydrogen bonding may be inhibited by the presence of bis(tributyltin) oxide which will hydrogen bond to the ethanol molecules to some extent, disrupting what was a very ordered system. This would result in a short range hydrogen bonding system occurring when bis(tributyltin) oxide is present, compared to the relatively long range hydrogen bonding which appears to occur in the laponite-ethanol system. This can be compared with the process involved in the intercalation/adsorption of water by smectite clays. The adsorption of water is affected by the exchangeable cation present in the interlayer region^{5,7,8} (Section 1.3.3) sodium enhancing a ordered arrangement of the water layers, calcium restricting the formation of water layers after a certain number of layers have been formed. In the

case of the bis(tributyltin) oxide/laponite reaction, bis(tributyltin) oxide may be present in small quantities in the interlayer region and restricting the uniform arrangement of ethanol molecules.

5.4.3.3 XPS

Table 5.7 shows the results of Sn(3d5) XPS analysis of the tin-clay materials. Only 13 - 14 % of the tin expected to be present on the clay surface was detected by XPS. Interestingly, comparable concentrations of tin are found on the surfaces of both clays and this supports the theory which suggests that for both clays adsorption of bis(tributyltin) oxide is primarily at surface sites. The binding energy at which the tin was detected encompasses the binding energy at which tin in SnO₂ is found, as well as other tin(IV) species¹¹³. As for the reactions at room temperature, the low percentage of tin detected on the surface of the smectite clays may be due to desorption of the tin(IV) species.

Table 5.7 XPS results of the tin-clay products formed during reaction under microwave conditions

product	% tin expected* 487.1 eV	% tin found and binding energy (eV)
bis(tributyltin) oxide-mont	1.0	0.13, 487.2
bis(tributyltin) oxide-laponite	1.0	0.14, 487.2

* as suggested by UV results

5.4.3.4 FTIR

As a result of the reaction of smectite clays and bis(tributyltin) oxide under microwave conditions, 3 wt% of bis(tributyltin) oxide is present on the surface of the smectite clays, from UV results. For the reactions at room temperature (Section 5.3) only 1% tin was present, FTIR did not detect any tin compounds in the solid material and it was assumed that the tin concentration was below the detection limit. However for the bis(tributyltin) oxide-montmorillonite material obtained under microwave conditions, a slight broadening of the montmorillonite peak in the region from 600 cm⁻¹ - 520 cm⁻¹ suggests the possibility of a Sn-O bond, as would occur in the spectra of SnO and SnO₂. The Sn(3d5) binding energy for Sn(II) compounds is not found in

the same range as for the Sn(IV) compounds and thus the FTIR absorbance peak may be due to the presence of SnO₂. There is no evidence of butyl groups in the product. Proton attack on aryltin bonds is well known^{92,93}. Sites of Brønsted acidity on the clay may provide protons to electrophilically attack the carbon bonded. In the case of bis(tributyltin) oxide, it seems feasible to suggest that similar attack of the tin carbon bond would give butane as an organic product which would evaporate from the tin surface and therefore be undetectable by any of the methods of analysis used.

No change in the laponite FTIR spectrum is observed after the laponite/bis(tributyltin) oxide adsorption reaction.

Insufficient concentrations of organo-tin compounds in the tin-clay products meant that ¹¹⁹Sn MASNMR, ¹³C MASNMR and Mössbauer analysis could not be conducted.

As found for the room temperature reactions, adsorption of bis(tributyltin) oxide by laponite and montmorillonite, under microwave conditions, results in adsorption of bis(tributyltin) oxide primarily at surface and edge sites for the smectite adsorbents. Analysis of the bis(tributyltin) oxide-smectite materials show that bis(tributyltin) oxide reacts to form a Sn(IV) species on the smectite surface. A high degree of desorption of the surface sorbed tin(IV) species appears to occur before analysis of the tin-smectite material takes place.

5.4.4 Adsorption of bis(tributyltin) oxide by quaternary ammonium exchanged clays under microwave conditions

The adsorption of bis(tributyltin) oxide by the following quaternary ammonium cations under microwave conditions was attempted as described in Section 5.4.1 for the following quaternary ammonium exchanged clays: HDTMA-montmorillonite, TMPA-montmorillonite, HDTMA-laponite, and TMPA-laponite. Table 5.8 below shows the results of the reactions. Montmorillonite and laponite adsorption are shown in the table to enable comparison.

Table 5.8 Uptake of bis(tributyltin) oxide by adsorbents and the accompanying change in basal spacings

material	percentage uptake of bis(tributyltin) oxide	d(001) Å*
montmorillonite	15	12.44 (12.65)
TMPA-montmorillonite	15	14.24 (14.24)
HDTMA-montmorillonite	30	17.66 (18.01)
laponite	15	14.69 (12.95)
TMPA-laponite	0	14.02 (14.71)
HDTMA-laponite	30	14.02 (14.01)

* Figure in bracket is basal spacing of material before reaction

5.4.5 Characterisation of tin-Quat-smectite materials

5.4.5.1 XRD

For all the reactions, except the laponite reaction which has already been discussed in Section 5.4.1, the observed uptake of bis(tributyltin) oxide was not accompanied by a significant increase in basal spacing. In the case of the non-exchanged smectite clays, this led to the conclusion that adsorption occurred principally on the clay surfaces. For the quaternary ammonium exchanged clays, the adsorption of bis(tributyltin) oxide may not have taken place at edge and surface sites only. The interlayer openings caused by the presence of the quaternary ammonium cation and energy obtained from the microwave radiation may have been sufficient to enhance adsorption of the organo-tin compounds in the interlayer region. The adsorption of bis(tributyltin) oxide may well have occurred via van der Waals interactions between the alkyl chains of the quaternary ammonium cations and the butyl chains of bis(tributyltin) oxide, due to superheated conditions.

Results for the TMPA-laponite and the HDTMA-montmorillonite systems are interesting in that the basal spacing seem to significantly decrease on interaction with ethanolic solutions of bis(tributyltin) oxide. For the TMPA-laponite/bis(tributyltin) oxide reaction, the decrease in basal spacing on adsorption of bis(tributyltin) oxide,

implies a change in the orientation of the Quat on exposure to the bis(tributyltin) oxide solution. No adsorption of the organo-tin compound occurs. For the HDTMA-montmorillonite/bis(tributyltin) oxide reaction, adsorption of bis(tributyltin) oxide occurred. This suggests that the presence of the bis(tributyltin) oxide solution confers the re-orientation of the quaternary ammonium cations in the interlayer region of these two adsorbents. Reactions of the Quat-clays with ethanol alone were not conducted. Alternative orientations of the quaternary ammonium cations may be obtained by further keying into the silicate layer or the taking up of a flatter orientation resulting in a decrease in the basal spacing. The change in orientation is probably driven by the ethanol molecules interacting with the quaternary ammonium cations. It is not yet clear why such changes in basal spacing do not occur for all the Quat-smectites examined in this study.

5.4.5.2 XPS

Table 5.9 shows the results of Sn(3d5) XPS analysis of the tin-Quat-clay materials after reaction. As in previous experiments the percentage uptake as detected by XPS was lower than suggested by UV.

Table 5.9 Binding energies (Sn 3d5) and percentage of tin compounds present after reaction of bis(tributyltin) oxide with various Quat-clays

product	% tin expected* at 487.1 eV	% tin found and binding energy (eV)
[(Bu) ₃ Sn] ₂ O-HDTMA-montmorillonite	2.0	0.4, 486.7
[(Bu) ₃ Sn] ₂ O-TMPA-montmorillonite	1.0	0.1, 487.0
[(Bu) ₃ Sn] ₂ O-HDTMA-laponite	2.0	0.3, 486.8

* Amount expected to be detectable by XPS if percentage adsorption recorded by UV had occurred

The amount of tin found in the solid tin-exchanged clay materials again suggests that little bis(tributyltin) oxide is present on the surface of the adsorbent. However, significantly more is present than that after reaction of bis(tributyltin) oxide with the non-exchanged clays under similar conditions (Section 5.4.1). The binding energies at which the tin was detected are slightly higher than that found for the bis(tributyltin) oxide precursor. It seems reasonable to assume that the small amount of

bis(tributyltin) oxide has reacted to form a new tin(IV) compound since there no binding energies at 486.1 eV. Thus the binding energy of 486.7 eV - 487.0 eV \pm 0.2 eV is probably attributable to a new tin(IV) compound.

5.4.5.3 FTIR

As in Section 5.3.3 the FTNIR spectra of the tin-Quat-clay materials did not differ from the spectra of the relevant parent exchanged clay, particularly not in the 550 cm⁻¹ - 450 cm⁻¹ region suggesting SnO₂ is not present in concentrations detectable by the FTIR experiment.

5.4.5.4 Mössbauer spectroscopy

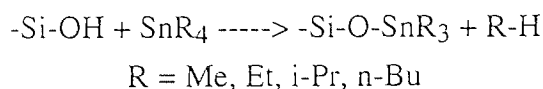
The detection of a relatively high concentration of tin in the tin-Quat-clay materials by XPS studies (Table 5.10) was encouraging, thus the product of the bis(tributyltin) oxide/HDTMA-montmorillonite reaction was analysed by ¹¹⁹Sn Mössbauer spectroscopy. Unfortunately no tin was detected in the sample and thus no further information was gained about the products of these reactions.

Adsorption of bis(tributyltin) oxide by Quat-smectites involves the reaction of bis(tributyltin) oxide to form a new tin(IV) compound. There is no evidence of de-alkylation to SnO₂. The site of adsorption is not yet clarified.

5.5 The de-alkylation of organo-tin compounds

5.5.1 Introduction

The adsorption of organo-tin compounds by partially dehydroxylated silica, SiO₂, has recently been studied by Nédez et al.¹¹². Tetraalkyltin compounds, R₄Sn and tributylhydrotin were reacted with the surface of silica at room temperature and at temperatures between 100 °C and 200 °C. Interaction between the complexes and the silica surface, and evolution of gases, was followed by IR, and ¹³C and ¹¹⁹Sn MAS NMR spectroscopies. At room temperature the tin compounds were found to be reversibly physisorbed. It was suggested that a hydrogen-type bond is formed between the terminal methyl group of the alkyl ligands and/or the hydride ligand and the surface Si-O groups. Above 100 °C a surface complex of -SiO-SnR₃ is formed with the release of one mole of alkane per mole of tin compound:



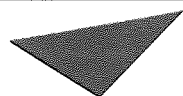
This reaction also occurs at room temperature for Bu_3SnH but at a very slow rate. The alkyl chains are said to fold back towards the surface of the silica and interact via hydrogen type bonding. The reaction scheme for the reaction is shown in Figure 5.8.

5.5.2 Adsorption of bis(tributyltin) oxide by smectite clays under microwave conditions: the effect of time.

Section 5.4 showed that reaction of smectite clays with bis(tributyltin) oxide under microwave conditions yields a product in which any tin compound on the surface of the clay is probably present as tin (IV) oxide. The work of Nédez et al.¹¹², initiated a study of the ability to monitor the reactions of bis(tributyltin) oxide, during the microwave reaction of bis(tributyltin) oxide in ethanolic solution and smectite clays. Attempts to use the high temperatures used in the experiments of Nédez et al., were made by using microwave heating in order to investigate the adsorption of bis(tributyltin) oxide from ethanolic solution by montmorillonite and laponite unmodified clays. The reactions were conducted at four different time scales to probe the de-alkylation processes. The solid tin-clay materials were analysed by FTNIR initially, and then XPS and XRD when results suggested such analysis would be useful.

The experiments with the smectite clays and ethanolic bis(tributyltin) oxide were repeated as described in Section 5.4, but the time scale of the experiments were varied such that each clay reaction system was subjected to 1, 2, 3 and 5, 1 minute bursts of microwave radiation.

UV results suggested that adsorption occurred as shown in Table 5.10



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Figure 5.8 Proposed mechanism for the de-alkylation of organo-tin compounds, Nédez et al.¹¹²

Table 5.10 Results of the effect of time on adsorption of bis(tributyltin) oxide from ethanol onto smectite clays under microwave conditions

clay	time of reaction (minutes)	percentage adsorption
laponite	1	15
	2	15
	3	15
	5	15
montmorillonite	1	8
	2	8
	3	10
	5	15

5.5.3 Characterisation of the tin-smectite materials

5.5.3.1 FTIR

The solid tin-clay materials were analysed by diffuse reflectance FTIR to detect the presence of the tin compounds on the clay surface. If the UV data is correct then 1.5 - 2.5% of tin in the form of bis(tributyltin) oxide, or 0.5 - 1% of tin(IV) oxide, should be present on the clay surface. Such concentrations may not be detectable by FTIR.

The FTIR spectra of the tin-laponite material formed during the reaction of bis(tributyltin) oxide with laponite, suggest no reaction has taken place. That is, the spectra of the laponite clay; laponite in ethanolic media subjected to microwave radiation (1, 2, 3 and 5, one minute bursts); and laponite with bis(tributyltin) oxide in ethanolic media after 1, 2, 3 and 5, one minute bursts of microwave radiation are exactly the same.

Spectra of the products of the reaction of bis(tributyltin) oxide with montmorillonite gave quite interesting results, the spectra are shown in Figures 5.9 through 5.11.

Spectra of the products of the reactions after exposure to microwave radiation for 1 and 3 minutes are similar and show broadening of the peaks in the 620 cm^{-1} -450 cm^{-1} region. Further broadening is observed for the product of the 5 minute reaction. This broadening is due to the presence of a Sn-O bond in the tin(IV) species on the montmorillonite surface. Again the lack of peaks in the 1550 cm^{-1} - 450 cm^{-1} attributable to C-H bonds, would suggest the product contains no alkyl groups and that a small concentration of SnO_2 is produced.

5.5.3.2 XPS

Representative samples of the reaction products were sent for preliminary XPS analysis, the results are shown in Table 5.11

Table 5.11 Sn(3d5) XPS analysis of the presence of tin in the products of the timed reactions and the binding energy at which they were detected.

product and time of reaction in minutes	% tin expected* 486.1 eV	% tin found and binding energy (eV)
bis(tributyltin) oxide-laponite		
1	1.0	0.16, 487.0
5	1.0	0.13, 487.2
bis(tributyltin) oxide-mont		
1	1.0	0.12, 486.8
5	1.0	0.14, 487.2

* as expected from UV results

XPS binding energies are normally within an accuracy of ± 0.2 eV but at these low concentrations accuracy of $\pm 0.3 - 0.5$ eV is more likely. The energies found for the tin-laponite materials at two of the four different times studied, seem to correlate with the FTIR results which suggest that a low percentage of tin species is present in the laponite-tin product. As in Section 5.4.1 the binding energies observed for the products are those that would arise if a new tin(IV) species were present. No binding energies in the region of 486.1 eV [attributed to bis(tributyltin) oxide] were detectable.

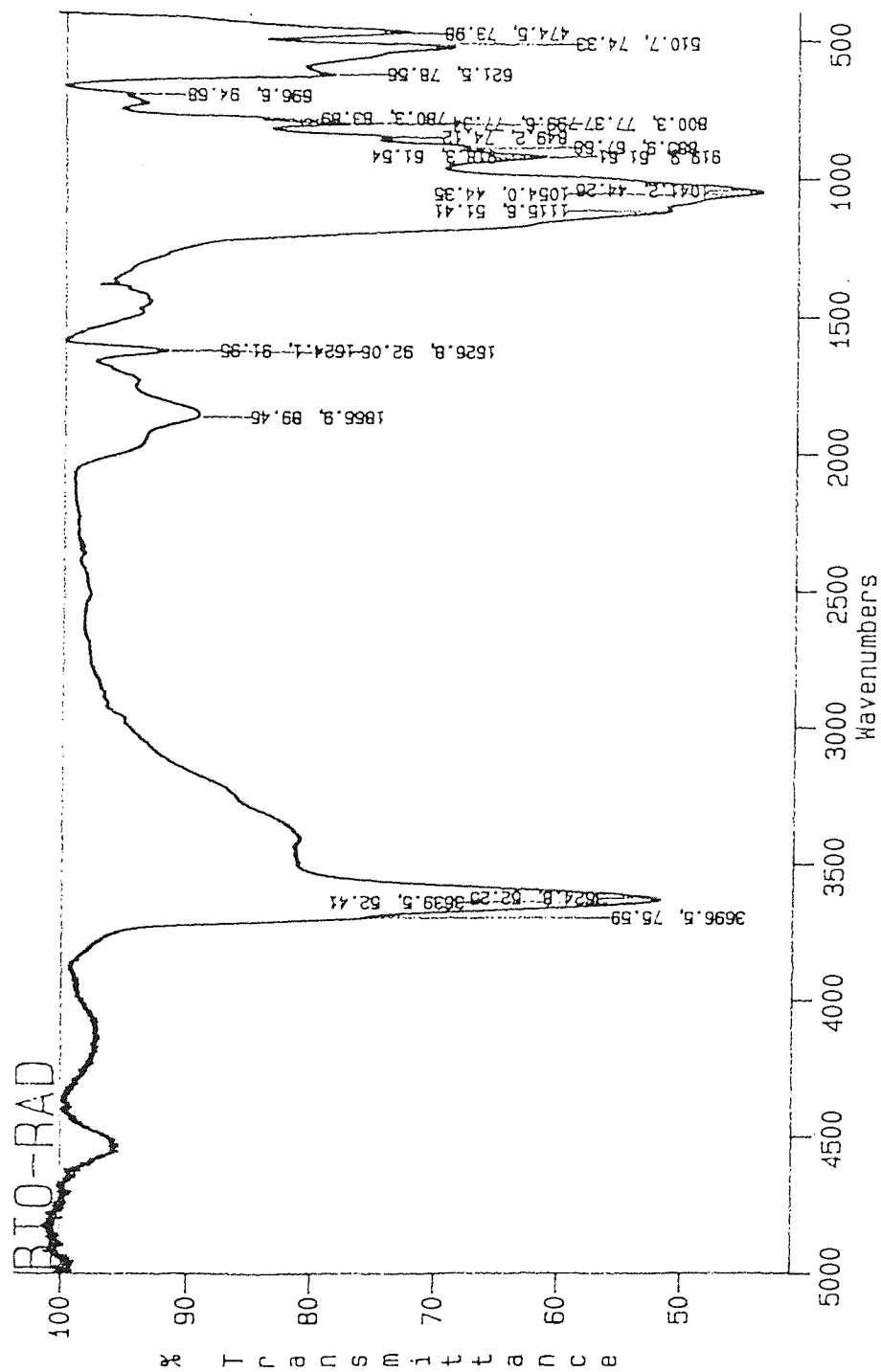


Figure 5.9 FTNIR of bis(tributyltin)oxide montmorillonite material after 1 minute of reaction

Results therefore suggest that after one minute a Sn(IV) species with binding energy 487.0 - 487.2 eV \pm 0.5 eV is formed which is stable to microwave radiation for five minutes of exposure.

The results of the analysis of the bis(tributyltin) oxide-montmorillonite are similar to those of bis(tributyltin) oxide-laponite. For both smectite clay reactions, the XPS experiment suggests that a tin(IV) species is present in the tin-clay material after 1 and 5 minute of reaction. In the case of the bis(tributyltin) oxide/montmorillonite reaction, the tin binding energies may result from the presence of one or two tin species. At low concentrations the two peaks may arise from the same tin(IV) species which from the FTIR data may be SnO₂. However, if the two peaks arise from the presence of two different tin(IV) species on the clay surface, then the reaction may have progressed as suggested for earlier experiments (Section 5.3), with detection of the intermediate tin(IV) species occurring. That is, bis(tributyltin) oxide undergoes hydration and/or de-alkylation reactions to form one tin(IV) species on the surface of the mineral. Continued reaction results in a clay mineral with a second tin(IV) species, present on the clay surface.

5.5.3.3 XRD

Representative samples of the reaction were submitted for XRD analysis, Table 5.12 shows the results.

XRD results for the montmorillonite reactions suggest that though a product with a tin(IV) species that is not bis(tributyltin) oxide is formed, the reaction does not result in expansion of the interlayer region and is therefore a surface reaction. As described in Section 5.4, an acid clay may have been formed resulting in a reduction in basal spacing.

In the reaction of laponite with bis(tributyltin) oxide, XRD results suggest that the intercalation of ethanol (see Section 5.4) is a relatively slow reaction, i.e. the reaction is able to be monitored by reactions in a microwave oven over a time scale of five minutes. The reaction appears to involve the gradual formation of ethanol layers in the laponite interlayer region.

Adsorption of bis(tributyltin) oxide by montmorillonite under microwave conditions may not be complete in 5 minutes (Table 5.10). Within 1 minute tin(IV) oxide may have been produced and adsorbed on the clay surface. The adsorption, hydration and

Table 5.12 Basal spacings of the products of the reactions between bis(tributyltin) oxide and smectite clays under microwave conditions.

tin-clay material and time of reaction (minutes)	d(001) Å
montmorillonite-bis(tributyltin) oxide	
1	12.44
5	12.44
montmorillonite alone	12.65
laponite-bis(tributyltin) oxide	
1	13.90
5	14.69
laponite alone	12.95

de-alkylation reactions continue throughout the 5 minutes (FTIR). The hydration/de-alkylation reactions may be slow enough to detect the intermediate tin(IV) species by XPS. The decrease in basal spacing which paralleled the release of sodium ions from the interlayer region in a previous experiment (Section 5.4), occurred in under one minute. An acid clay may have been produced.

Adsorption of bis(tributyltin)oxide by laponite under microwave conditions was complete in 1 minute with regard to the amount of bis(tributyltin)oxide adsorbed (Table 5.10). A tin(IV) species was surface sorbed. However, complete adsorption of ethanol into the interlayer region takes more than one minute to occur. It may be that if the reaction had proceeded for longer than the five minute limit of this experiment, further adsorption of ethanol may have led to further expansion of the silicate layers.

5.6 Conclusions and Further Work

Triphenyltin hydroxide was not adsorbed by any of the adsorbents at the conditions used in this study.

In this study of adsorption of organo-tin compounds by Quat-smectites at ambient temperatures, it was found that the Quat-smectites used were ineffective adsorbents

for both bis(tributyltin)oxide and triphenyltin hydroxide. Thus the findings of Meer¹⁰⁹ may be disregarded.

In the adsorption of bis(tributyltin)oxide from ethanol by smectite clays at ambient conditions, the interactions were found to be typical of weak adsorbate-adsorbent interactions, Type V when montmorillonite is the adsorbent and Type III or V when laponite is the adsorbent. Adsorption appears to be accompanied by a conversion of bis(tributyltin) oxide to a different tin(IV) species via hydration and/or de-alkylation reactions. In the case of montmorillonite, adsorption occurs on the surface and edge sites of the clay. Adsorption by laponite is complex and appears to involve adsorption of ethanol into the interlayer region as well as adsorption of bis(tributyltin)oxide at surface and edge sites.

In the study of adsorption of organo-tin compounds from ethanol by Quat-smectites when exposed to microwave radiation, it was found that the Quat-smectites adsorbed bis(tributyltin)oxide. The adsorption of bis(tributyltin) oxide by the Quat-clays under microwave conditions varies with the type of Quat used rather than the type of clay. Both HDTMA-smectites adsorb comparatively more bis(tributyltin) oxide than TMPA-clays or non-exchanged smectites under microwave conditions. At this stage it is difficult to predict whether adsorption of bis(tributyltin)oxide is primarily at surface or interlayer sites, as no increase in basal spacing results from adsorption but interlayer space is available. It is suggested that if interlayer adsorption occurs it does so via van der Waals interactions between alkyl groups of the adsorbate and the adsorbent. The adsorbed bis(tributyltin)oxide is thought to undergo hydration and/or de-alkylation reactions. Adsorption of bis(tributyltin)oxide from ethanol by TMPA-laponite and HDTMA-montmorillonite results in the re-orientation of the quaternary ammonium cations in the interlayer region. In the analysis of the tin-Quat-clay material, significant concentrations of tin compound are detected by XPS, thus adsorption occurs at the surface, but there is no evidence for adsorption in the interlayer region.

In the adsorption of bis(tributyltin)oxide from ethanol by smectite clays under microwave conditions adsorption occurs as that at room temperature. Microwave adsorption studies show that adsorption of bis(tributyltin) oxide is primarily at surface sites for both clays. In the case of laponite, the interlayer adsorbate is ethanol with bis(tributyltin) oxide adsorbing primarily at surface sites.

Sodium analysis of the supernatants resulting from the adsorption of bis(tributyltin) oxide by the smectite clays under microwave conditions shows that the laponite interlayer region retains the sodium cations on reaction. These results are contrary to

the montmorillonite results which indicate a release of a high concentration of the sodium cations. No pH changes are detected in the montmorillonite reaction and thus there is no evidence of the formation of an acid clay. Thus the mechanism for the adsorption of bis(tributyltin) oxide from ethanol by montmorillonite under microwave conditions remains unexplained.

In the study of the effect of time on the adsorption of bis(tributyltin) oxide by smectite clays under microwave conditions, it was found that for laponite, maximum bis(tributyltin) oxide surface adsorption is achieved in under one minute. A small concentration of tin(IV) species, thought to be tin(IV) oxide, was detected on the surface of the clay. The accompanying intercalation of ethanol into the laponite interlayer region is slow and can be followed by XRD analysis. However, for montmorillonite, at five minutes the percentage of bis(tributyltin) oxide adsorbed may not be the maximum adsorption achievable. One or two tin(IV) species may be present on the surface of the clay material, one of which is thought to be tin(IV) oxide. The nature of the other tin(IV) species is not yet determined.

Further work should involve a study of the swelling properties of sodium exchanged, calcium exchanged and sodium-calcium exchanged montmorillonites in ethanolic media. This would clarify, the nature of the sodium-calcium-montmorillonite used in these studies.

The results of the apparent desorption or re-orientation of TMAPA cations in TMAPA-laponite and the HDTMA cations in HDTMA-montmorillonite under microwave conditions (Section 5.3.2.2) should be clarified by monitoring the ethanolic media for TMAPA cations or by studying the interlayer chemistry of these particular Quat-clays.

Study of the apparent loss of the alkyl groups from bis(tributyltin) oxide would be useful in the clarification of the products of the adsorption of bis(tributyltin) oxide. The preparation of organo-tin-clay materials containing high concentrations of tin would enable vital ^{118}Sn MASNMR, ^{13}C MASNMR and Mössbauer spectroscopic analysis. Carrying out the reaction in sealed vessels from which the nature of the gaseous products could be studied in situ by, for example, FTIR or GC/MS, would yield information on the nature of the mechanism of adsorption. Alternatively carrying out similar studies with a derivative less likely to give gaseous alkane products, for example bis(trihexyltin) oxide, may show evidence of the de-alkylation of bis(tributyltin) oxide on exposure to clays and Quat-clays in ethanolic media and under microwave and ambient conditions.

For the adsorption of organo-tin compounds, five minutes of microwave radiation was assumed to be an adequate amount of time for the reaction to proceed to near completion. The assumption was made on the basis of research conducted by Bond⁹² and Ashcroft⁹³. Any further work in this field could begin by clarifying that this is indeed the case.

Chapter 6

Adsorption Characteristics of Transition Metal Complex Exchanged Smectites

6.1 Introduction

The synthesis of transition metal complex exchanged hectorites and studies of their adsorbent characteristics were outlined in Section 1.4.2. It was shown by Mortland and co-workers^{43,45} that 1,10-phenanthroline and 2,2'-bipyridyl complexes of iron(II) and copper(II) readily undergo exchange reactions with hectorite clay. The resulting exchanged clays were able to adsorb water and benzene vapours. The work described in this chapter is an expansion of the work of Mortland and co-workers to include the synthesis of transition metal complex exchanged montmorillonite and laponite. Adsorption of phenol and 2,4,6-trichlorophenol from aqueous solution is measured. Adsorption of these phenols from solution by the aforementioned adsorbents has not previously been studied. 2,2'-bipyridyl complexes of Fe(II), Cu(II), Co(II), and Co(III) and tri-(2-pyridyl)amine complexes of Fe(II), Co(II) were used in the synthesis of the transition metal complex exchanged smectites.

6.2 Synthesis of 2,2'-bipyridyl and tri-(2-pyridyl)amine transition metal complexes

6.2.1 Ligand synthesis

The structure of the ligands used in this study are represented in Figure 6.1. 2,2'-bipyridyl was used as supplied.

Tri-(2-pyridyl)amine was synthesised using a literature method¹¹⁸. Di-(2-pyridyl)amine (5.5 g) was refluxed in xylene for 16 hours with 2-bromopyridine (5.2 g) in the presence of copper bronze (2.0 g), a trace of potassium iodide, and anhydrous potassium carbonate (6.0 g). The solvent and excess 2-bromopyridine was removed by steam distillation and the residue extracted four times with boiling water (50 cm³). A white solid form was obtained on cooling which was recrystallised from water to give a white crystalline solid.

Appearance: white crystalline solid. Melting point = 129 °C, literature value = 130 °C.

Elemental analysis found: C, 72.6%; H, 4.93%; N, 22.6%

Elemental analysis expected: C, 72.6%; H, 4.87%; N, 22.6%

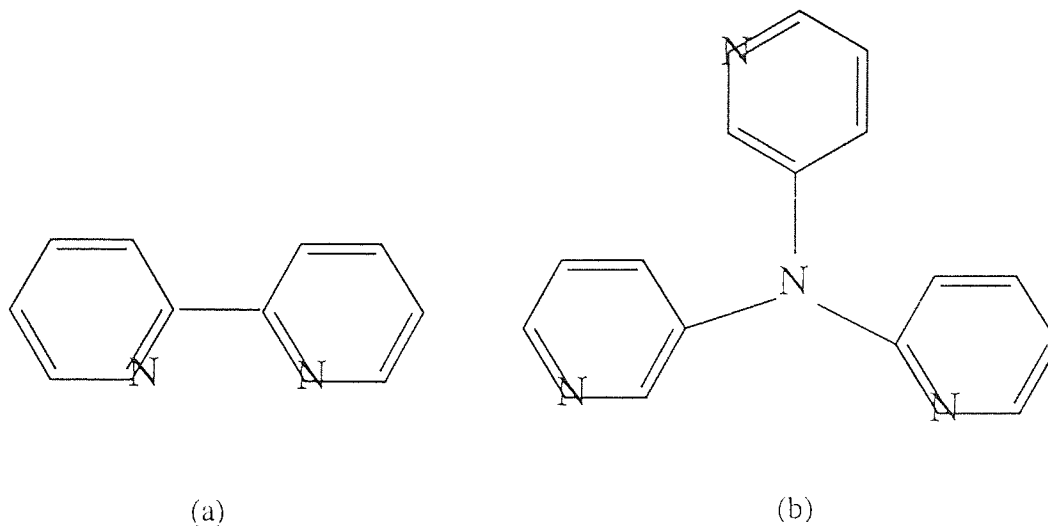


Figure 6.1 The structure of (a) 2,2'-bipyridyl and (b) tri-(2-pyridyl)amine

6.2.2 Complex preparation

2,2'-bipyridyl complexes of Fe(II), Cu(II), Co(II) and Co(III); and tri-(2-pyridyl)amine complexes of Fe(II) and Co(II) were synthesised as described below. 2,2'-bipyridyl transition metal complexes of Fe(II), Cu(II), Co(II) and Co(III) were synthesised using a literature method¹¹⁹. Tri-(2-pyridyl)amine transition metal complexes of Fe(II) and Co(II) were synthesised using a literature method¹²⁰.

6.2.2.1 Tris 2,2'-bipyridyl iron(II) perchlorate

2,2'-bipyridyl (0.2 g) was dissolved in hot water (300 cm³) and treated with excess iron(II) sulphate and sodium perchlorate solution. The red solution was heated on a hot plate for one hour and then left to cool. The red crystalline perchlorate which separated was filtered off, washed with distilled water and dried in vacuo.

Tris 2,2'-bipyridyl iron(II) perchlorate is known to be a low-spin octahedral complex with electron configuration of the d orbitals being t_{2g}^6 .

6.2.2.2 Tris 2,2'-bipyridyl copper(II) perchlorate

Ethanollic solutions of 2,2'-bipyridyl and copper perchlorate in a molar ratio of 3:1 were mixed, the solid which separated was filtered off, washed well with water and dried in vacuo.

Tris 2,2'-bipyridyl copper(II) perchlorate has been found to be reluctant to form octahedral complexes with 2,2'-bipyridyl. It is more common that 5 co-ordinate complexes with a trigonal bipyramidal structure are formed. The complex synthesised is likely to have chemical formula $[\text{Cu}(\text{bipy})_2(\text{ClO}_4)](\text{ClO}_4)$.

6.2.2.3 Tris 2,2'-bipyridyl cobalt(II) perchlorate trihydrate

Cobalt(II) chloride hexahydrate (0.6 g) was dissolved in ethanol (25 cm³), filtered and boiled to remove air. It was then treated with 2,2'-bipyridyl (1.2 g) in hot ethanol (20 cm³) which formed a brown solution. Nitrogen was passed through the mixture which was then diluted with distilled water (50 cm³) and excess sodium perchlorate was added. After 15 minutes in ice, the crystals which formed were filtered off, washed with water and dried in vacuo.

Tris 2,2'-bipyridyl cobalt(II) perchlorate trihydrate is a high-spin octahedral complex with electron configuration of the d orbitals being $t_{2g}^5e_g^2$.

6.2.2.4 Tris 2,2'-bipyridyl cobalt(III) perchlorate

Cobalt(III) chloride hexahydrate (2.4 g) and 2,2'-bipyridyl (4.7 g) were heated with of distilled water (50 cm³) until complete solution occurred. This yellow solution was treated with hydrogen peroxide (10 cm³, 30%) and hydrochloric acid (10 cm³, d 1.18) and the mixture evaporated to a syrupy consistency. Distilled water (50 cm³) was then added, and the solution treated with perchloric acid (10 cm³, 60%). The yellow crystalline perchlorate was then separated. This was recrystallised from hot water and air dried.

Tris 2,2'-bipyridyl cobalt(III) perchlorate is known to be a low-spin octahedral complex with electron configuration of the d orbitals being t_{2g}^6 .

6.2.2.5 Bis tri-(2-bipyridyl)amine iron(II) perchlorate

Iron perchlorate hexahydrate (0.19 g) in ethanol (10 cm³) was mixed with an acetone solution (10 cm³) of the tri-(2-pyridyl)amine (0.24 g). The orange brown solid which crystallised from the acetone-ethanol solution was air dried.

Bis tri-(2-bipyridyl)amine iron(II) perchlorate is a low-spin octahedral complex¹²¹ with electron configuration of the d orbitals being t_{2g}^6 .

6.2.2.6 Bis tri-(2-bipyridyl)amine cobalt(II) perchlorate

Cobalt perchlorate hexahydrate (0.19 g) in ethanol (10 cm³) was mixed with an acetone solution (10 cm³) of the tri-(2-pyridyl)amine (0.24 g). The orange solid which crystallised from the acetone-ethanol solution was air dried.

Bis tri-(2-bipyridyl)amine cobalt(II) perchlorate has been shown to be principally a high-spin octahedral complex. The presence of some low-spin isomer has been detected and reported by Bond et al.¹²¹. The electron configuration of the d orbitals being $t_{2g}^5e_g^2$ (high spin) or $t_{2g}^6e_g^1$ (low spin).

6.3 Characterisation of transition metal complexes

The synthesis and characterisation of these complexes is well documented. Thus, the characterisation of the transition metal complexes was conducted by colour and FTIR analysis.

6.3.1 Colour

Table 6.1 summarises the colours of the synthesised complexes.

Table 6.1 Colours of synthesised complexes

Complex	Colour
Tris 2,2'-bipyridyl iron(II) perchlorate	red/maroon
Bis 2,2'-bipyridyl copper(II) perchlorate	blue
Tris 2,2'-bipyridyl cobalt(II) perchlorate trihydrate	sun yellow
Tris 2,2'-bipyridyl cobalt(III) perchlorate	yellow/orange
Bis tri-(2-bipyridyl)amine iron(II) perchlorate	orange/brown
Bis tri-(2-bipyridyl)amine cobalt(II) perchlorate	orange

The colours of the synthesised transition metal complexes are as reported in the literature¹¹⁸⁻¹²⁰.

6.3.2 FTIR

FTIR analysis of all complexes shows the presence of the perchlorate ion - 1100 cm^{-1} (ν_3) - and absorption characteristic of the relevant 2,2'-bipyridyl or tri-(2-pyridyl)amine molecule. Additional spectral features are noted below for specific complexes:

The spectrum of bis 2,2'-bipyridyl copper(II) perchlorate, $[\text{Cu}(\text{bipy})_2(\text{ClO}_4)](\text{ClO}_4)$, indicates that it is the $[\text{Cu}(\text{bipy})_2]^{2+}$ form that has been made and not the $[\text{Cu}(\text{bipy})_3]^{2+}$.

The crystal structures of the complexes are known. The bonding of the 2,2'-bipyridyl complexes is tris-bidentate, with the exception of the Cu(II) complex in which is bis-bidentate. The bonding of the tri-(2-bipyridyl)amine complexes is given as bis-terdentate.

Analysis by FTIR suggested that all complexes had been successfully synthesised.

6.4 Preparation of transition metal complex exchanged smectites

Transition metal complex exchanged montmorillonites and laponites were prepared as described in Section 3.2.2 with addition of the transition metal complex to satisfy the c.e.c of the smectite.

6.5 Characterisation of transition metal complex exchanged smectites

Representative samples of the transition metal complex exchanged smectites were analysed by XRD, Atomic absorption and FTNIR.

6.5.1 Percentage exchange (AA)

Table 6.2 below shows the percentage exchange occurring in representative samples.

Table 6.2 Percentage exchange observed for selected transition metal complex exchanged smectites

Material	percentage exchange % Na ⁺ displaced	basal spacing d(001), Å
[Cu(bipy) ₂](ClO ₄) ₂ -laponite	80%	17.7
[Cu(bipy) ₂](ClO ₄) ₂ -montmorillonite	75%	17.7
[Co(bipy) ₃](ClO ₄) ₃ -laponite	80%	17.7
[Co(bipy) ₃](ClO ₄) ₃ -montmorillonite	70%	17.7

The examples shown in Table 6.2 show that a high percentage of exchange occurs during reaction. Both clays also show that significantly less than 100% exchange takes place during the reaction. This may be due to the size of the transition metal complex cations. That is, while the charge on the cation may be 2+, resulting theoretically in the displacement of 2 sodium cations, the size of the exchanging cation may take up more than 2 exchange sites. This may reduce the possibility of successive exchanging cations displacing the third sodium cation 'trapped' by the first exchanging cation. Figure 6.2 shows a schematic representation of the exchange reaction between smectite clays and transition metal complexes.

6.5.2 Basal spacing (XRD)

The basal spacings of all the [M(bipy)₃]ⁿ⁺ exchanged smectites, where M = Fe(II), Co(II) and Co(III) and n the charge on the transition metal, and [Cu(bipy)₂]²⁺ exchanged smectites were found to be 17.7 Å, corresponding to an opening of the silicate layers by ~5 Å for both clays. The exception was [Co(bipy)₃]²⁺ exchanged laponite with a basal spacing of 19.2 Å, and a silicate layer opening of 6.2 Å. Studies of 2,2'-bipyridyl complexes of Fe(II) and Cu(II) exchanged onto hectorite clay by Mortland et al.⁴³, showed that increases in basal spacings of 8 Å accompanied the exchange reaction. This was stated to be in accordance with monolayer arrangement of the transition metal complex cations. Here it is assumed that the same monolayer arrangement occurs but that for the clays studied, the cations take up an arrangement that results in an interlayer opening of 5 - 6 Å.

The opening of the interlayer region observed for the $[\text{Co}(\text{bipy})_3]^{2+}$ exchanged laponite was 6.2 Å. High-spin-low-spin equilibria have been reported to occur in

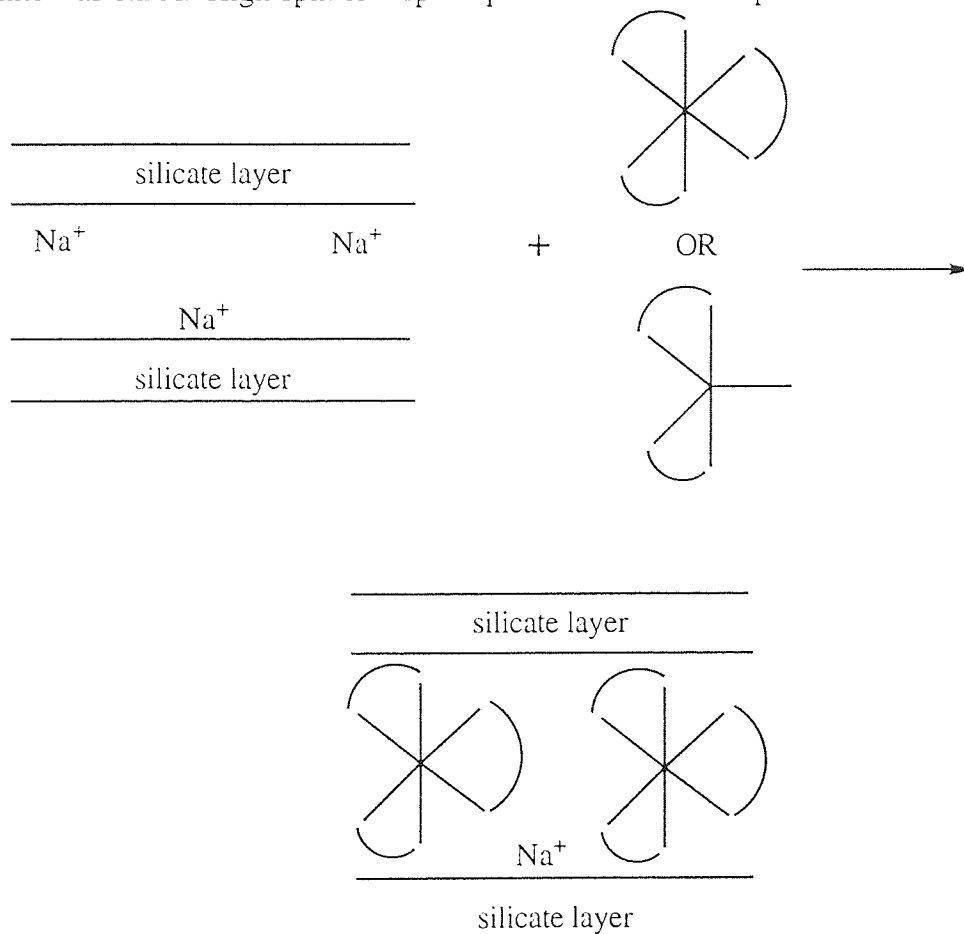


Figure 6.2 A schematic representation of the reaction between smectite clays and transition metal complexes

these complexes¹²². The laponite clay may cause this high-spin-low-spin crossover. The low-spin complex would be subject to the Jahn-Teller effect. This would result in the increase of the Co^{2+} radius and therefore an increase in the basal spacing.

Basal spacings of the $[\text{M}(\text{tripyam})_2](\text{ClO}_4)_n$ exchanged clay products, where $\text{M} = \text{Fe}(\text{II})$ and $\text{Co}(\text{II})$, and n the number of moles of perchlorate needed to balance the charge of the transition metal cation, were not obtained.

6.5.3 Colour

Table 6.3 below shows the colours of the transition metal complexes and their respective exchanged smectites.

Table 6.3 The colours of the transition metal complexes and their respective exchanged smectites*

Complex	Colour	Colour of clay
Tris 2,2'-bipyridyl iron(II) perchlorate	red/maroon	
[Fe(bipy) ₃] ²⁺ - smectites		red/maroon
Bis 2,2'-bipyridyl copper(II) perchlorate	blue	
[Cu(bipy) ₂] ²⁺ - smectites		blue
Tris 2,2'-bipyridyl cobalt(II) perchlorate trihydrate	sun yellow	
[Co(bipy) ₃] ²⁺ - smectites		sun yellow
Tris 2,2'-bipyridyl cobalt(III) perchlorate	yellow/orange	
[Co(bipy) ₃] ³⁺ - smectites		yellow/orange
Bis tri-(2-bipyridyl)amine iron(II) perchlorate	orange/brown	
[Fe(tripyam) ₂] ²⁺ - montmorillonite		orange/brown
Bis tri-(2-bipyridyl)amine cobalt(II) perchlorate	orange	
tri-(2-bipyridyl)amine complex of Co(II)		
exchanged montmorillonite		pink

*smectites denotes both laponite and montmorillonite.

N.B. Tri-(2-bipyridyl)amine transition metal complex exchanged laponites were not synthesised.

The colours of the 2,2'-bipyridyl transition metal complex exchanged clays was the same as the complex precursors. This indicated that the bonding of the transition metal complexes does not change on exchange with the sodium cations in the smectite clays.

Obviously, the interesting observation to be made here is the change in the colour of the tri-(2-bipyridyl)amine complex of cobalt(II) when present on the surface of the montmorillonite clay. Similar observations were made by Bond et al.¹²¹ when the

same complex was exchanged onto laponite clay. The reason for the colour change was suggested to be due to a change from terdentate to bidentate ligands. Shaking of the orange complex in aqueous media has been shown to result in a pink solution. The species formed from this reaction and the species participating in the exchange reaction is proposed to be diaquo{bis[tri-2-pyridylaminecobalt(II)]} with bidentate amine ligands¹²¹. Aquation of $[\text{Co}(\text{tripyam})_2](\text{ClO}_4)_2$ is facilitated by the fact that the two Co-N bonds of $[\text{Co}(\text{tripyam})_2](\text{ClO}_4)_2$ are significantly longer at 2.152 Å than the other four at 2.100 Å¹²¹. Evidence of the cation being the stated diaquo species will need to be obtained by UV-Vis diffuse reflectance.

6.5.4 FTIR/FTNIR

All transition metal complex exchanged montmorillonites were analysed by FTNIR. Peaks arising from the presence of the relevant complex and from the presence of the montmorillonite clay were present in all products. The absence of the broad perchlorate peak in all transition metal complex exchanged montmorillonites suggests that the transition metal complex cations only are present in the interlayer region. That is, the concentration of transition metal complex ion pairs and sodium perchlorate in the exchanged montmorillonite product is below the detection limit of the FTIR experiment. This is strong evidence for the cation exchange reaction occurring for all the complexes synthesised.

Characteristic peaks for montmorillonite in the near infra-red region, 5000-4000 cm^{-1} , are 4120 cm^{-1} , 4500 cm^{-1} , 4760 cm^{-1} . Changes in the montmorillonite spectra resulting from the exchange reaction are summarised for each transition metal complex exchanged clay in the Table 6.4 below.

The major observation from this data is the absence of the peak at 4760 cm^{-1} due to presence of the montmorillonite. The assignment of this peak is not documented in the literature. Since it is no longer present after the exchange reaction, it is possible that it arises due to the presence of interlayer water. The absence of the peak will therefore be due to the displacement of water from the interlayer region during the exchange reaction.

It is probable that peaks at 4360, 4680, 4840, 4940 cm^{-1} are combination bands for the pyridyl group in the ligands of the complexes. With the exception of the $[\text{Co}(\text{tripyam})_2](\text{ClO}_4)_2$ and its respective exchanged montmorillonite, no large changes in the spectra occur in the 4000 - 400 cm^{-1} region when the transition metal complexes are exchanged onto the clay. It can be assumed that the complex is not

undergoing any major changes on reaction, i.e. that the bonding remains unchanged on exchange. Figure 6.3 shows representative spectra.

Table 6.4 FTNIR peaks of the transition metal exchanged montmorillonites, 5000-4000 cm^{-1} region only

Material	Peaks present cm^{-1}					
	4100w	4360m	4680m	4760w	4840m	4940w
$[\text{Fe}(\text{bipy})_3]^{2+}$ - mont	n	y	y	n	y	y
$[\text{Cu}(\text{bipy})_2]^{2+}$ - mont	n	y	y	n	y	y
$[\text{Co}(\text{bipy})_3]^{2+}$ - mont	y	y	y	n	n	y
$[\text{Co}(\text{bipy})_3]^{3+}$ - mont	b	y/w	y	n	y	n
$[\text{Fe}(\text{tripyam})_2]^{2+}$ - mont	n	y	y	n	y	y
$[\text{Co}(\text{tripyam})_2]^{2+}$ - mont *	b	n	y	n	y	y

w - weak intensity peak, m - medium intensity peak, b - broad peak, y - present in spectra, n - not present in spectra.

* - the exact nature of this complex is discussed in Section 6.5.3.

In the case of the $[\text{Co}(\text{tripyam})_2]^{2+}$ - montmorillonite there are the only two peaks arising from the presence of the complex which are assignable to both spectra in the 4000-400 cm^{-1} region (peaks at 1289 and 1330 cm^{-1} on complex; 1287 and 1329 cm^{-1} on exchanged clay). The difference between the $[\text{Co}(\text{bipy})_3]^{2+}$ - montmorillonite and $[\text{Co}(\text{tripyam})_2]^{2+}$ - montmorillonite spectra in the 5000 - 4000 cm^{-1} region (Table 6.4) is quite interesting and parallels differences in the 4000 - 400 cm^{-1} region of the FTIR spectrum and the difference in colour observed on exchange. The differences in the FTIR/NIR spectra may well be additional evidence for the presence of a new cationic species, possibly diaquo{bis[tri-2-pyridylaminecobalt(II)]}, in the exchange reaction mixture, as explained in Section 6.5.3. Figure 6.3d shows the spectrum of the tri-(2-pyridyl)amine complex of cobalt exchanged onto montmorillonite.

The combination of the colour of the exchanged smectite products, percentage exchange observed, XRD results and FTNIR results strongly suggest that the 2,2'-bipyridyl transition metal complex exchanged smectite products have been successfully synthesised.

The colour of the $[\text{Fe}(\text{tripyam})_2](\text{ClO}_4)_2$ exchanged clay was the same as the complex. Therefore the bonding of the complex does not change as a result of the exchange reaction in this case. This suggests that the $[\text{Fe}(\text{tripyam})_2]^{2+}$ exchanged montmorillonite was successfully synthesised.

For the $[\text{Co}(\text{tripyam})_2]^{2+}$ - montmorillonite, the colour of the complex exchanged clay was different to the complex. This combined with the observed differences in the IR spectra of the complex and exchanged clay suggests that the cationic species may actually be diaquo{bis[tri-2-pyridylaminecobalt(II)]}.

Basal spacings of the products of the exchange reactions with tri-(2-pyridyl)amine complexes of iron (II) and cobalt(II) and smectite clays were not obtained.

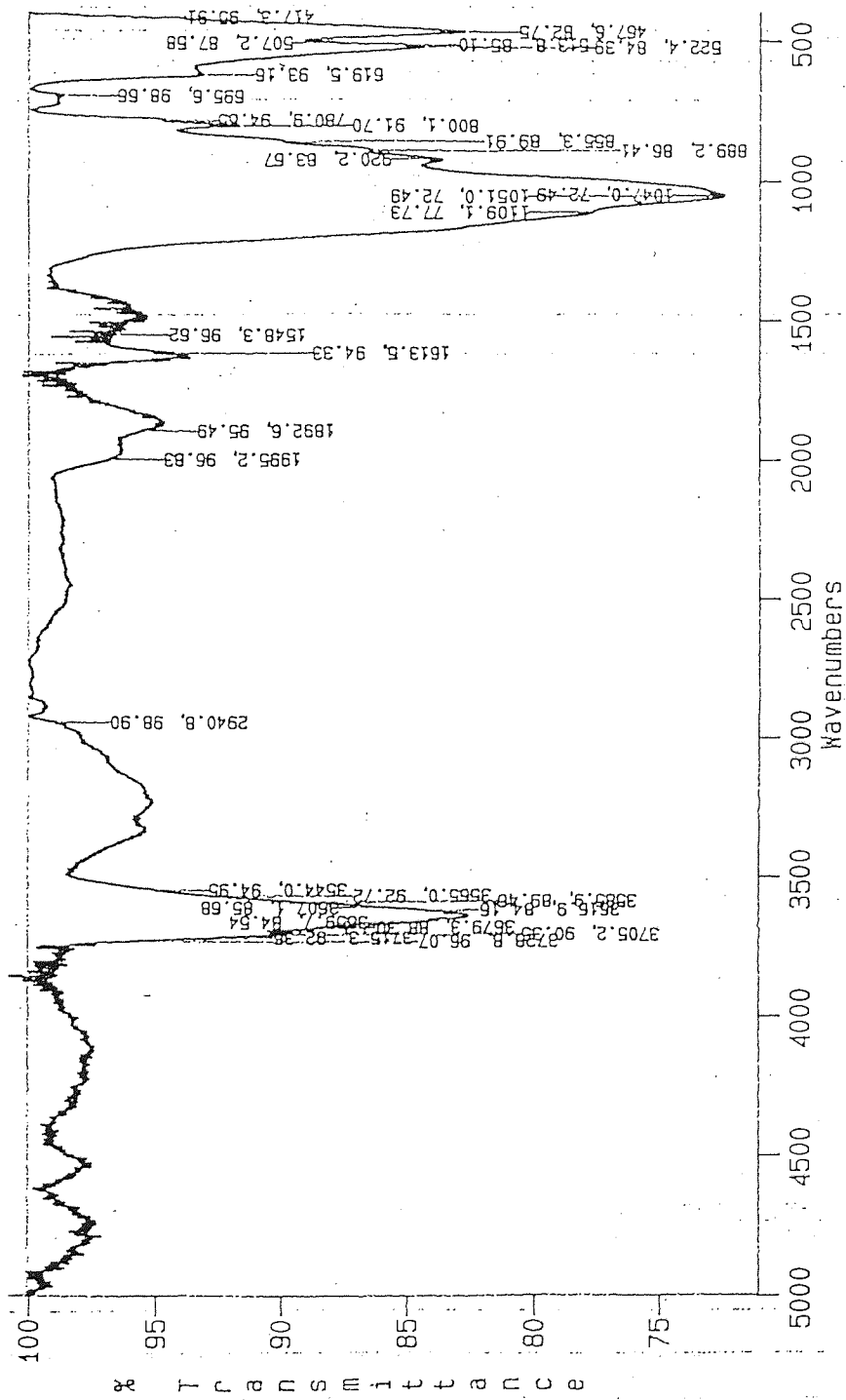


Figure 6.3a The FTNIR spectrum of montmorillonite

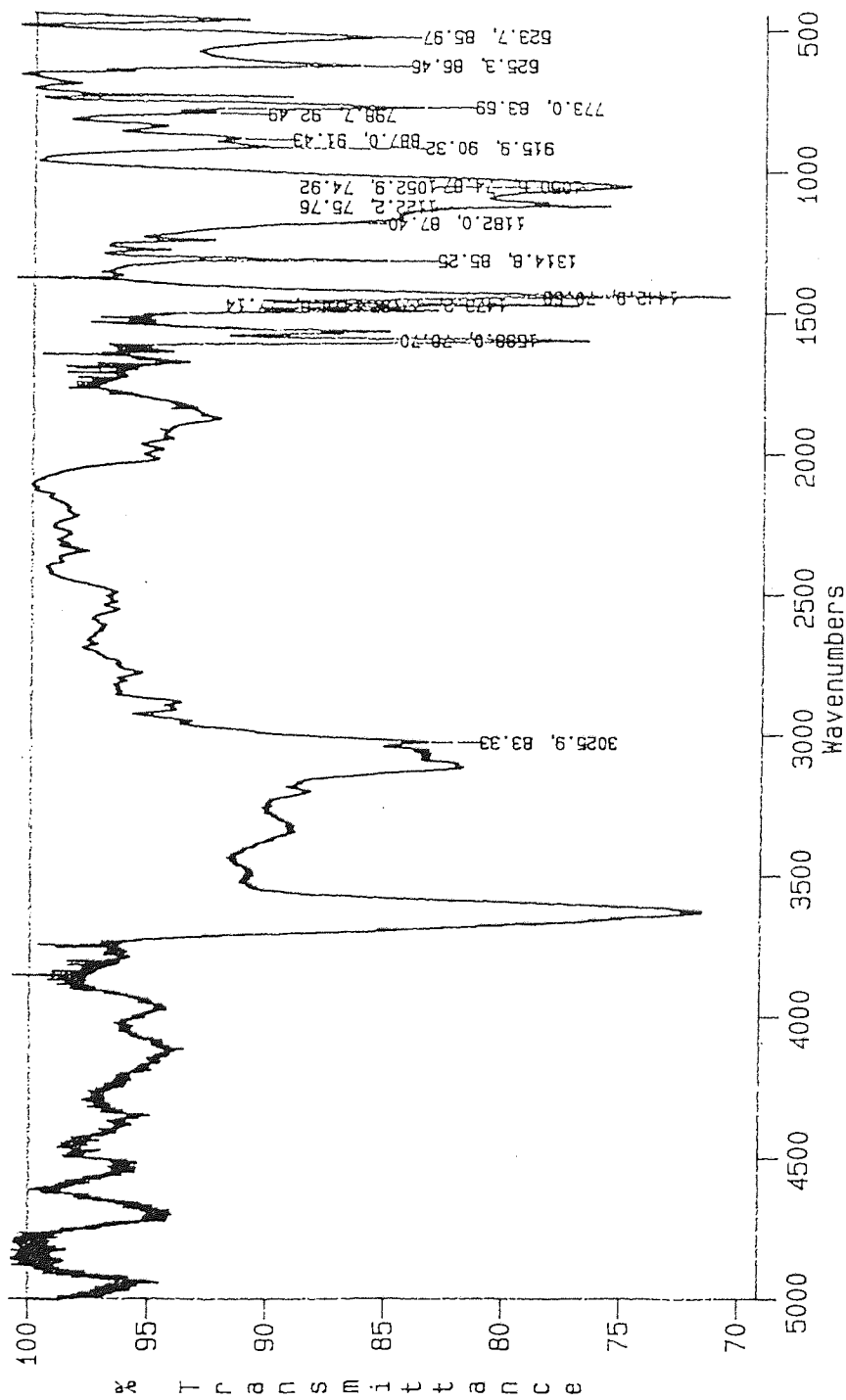


Figure 6.3c The FTIR spectrum of $[Co(bipy)_3]^{2+}$ - montmorillonite

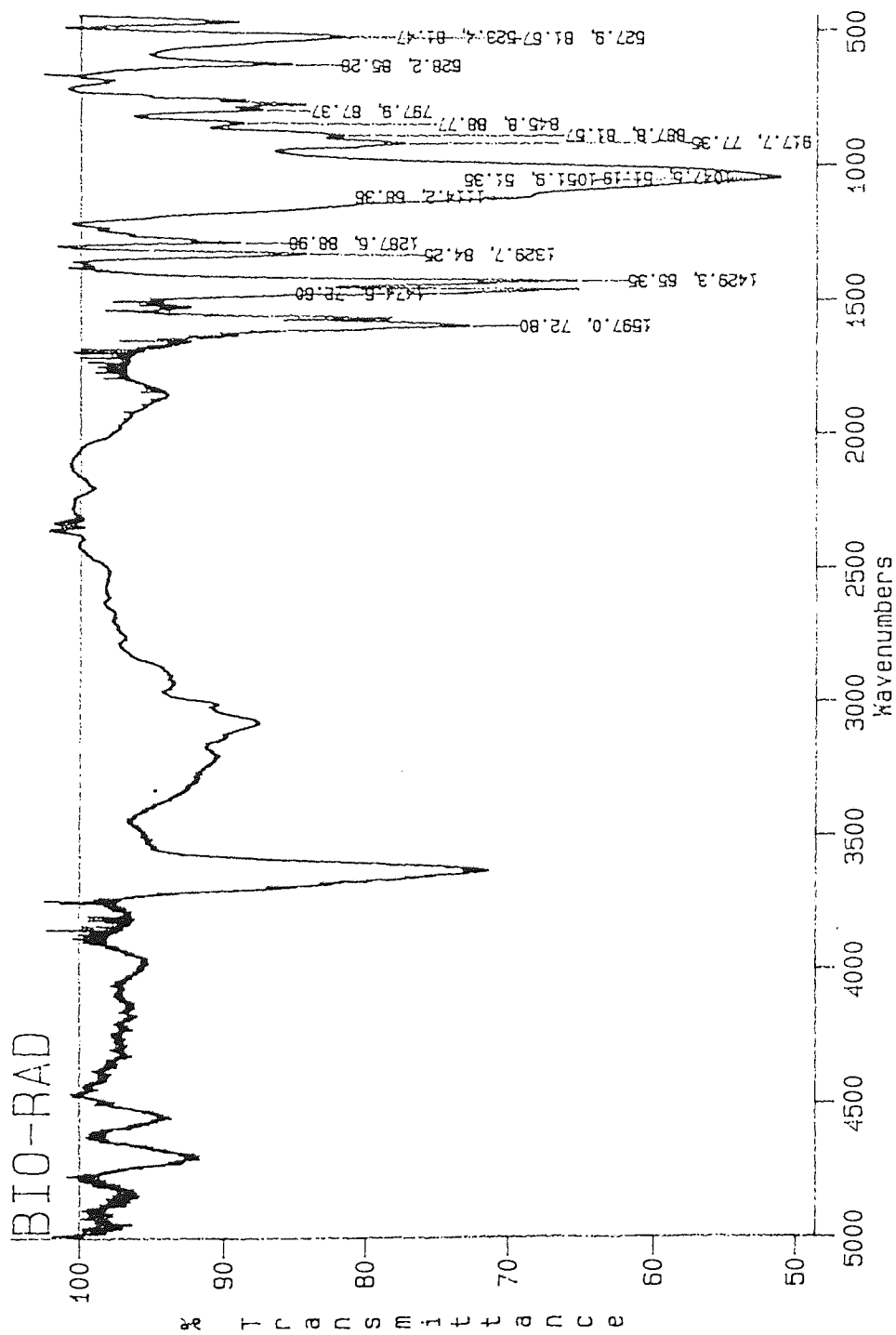


Figure 6.3d The FTNIR spectrum of the tri-(2-pyridyl)amine complex of cobalt(II) exchanged with montmorillonite

6.5 The reaction of 2,2'-bipyridyl with montmorillonite

A small concentration of iron (5.1%), in oxidation states II (0.7%) and III (4.4%)⁸⁶, is known to be present in the octahedral layer of montmorillonite due to isomorphous substitution reactions of the clay during formation. In this short experiment it was intended to examine the ability to complex the iron present in the octahedral layer with 2,2'-bipyridyl.

Montmorillonite (2 g) and 2,2'-bipyridyl (0.28 g) were added to 100 cm³ distilled water and shaken at room temperature for one week at 300 rpm. The reaction mixture was filtered and air dried. A pale pink powdered product (1.4 g) was obtained. The product was analysed by FTNIR.

The FTNIR spectrum is almost identical to that of the [Fe(bipy)₃](ClO₄)₂ exchanged montmorillonite spectrum though peaks at 4940 cm⁻¹ and 4840 cm⁻¹ are not as sharp as in [Fe(bipy)₃](ClO₄)₂ exchanged montmorillonite spectrum. This, combined with the observed colour change of the clay, strongly suggests that the 2,2'-bipyridyl is able to complex the iron present in the octahedral layer of the montmorillonite clay. More detailed study of the NIR region of the FTNIR spectrum for these materials will be needed to concentrate on the shifts or changes in the peaks at 4100 - 4120 cm⁻¹. Peaks in this region have previously assigned to Mg-OH and Fe-OH combination vibrations^{90,91}. The fact that no change is detected in the spectra in this region on reaction of the montmorillonite with 2,2'-bipyridyl, suggests that this peak is assignable to Mg-OH only for this particular montmorillonite clay.

Unfortunately this work could not be taken any further but analysis by UV-Vis diffuse reflectance would show evidence of complex formation. XRD and Mössbauer analysis would be informative as to the sites and extent of this complexation reaction.

6.6 Adsorption by transition metal complex exchanged smectites

6.6.1 Equilibration time and methods of phenol and 2,4,6-trichlorophenol analysis

Tris 2,2'-bipyridyl iron(II) perchlorate exchanged montmorillonite (0.1 g) was added to an aqueous solution containing 0.08 mmol phenol/100 cm³ distilled water, four such reaction mixtures were prepared. The flasks were stoppered and sealed with

teflon tape and placed on a mechanical shaker, set at 300 rpm. One was removed every 90 minutes, filtered and analysed by UV spectrophotometry at 268 nm.

However, the UV experiment was found to be unable to distinguish between the phenol present and the 2,2'-bipyridyl of the transition metal complex. Thus, an alternative method of analysis was sought.

The equilibration experiment was repeated with the phenol concentration being analysed by HPLC at the conditions described in Section 2.3. HPLC was found to be a satisfactory method for the analysis of these experiments. The time taken for the phenol solutions to reach equilibrium concentration was found to be 4.5 hours and separations of the aromatics present was achieved with little difficulty.

A repeated experiment with 2,4,6-trichlorophenol showed that UV was able to distinguish between the 2,2'-bipyridyl of the transition metal complex and 2,4,6-trichlorophenol. Thus 2,4,6-trichlorophenol adsorption was followed using UV analysis at 293 nm.

6.6.2 Adsorption isotherms

Adsorption of phenol and 2,4,6-trichlorophenol was measured as described in Section 3.6. Phenol concentration was measured by HPLC and 2,4,6-trichlorophenol concentration by UV as described in Section 6.5.1.

6.6.2.1 Adsorption by exchanged montmorillonites

Table 6.5 summarises the results of adsorption of phenol and 2,4,6-trichlorophenol by transition metal complex exchanged montmorillonites and Figure 6.4 shows the adsorption isotherms.

The 2,2'-bipyridyl transition metal complex exchanged clays all adsorb the two phenols. In all cases the 2,2'-bipyridyl transition metal complex exchanged montmorillonites show a greater affinity, both in terms of adsorption capacity and strength of interaction, towards the 2,4,6-trichlorophenol. This increased interaction may result from π - π interactions of the benzene rings of the 2,2'-bipyridyl ligand of the exchanged clay and the 2,4,6-trichlorophenol. The low solubility of the 2,4,6-trichlorophenol in water decreases the influence of adsorbate-solvent interactions and effectively results in the partitioning of the 2,4,6-trichlorophenol to the organic portion

Table 6.5 Summary of adsorption of phenol and 2,4,6-trichlorophenol by transition metal complex exchanged montmorillonites

	Adsorption isotherm type	
	phenol	2,4,6-trichlorophenol
Exchanged montmorillonites		
[Fe(bipy) ₃] ²⁺ - montmorillonite	V	I
[Cu(bipy) ₂] ²⁺ - montmorillonite	V/C	C - possible bilayer
[Co(bipy) ₃] ²⁺ - montmorillonite	III	C
[Co(bipy) ₃] ³⁺ - montmorillonite	C	I
[Fe(tripyam) ₂] ²⁺ - montmorillonite	un	V
[Co(tripyam) ₂] ²⁺ - montmorillonite ?	un	C

un - isotherm type unassignable

of the adsorbent - the 2,2'-bipyridyl ligand. This will, no doubt, play some part in the mechanism of adsorption. The orientation of 2,4,6-trichlorophenol is likely to be dependant on the orientation of the 2,2'-bipyridyl ligands to allow for benzene ring - pyridine ring interactions, and it is possible that the 2,4,6-trichlorophenol orients itself in the pockets of the ligand positions. Similar interactions were postulated to occur in the studies of benzene vapour adsorption by [M(phen)₃]²⁺ exchanged hectorites, where M = Fe⁴³.

In the Mortland et al. study, Type II and Type III adsorption was observed to occur. The results here suggest that 2,4,6-trichlorophenol is able to interact with the 2,2'-bipyridyl of the iron(II) and cobalt(III) transition metal complex exchanged montmorillonites to a greater degree (Type I isotherms) than that observed by Mortland et al., possibly as a result of the 2,2'-bipyridyl being relatively electron rich and the

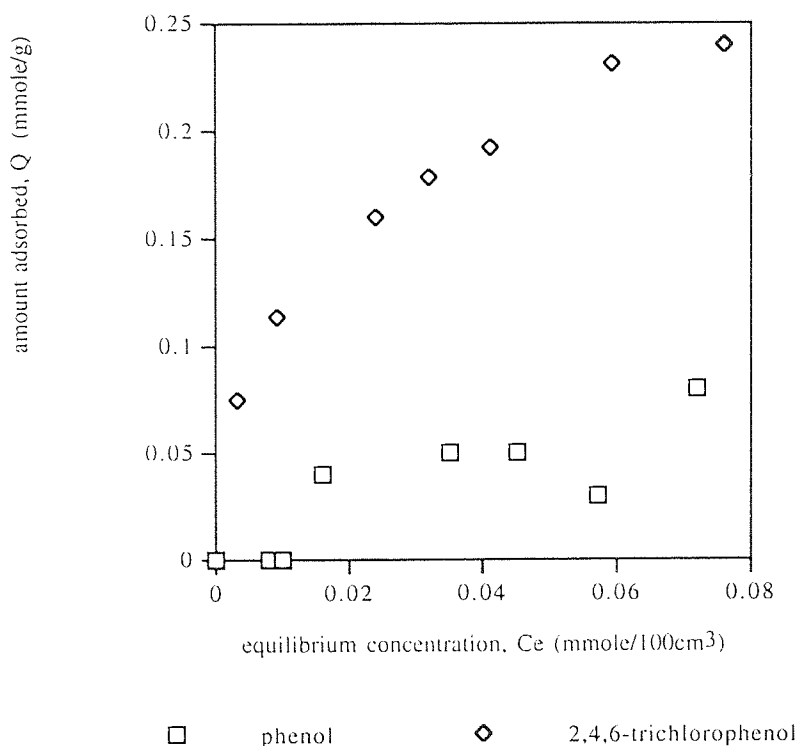


Figure 6.4a Adsorption of phenols by tris 2,2'-bipyridyl iron(II) perchlorate exchanged montmorillonite

2,4,6-trichlorophenol being relatively electron deficient. The electron richness of the ligand may result from the back bonding involved in complex formation. The two low spin, t_{2g}^6 , complexes $[\text{Fe}(\text{bipy})_3]^{2+}$ and $[\text{Co}(\text{bipy})_3]^{3+}$ may give rise to a higher degree of back bonding than the other 2,2'-bipyridyl transition metal complexes studied. This would result in the flow of π electrons from the metal to the ligand being greater for the low-spin complexes. This in turn would result in an increase in the electron density of the ligand which may enhance pyridine ring - benzene ring interactions between the transition metal complex exchanged clay and the 2,4,6-trichlorophenol, Figure 6.5.

Interactions of 2,4,6-trichlorophenol with the 2,2'-bipyridyl ligand of copper(II) and cobalt(II) transition metal complex exchanged montmorillonites were not as strong as those for 2,2'-bipyridyl transition metal complex of iron(II) and cobalt(III) exchanged clays. Both $[\text{Cu}(\text{bipy})_2]^{2+}$ exchanged montmorillonite and $[\text{Co}(\text{bipy})_3]^{2+}$ exchanged montmorillonite adsorbed 2,4,6-trichlorophenol via a partitioning process. $[\text{Cu}(\text{bipy})_2]^{2+}$ exchanged montmorillonite appears to adsorb 2,4,6-trichlorophenol in a

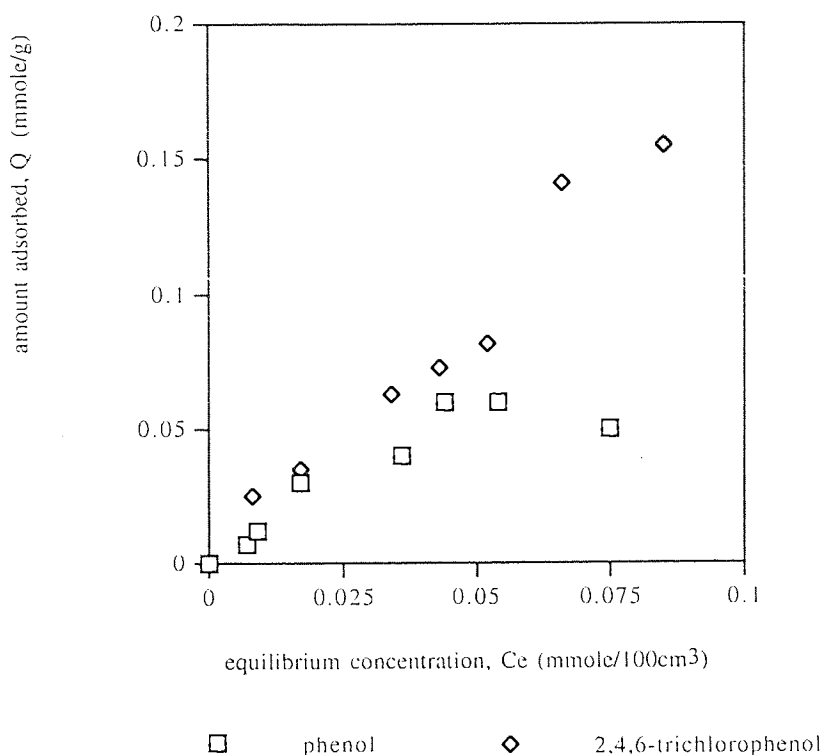


Figure 6.4b Adsorption of phenols by bis 2,2'-bipyridyl copper(II) perchlorate exchanged montmorillonite

bilayer or two-step manner. The mechanism for bilayer adsorption is straight forward. The two-step adsorption may occur when interactions at one type of adsorption site occurs before adsorption at the second adsorption site. It is likely that surface adsorption of 2,4,6-trichlorophenol occurs before interlayer adsorption if two-step adsorption is occurring.

Adsorption of phenol by the 2,2'-bipyridyl transition metal complex exchanged montmorillonites generally occurred as weak adsorbate-adsorbent interactions. The phenol formed weaker interactions with the 2,2'-bipyridyl ligand than those postulated for 2,4,6-trichlorophenol probably due, as discussed in previous chapters and to a certain extent above, to the high adsorbate-solvent interactions between phenol and water.

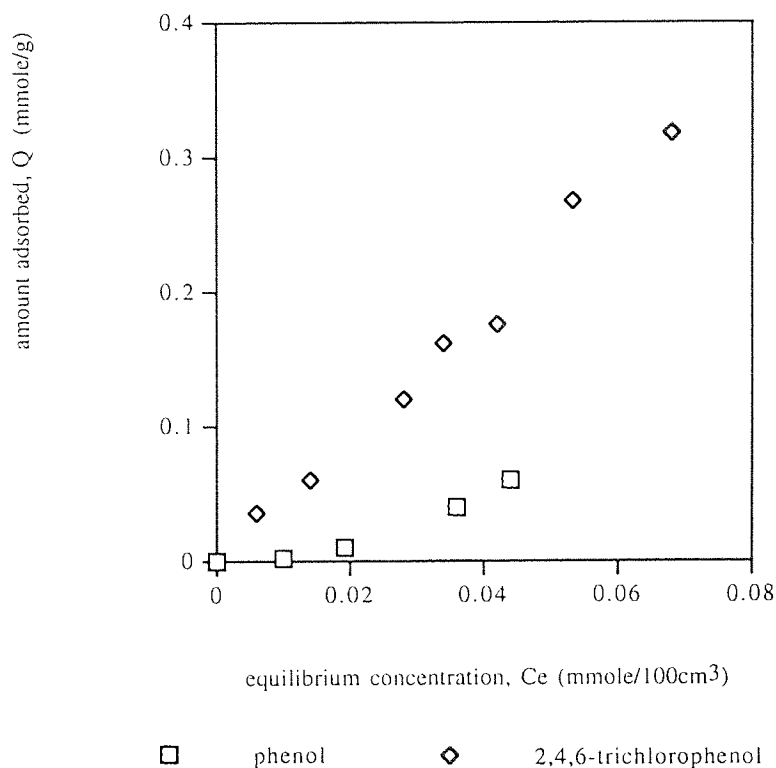


Figure 6.4c Adsorption of phenols by tris 2,2'-bipyridyl cobalt(II) perchlorate exchanged montmorillonite

It is unlikely that the phenol was exposed to any of the silicate layers with the presence of these large cations. This suggests that the exposure of the silicate layer plays little part in the mechanism of phenol adsorption for the transition metal complex exchanged smectites studied here.

Adsorption of 2,4,6-trichlorophenol by tri-(2-pyridyl)amine complexes of iron(II) and cobalt(II) was by weak adsorbate-adsorbent interactions. Even at low concentrations the adsorbate-adsorbent interactions are weak, indicating difficulty in approaching the adsorption sites. The interactions are significantly different to that observed for the 2,2'-bipyridyl iron(II) and Co(III) complex exchanged montmorillonites. This may be due to the complex orientation of the tri-(2-pyridyl)amine ligand compared to the 2,2'-bipyridyl ligand. Terdentate ligands impose structural limitations on complexes. In the case of the tri-(2-pyridyl)amine ligand it may prove more difficult for a significant number of 2,4,6-trichlorophenol molecules to orient and interact with the tri-(2-pyridyl)amine ligand than to orient and interact with the 2,2'-bipyridyl ligand especially if 2,4,6-trichlorophenol orients itself in the pockets of the 2,2'-bipyridyl

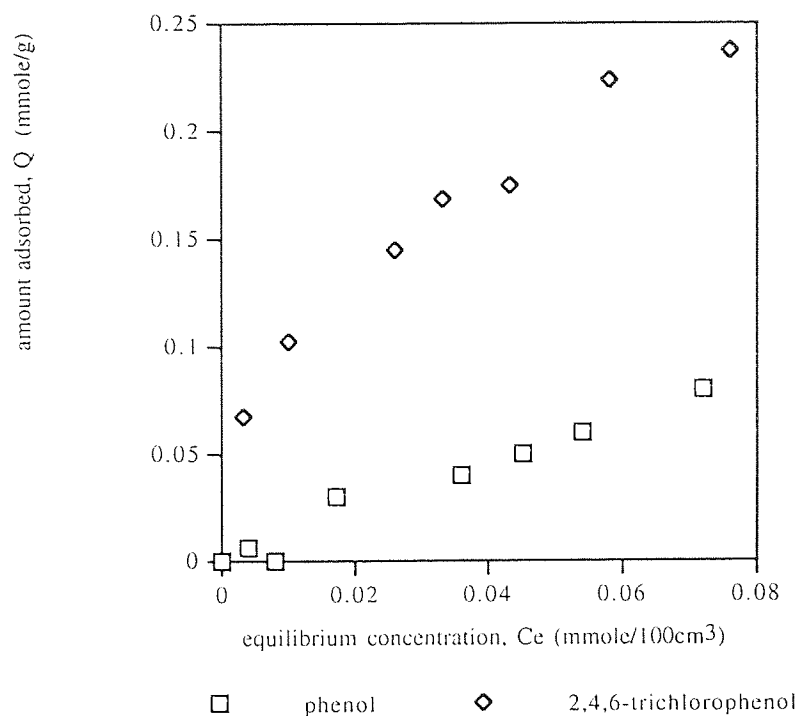


Figure 6.4d Adsorption of phenols by tris 2,2'-bipyridyl cobalt(III) perchlorate exchanged montmorillonite

ligand positions. Such orientation may be impossible with the tri-(2-pyridyl)amine ligands. At best interactions will be directly with one pyridyl group of the tri-(2-pyridyl)amine in a face to face manner, rather than with a possible two ligands in the pockets of the 2,2'-bipyridyl ligands in the 2,2'-bipyridyl transition metal complexes.

Adsorption of phenol by tri-(2-pyridyl)amine complexes of iron (II) and cobalt (II) was undefinable. Adsorption was observed but adsorption isotherm types could not be assigned.

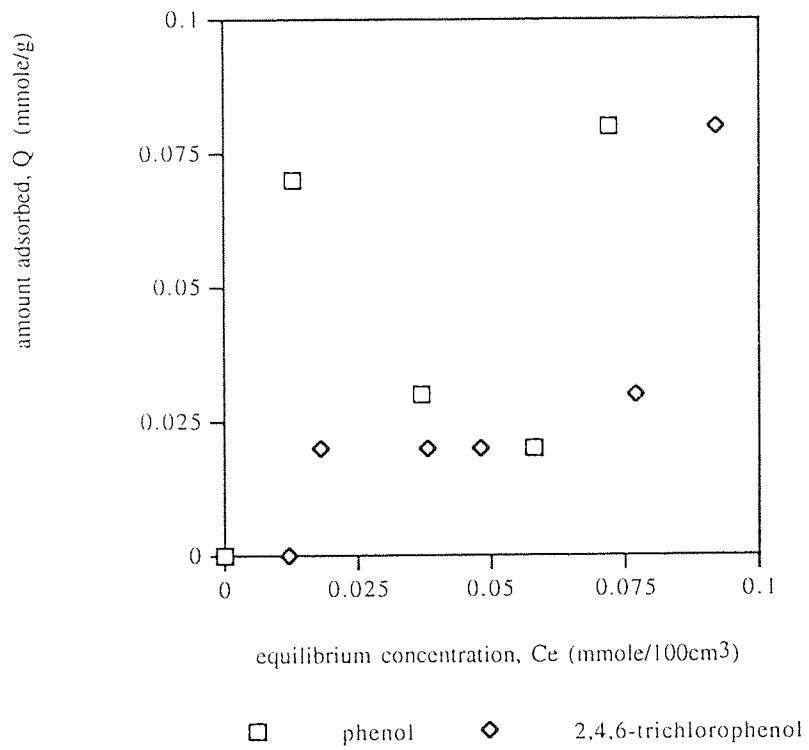


Figure 6.4e Adsorption of phenols by bis tri-(2-pyridyl)amine iron(II) perchlorate exchanged montmorillonite

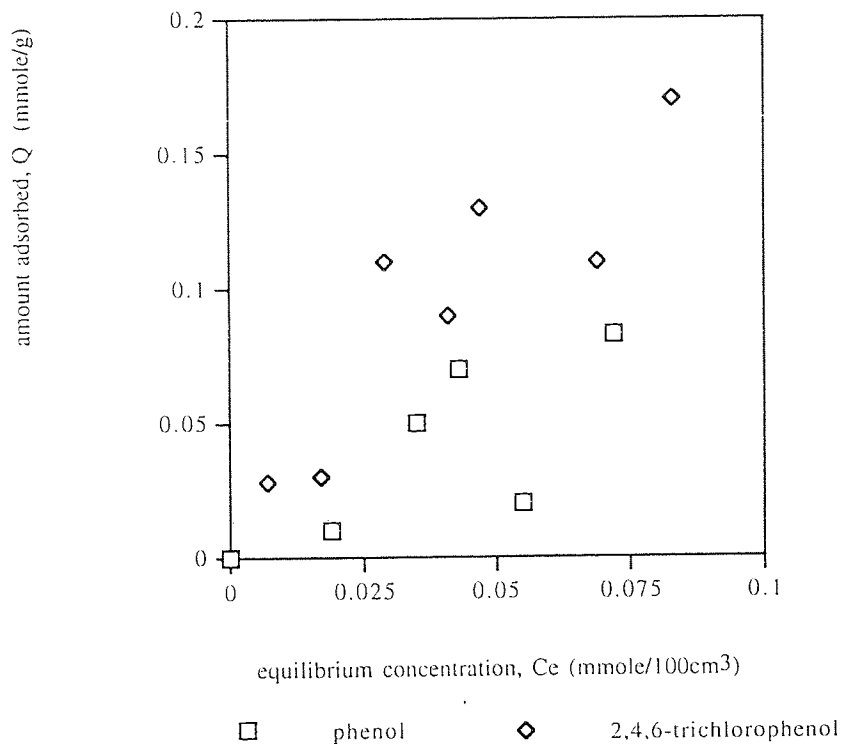


Figure 6.4 f Adsorption of phenols by tri-(2-pyridyl)amine complex of cobalt(II) exchanged montmorillonite

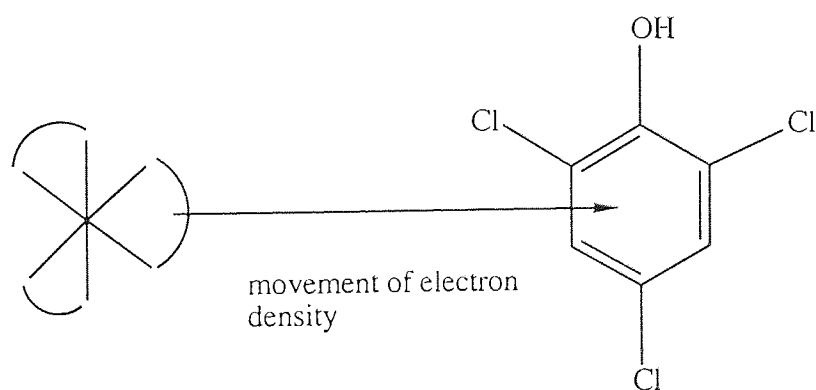


Figure 6.5 A schematic representation of interactions between 2,4,6-trichlorophenol and the 2,2'-bipyridyl iron(II) complex

6.6.2.2 Adsorption by 2,2'-bipyridyl transition metal exchanged laponites

Adsorption isotherms measuring transition metal complex exchanged laponites adsorption of phenol suggested that little if any adsorption occurred for any of the materials. This is quite a surprising result. Characterisation of the exchanged laponites is needed before any explanation of the unexpected results is put forward. Adsorption of 2,4,6-trichlorophenol was not measured.

6.7 Conclusions and Further work

Conclusions

2,2'-bipyridyl complexes of iron(II), copper(II), cobalt(II) and cobalt(III) were successfully exchanged onto montmorillonite and laponite clays. The tri-(2-pyridyl)amine complex of iron(II) was probably exchanged onto montmorillonite clay. The cationic species present in the tri-(2-pyridyl)amine cobalt(II) complex exchanged montmorillonite is proposed to be diaquo{bis[tri-2-pyridylaminecobalt(II)]} with bidentate amine ligands.

In the adsorption of 2,4,6-trichlorophenol by the transition metal complexes, adsorption by $[\text{Fe}(\text{bipy})_3]^{2+}$ exchanged montmorillonite and $[\text{Co}(\text{bipy})_3]^{3+}$ exchanged montmorillonite occurred via strong adsorbate-adsorbent interactions as indicated by Type I isotherms. The interactions are thought to occur via π - π interactions between the aromatic rings of the ligand and the 2,4,6-trichlorophenol. The electron density of the 2,2'-bipyridyl ligand is thought to be increased due to the increased back bonding occurring in the two low-spin, t_{2g}^6 , complexes. Adsorption by $[\text{Cu}(\text{bipy})_2]^{2+}$, $[\text{Co}(\text{bipy})_2]^{2+}$, $[\text{Fe}(\text{tripyam})_2]^{2+}$ and the tri-(2-pyridyl)amine complex cobalt(II) exchanged montmorillonites was via relatively weak interactions as indicated by partitioning or Type V isotherms.

Adsorption isotherms of phenol adsorbed by the transition metal complex exchanged montmorillonites indicated that adsorbate-adsorbent interactions were weak. The isotherms were of types C, V or III for the 2,2'-bipyridyl transition metal complex exchanged montmorillonites and undefinable for the tri-(2-pyridyl)amine transition metal complex exchanged montmorillonites.

A possible reason for the distinction in adsorption efficiencies of the phenol and 2,4,6-trichlorophenol for all adsorbents may be ability for the 2,4,6-trichlorophenol to

interact with the ligands to a greater degree than the phenol due to the ligands being relatively electron rich and the 2,4,6-trichlorophenol being relatively electron deficient. This combined with the low 2,4,6-trichlorophenol-water (adsorbate-solvent) interaction may explain the increased interaction with the adsorbent.

The iron(II) present in the octahedral layers of the montmorillonite clay may be complexed by a simple reaction with 2,2'-bipyridyl. FTNIR analysis shows no change in the absorbance of the peak suggested to be due to the presence of Fe-OH.

Further Work

Thorough characterisation of the transition metal complex exchanged clays by atomic absorption, elemental analysis, UV-Vis diffuse reflectance, ESR; and further XRD and FTNIR analysis. Such characterisations may allow some insight into the differences in adsorption capacities and strengths of interactions observed with these adsorbents.

In order to ascertain whether interactions between 2,4,6-trichlorophenol and $[\text{Fe}(\text{bipy})_2]^{2+}$ exchanged montmorillonite are π - π interactions and result irrespective of adsorbate-solvent interactions further adsorption isotherms should be measured. Studies should include adsorption from different solvents and, study of various chlorinated phenols with comparable water solubility properties but varying electron deficiency properties to 2,4,6-trichlorophenol. Studies of the π - π interactions between the $[\text{Fe}(\text{bipy})_2]^{2+}$ and 2,4,6-trichlorophenol following similar methods to those described in Chapter 7 may help in the elucidation of the mechanisms involved in adsorption.

The random adsorption observed when phenol is exposed to the tri-(2-pyridyl)amine transition metal complex exchanged laponites and montmorillonites should be studied further and compared to adsorption of 2,4,6-trichlorophenol.

The complexation of iron(II) in the octahedral layer of montmorillonite is not surprising but warrants further study both with a view to the characterisation of the new material (XRD, Mössbauer, ESR, UV-Vis diffuse reflectance) and any adsorption characteristics.

Chapter 7

Electron Donor-Acceptor (charge transfer) complexes for the enhancement of adsorbate-adsorbent interactions

7.1 Introduction

7.1.1 Electron Donor-Acceptor (Charge-Transfer) complexes

The term Electron Donor-Acceptor (EDA) complex is used to describe complexes formed by the weak interaction of electron donors with electron acceptors. The electron donor molecule may be a molecule with high electron density by virtue of possessing a lone pair of electrons (an n donor), or a pair of electrons in a p orbital of a double bond or of an aromatic system (a π donor). The electron acceptor molecule may be described as one which is electron deficient due to the presence of electron withdrawing groups and/or possesses a vacant p orbital. The most common organic acceptors are π acceptors. They include aromatic systems containing electron withdrawing groups, for example, quinones and acid anhydrides. The complex is formed by the transfer of electron density from the donor component to the acceptor component. The observed electronic absorptions in addition to the absorption of the components are due to intermolecular charge-transfer transitions. Thus, the presence of an EDA complex may be detected by UV-Vis spectrophotometry. These complexes generally exhibit a spectrum (called a charge transfer spectrum) that is not the same as the sum of the spectra of the two individual molecules. The first excited state of the complex is relatively close in energy to the ground state, this results in a peak in the visible or near-UV region, which often has a high extinction coefficient.

Many EDA complexes are unstable and exist only in solutions in equilibrium with their components, but others are stable solids. In most EDA complexes the donor and acceptor molecules are present in an integral ratio, most often 1:1, but complexes with nonintegral ratios are also known. EDA complexes are often strongly coloured.

The term charge transfer complex is used when it appears that an interaction between two molecules occurs which cannot be attributed only to EDA interactions. The nature of charge-transfer bonding is not clearly understood, but it presumably involves some kind of donor-acceptor interaction. An example of a charge-transfer interaction is that of the complex formed between phenols and quinones¹²³. Although the donor (phenol) has electrons to contribute (both n and π donors are possible), the acceptor

does not have a vacant orbital but has some electron deficiency. The interaction observed is greater than that expected due to dipole-induced-dipole interactions but just how the electrons are accepted is not completely understood¹²⁴.

7.1.2 Application of electron donor-acceptor (charge-transfer) interactions to adsorption of 2,4,6-trichlorophenol

In the adsorption of 2,4,6-trichlorophenol by a number of quaternary ammonium exchanged montmorillonites, the isotherms obtained are typical of weak adsorbate-adsorbent interactions. Adsorption of 2,4,6-trichlorophenol by HDTMA-montmorillonite arises due to partitioning of the 2,4,6-trichlorophenol between the water solvent and the alkyl chains of the adsorbent. Adsorption of 2,4,6-trichlorophenol by HDTMA-laponite is via a strong adsorbate-adsorbent interaction which manifests itself as a Type I isotherm. These results were discussed in Chapter 3. Thus, there is still some room for the enhancement of 2,4,6-trichlorophenol - exchanged montmorillonite interactions. The introduction of conditions suitable for EDA interactions between synthesised quaternary ammonium exchanged montmorillonites and 2,4,6-trichlorophenol may well enhance the adsorbate-adsorbent interactions.

It is probable that 2,4,6-trichlorophenol has electron acceptor properties due to the presence of three strongly electron withdrawing chlorine groups on the ring. The interaction between the acceptor molecule, 2,4,6-trichlorophenol, and a donor molecule such as 1,3,5-trimethoxybenzene, may result in the formation of an EDA complex due to the transfer of electron density from the electron rich molecule to the electron deficient 2,4,6-trichlorophenol, see Figure 7.1. Such interactions are used as a test for the presence of aromatic hydrocarbons where picric acid (2,4,6-trinitrophenol) is the acceptor molecule. A positive result for the test is the formation of strong yellow coloured solutions or solids arising from the formation of the EDA complex.

Synthesis of quaternary ammonium compounds that could both participate in exchange reactions with montmorillonite clay, and have electron donor properties such that EDA complexes with 2,4,6-trichlorophenol could be formed, are attempted and the results discussed in this chapter. In Chapter 6 it was found that adsorption of 2,4,6-trichlorophenol by the $[\text{Fe}(\text{bipy})_3]^{2+}$ and $[\text{Co}(\text{bipy})_3]^{3+}$ exchanged montmorillonites occurred via strong adsorbate-adsorbent interactions. These interactions were thought to occur via π - π interactions between the aromatic rings of the ligand and the 2,4,6-trichlorophenol. The objective of this chapter was specifically to synthesise quaternary

ammonium compounds sufficiently electron rich to participate in EDA interactions with 2,4,6-trichlorophenol. Preliminary studies were to involve the synthesis of quaternary ammonium compounds containing the electron rich benzene ring. It was intended that the electron density of the benzene ring be further enhanced by substituting groups such as methyl and methoxy groups in the ortho and para positions on the benzene ring. This increase in electron density may facilitate EDA interactions with 2,4,6-trichlorophenol and enhance adsorbate-adsorbent interactions.

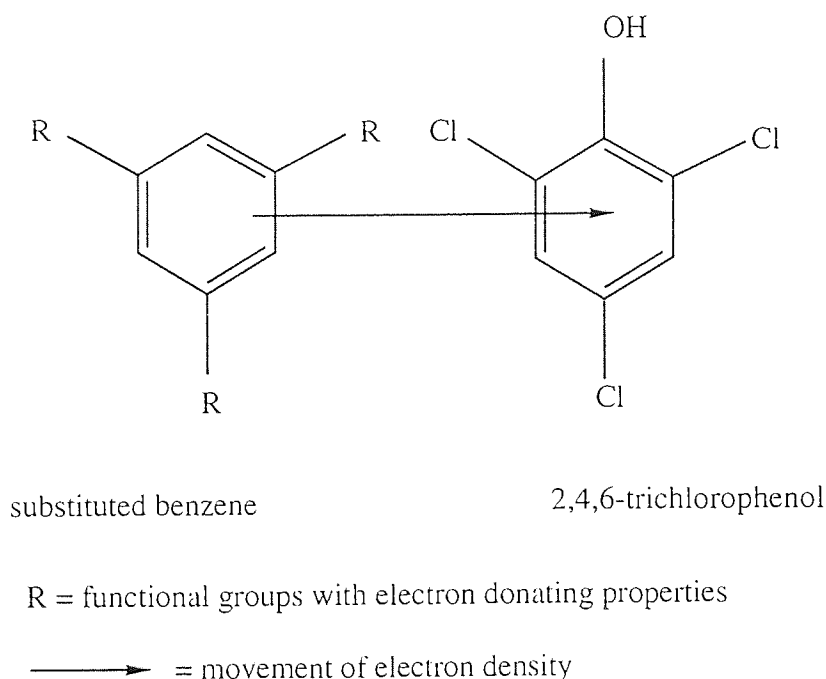


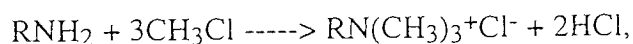
Figure 7.1 Electron Donor-Acceptor interactions between 2,4,6-trichlorophenol and substituted benzenes

7.2 Synthesis

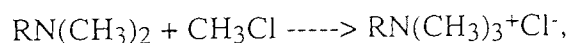
7.2.1 The synthesis of quaternary ammonium compounds

The industrial preparation of quaternary ammonium compounds can be carried out in four main ways¹²⁵:

(i) exhaustive alkylation of primary or secondary fatty amines,

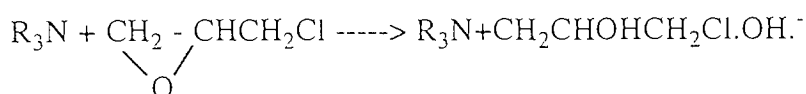


(ii) alkylation of a tertiary fatty amine,



(iii) alkylation of a low molecular weight tertiary amine (trimethylamine, pyridine) with a fatty halide,

(iv) treating tertiary amines or their salts with an epoxide in the presence of water



The largest tonnage of quaternary ammonium compounds is obtained via the exhaustive methylation process using a primary or secondary fatty amine and methyl chloride to yield $\text{RN}^+(\text{CH}_3)_3\text{Cl}^-$ and $\text{R}_2\text{N}^+(\text{CH}_3)_2\text{Cl}^-$ respectively. The reaction is usually carried out in the presence of a base to neutralise the HCl formed during the reaction. Optimum yields are obtained when the reaction is carried out under neutral conditions. The reaction is usually carried out in a polar medium, at temperatures varying between 65 °C and 95 °C.

For safety and equipment purposes it was decided that synthesis based on synthetic route (iii) would be undertaken, this method does not result in the production of HCl. This allowed use of a tertiary amine (triethylamine) which is a liquid at room temperature, removing the expense and difficulty of using gaseous methyl chloride. Thus, various methyl and methoxy benzyl chloride derivatives were reacted with triethylamine as described below to synthesise triethyl benzyl ammonium chlorides with good electron donor properties.

7.2.2 Synthesis of triethyl-2,4,6-trimethylbenzylammonium chloride

Quaternary ammonium compounds based on alkylated benzyl derivatives can be synthesised industrially by reacting a tertiary amine with benzyl chloride, or its derivatives, at 60 - 80 °C, in the presence of water¹²⁶. This reaction method was used as a basis to prepare triethyl-2,4,6-trimethylbenzylammonium chloride.

2,4,6-trimethylbenzyl chloride (0.1 mole, 16.87 g) and triethylamine (0.1 mole, 14 cm³) were mixed and heated, with stirring, until the temperature reached 80 °C. The mixture was maintained at this temperature for 30 minutes or until the mixture became too stiff to stir. 50 g of cold water was then added and the mixture was refluxed for 16 hrs. The water was then distilled off to remove unreacted organic material. The contents of the flask were allowed to cool, and were then filtered and washed with a small amount of water.

Yield = 37%. Melting point = 242.5 °C. Appearance = white crystalline solid.

Elemental analysis found: C = 52.3%, H = 11.7%, N = 10.1%

Elemental analysis expected: C = 71.2%, H = 10.4%, N = 5.19%.

Elemental analysis data suggest that an amine salt had been produced with formula $(C_2H_5)_3N.HCl$, this is a white crystalline solid, with a C, H, N ratio of 52.4%, 11.6%, 10.2% respectively, and a melting point of 261 °C (dec) which fits well with that found for the compound synthesised.

Benzyl alkyl ammonium compounds normally give yellow coloured solutions, have low melting points and are difficult to obtain in pure solid form. These factors coupled with the carbon depleted elemental analysis suggested that the desired compound was not formed.

The 1H and ^{13}C NMR and FTIR spectrum contained no peaks that could be attributed to the presence of an aromatic ring, and the FTIR showed N-H bonds were present.

A repeat of the experiment gave a duplicate of the results described above.

An alternative method for synthesis of such compounds is that as described above except iso-propanol, instead of water, is used as the solvent. This method was employed using 30 cm³ iso-propanol and the solvent was removed after the reaction using a rotary evaporator.

Yield = 30%. Appearance = cream/yellow, resinous mass, with excess iso-propanol present. By mass balance the product was calculated to contain 55% product, 45% alcohol. The product was found to be slightly soluble in water and foamed considerably, a property typical of quaternary ammonium compounds.

Due to the presence of iso-propanol, satisfactory elemental analysis and melting point data were not obtainable.

Though the FTIR of the product shows some differences compared with the FTIR of the reactants, these data alone do not suggest the desired product has been synthesised, since FTIR is not useful in diagnosing the presence of tertiary amino- or quaternary ammonium groups. In distinguishing between the 2,4,6-trimethylbenzyl chloride and the product, the differences observable in the FTIR would be firstly a more complex spectrum in the C-H absorption regions and the absence of the absorption band due to C-Cl in the spectrum of the product. Both of these features are apparent in the FTIR of

the product. In the C-H absorption regions 1470-1430 cm^{-1} and 1390-1370 cm^{-1} the spectrum is more complex and the absence of a medium peak at 556 cm^{-1} arises from the fission of the C-Cl bond during the quaternisation reaction.

^1H NMR and ^{13}C NMR analyses were carried out. The product chemical shifts were as follows:

^1H , δ ppm, I (= intensities)

triplet/multiplet (C6); 1.01 (I = 11.85), 0.99 (I = 23.14), 0.96 (I = 13.04), 0.94 (I = 5.91), 0.91 (I = 2.71)

quadruplet (C5); 2.77 (I = 3.44); 2.75 (I = 10.78); 2.72 (I = 11.01), 2.69 (I = 3.63)

singlet (C9) 1.83 (I = 9.77)

singlet (C10) 1.94 (I = 18.01)

singlet (C11) 4.03 (I = 6.07)

singlet (C3) 6.55 (I = 2.54)

complex multiplet (benzene ring) ; 6.45 (I = 1.73), 6.42 (I = 4.51), 6.39 (I = 0.32), 6.35 (I = 0.47), 6.33 (I = 0.72)

^{13}C , δ ppm, I (= intensities)

(C6) 19.2 (I = 2.90); (C5) 53.4 (I = -3.13); (C9) 19.8 (I = 2.80); (C10) 20.7 (I = 1.93); (C11) 40.1 (I = -0.89); (C3) 129.6 (I = 2.67); (C4) 130.6 (I = -0.50); (C1) 136.0 (I = -0.69); (C2) 136.4 (I = -1.27).

Figure 7.2 shows the molecule and carbon/hydrogen assignments.

The results of both NMR spectra suggest that the final, recrystallised compound, triethyl-2,4,6-trimethylbenzylammonium chloride, was synthesised and contained the starting material 2,4,6-trimethylbenzyl chloride, iso-propanol and triethylammonium salt.

7.2.3 Synthesis of triethyl-2,4,6-trimethylbenzylammonium iodide

Due to the high concentration of iso-propanol present on crystallisation, a short investigation of the conversion of the triethyl-2,4,6-trimethylbenzylammonium chloride to the iodide was carried out. In theory, the iodide will be less soluble in iso-propanol than the chloride and enable isolation of the triethyl-2,4,6-trimethylbenzylammonium iodide. This involved mixing the chloride with excess

sodium iodide and iso-propanol without heating. This resulted in a white suspension in sun yellow solution. The white suspension was filtered and the solvent left to evaporate off slowly in the refrigerator. The FTIR of the resulting iodide showed the main peaks of the quaternary ammonium compound, but also contained a significant amount of iso-propanol. Thus no advantage was gained in synthesising the iodide.

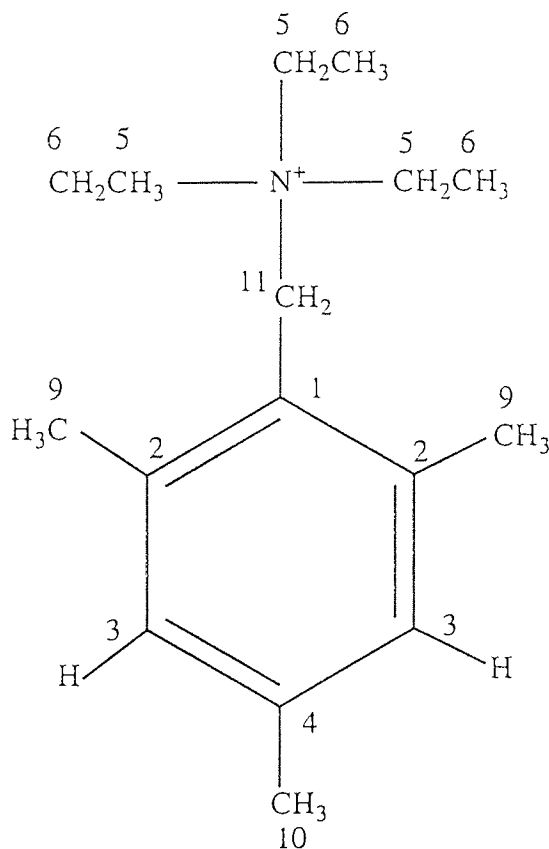


Figure 7.2 ^1H and ^{13}C NMR assignments for triethyl-2,4,6-trimethylbenzylammonium chloride

7.2.4 Synthesis of triethyl-4-methoxybenzylammonium chloride

Synthesis of triethyl-4-methoxybenzylammonium chloride was carried out as described in Section 7.2.2. 4-methoxybenzyl chloride (0.1 mole, 13.6 cm³) and triethylamine (0.1 mole, 14 cm³) were mixed and heated, with stirring, until the temperature reached 100 °C. The mixture was maintained at this temperature for 30 minutes or until the mixture became too stiff to stir. 65 cm³ iso-propanol was then added and the mixture was refluxed for 16 hrs. The solvent and unreacted organic material was then removed using a rotary evaporator. The contents of the flask were allowed to cool and evaporation allowed to continue slowly in the refrigerator over one week.

Yield = 53%. Appearance = yellow, resinous mass, with solvent of crystallisation still present. By mass balance the product was calculated to contain 80% product, 20% alcohol. As triethyl-2,4,6-trimethylbenzylammonium chloride, the product was found to be slightly soluble in water and foamed considerably.

While all the peaks expected are present, the FTIR spectra alone do not suggest the triethyl-4-methoxybenzylammonium chloride has been synthesised. Analysis of the spectra is complicated due to the difficulty in assigning the position of the C-Cl bond of the starting material.

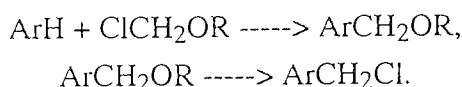
^1H and ^{13}C NMR analysis showed that little triethyl-4-methoxybenzylammonium chloride was synthesised in the reaction described above. The major product was found to be 4-methoxybenzyl alcohol, with starting materials and solvent also present.

7.2.5 Attempted synthesis of triethyl-2,4,6-trimethoxybenzylammonium-smectites

Methoxy groups are known to possess good electron donor properties. It was intended that the effect of three methoxy groups on a benzene ring be investigated with regard to donor properties and forming EDA complexes with 2,4,6-trichlorophenol.

2,4,6-trimethoxybenzyl halides are not readily available from chemical manufactures, it was therefore decided to attempt to synthesise the 2,4,6-trimethoxybenzyl halide precursor and react the precursor with triethylamine as described in Sections 7.2.2 and 7.2.4.

Conversion of benzene and methylbenzene derivatives to benzyl halides is known to occur via chloromethylation. This involves the use of chlorinated ethers. Such a reaction was first carried out by Sommelet²⁷. By treating benzene with α -monohalogenoalkyl ethers in the presence of AlCl_3 in CS_2 ; a mixture of benzyl chloride and benzyl ether was obtained. The ether is thought to be the primary product and is said to be readily converted to the chloromethyl derivative under the influence of HCl which is liberated during the reaction. The reaction was suggested to progress as follows:



Other catalysts used for this reaction are ZnCl_2 , SbCl_5 and SnCl_4 . SnCl_4 was found to be the most suitable catalyst.

Vavon and Bolle¹²⁸ suggested that aromatic hydrocarbons could be chloromethylated under homogeneous conditions, namely by treatment with monochloromethyl ether in acetic acid without a catalyst. However, under these conditions the reaction is much slower than in the presence of a catalyst. The substituted benzyl acetate formed is readily cleaved by the HCl or the ether.

The synthesis of 2,4,6-trimethoxybenzyl chloride is not recorded in the literature. The closest compound undergoing chloromethylation by this method was 2,4,6-trimethylbenzene in the synthesis of 2,4,6-trimethylbenzyl chloride.

The latter method¹²⁸ was investigated and slightly modified by Schonne et al.¹²⁹. This method was used for the first attempt at synthesis. The method involves placing 1,3,5-trimethoxybenzene (0.14 mole, 23.8 g) and chloromethyl methyl ether (0.16 mole, 13 cm³) in acetic acid (0.7 mole, 42 cm³) in a 200 cm³ round bottom flask, heating to 80 - 85 °C and refluxing for 18 hrs, the product is then distilled directly. 80% yields have been achieved in the synthesis of 2,4,6-trimethylbenzyl chloride.

Within half an hour of the start of the reaction procedure outlined above, a purple, heaving mass was obtained. The mixture was allowed to cool and left overnight. The mixture cooled as a glassy purple mass and was unchanged after one hour of heating.

The intense colour and viscosity of the product suggest that peroxides were formed which lead to some degree of polymerisation of the 1,3,5-trimethoxybenzene.

The above reaction was repeated under argon. The reactants were distilled where necessary, placed in the reaction vessel and refluxed for approximately 3 hrs, at this point the reaction mixture turned deep purple and on leaving overnight a red, liquid product resulted. Vacuum distillation of the liquid turned the solution purple. Three fractions were extracted:

- (i) an orange liquid boiling at 85 °C (under reduced pressure),
- (ii) a pale pink liquid boiling at 60 - 63 °C
- (iii) solid purple mass - non-boiling.

Both liquid fractions had an acetic acid odour, these were rotary evaporated to remove ether and after cooling were subjected to FTIR analysis which showed the presence of

acetic acid predominantly, with a low concentration of unreacted 1,3,5-trimethoxybenzene.

A third attempt at synthesis of the precursor was carried out after the method carried out by Summers¹³⁰ in the synthesis of 2,4,6-trimethylbenzylchloride. In this method chloromethyl methyl ether (freshly distilled) was dissolved in acetic acid and the mixture allowed to stand in a reaction flask, protected by a drying tube, for 48 hrs at 25 - 30 °C. It was then heated at 65 °C for 0.5 hrs (hydrogen chloride evolved). To this "aged" solution there was now added mesitylene (1,3,5-trimethylbenzene) and the mixture stirred at 60 - 70 °C for 4 hrs. Distillation under reduced pressure yielded up to 37% product and up to 72% polymer.

The preparation of 2,4,6-trimethoxybenzene was attempted using the method of Summers¹³⁰. Chloromethyl methyl ether (0.15 mole, 12.1 g), acetic acid (75 cm³), and 1,3,5-trimethoxybenzene (0.15 moles, 25.2 g) were used. The reaction mixture turned purple within 0.5 hr of heating.

A fourth attempt was made at the reaction. This was carried out as Summers¹³⁰ but without heating, the mixture remained yellow for 4 hrs. However, this would need to undergo heating to carry out distillation. On heating a purple mass resulted.

The purple glassy product resulting from this reaction, is produced as a result of a polymerisation reaction of 1,3,5-trimethoxybenzene with chloromethyl methyl ether. The reaction probably progresses in a similar way to that of the reaction of phenol with methanal to produce phenol-formaldehyde resins, of which the most common is bakelite, see Figure 7.3.

The mechanism for the reaction with 1,3,5-trimethoxybenzene is more complicated in this case due to the presence of three methoxy groups which will be render the benzene ring more susceptible to attack. Figure 7.4 shows the possible mechanisms.

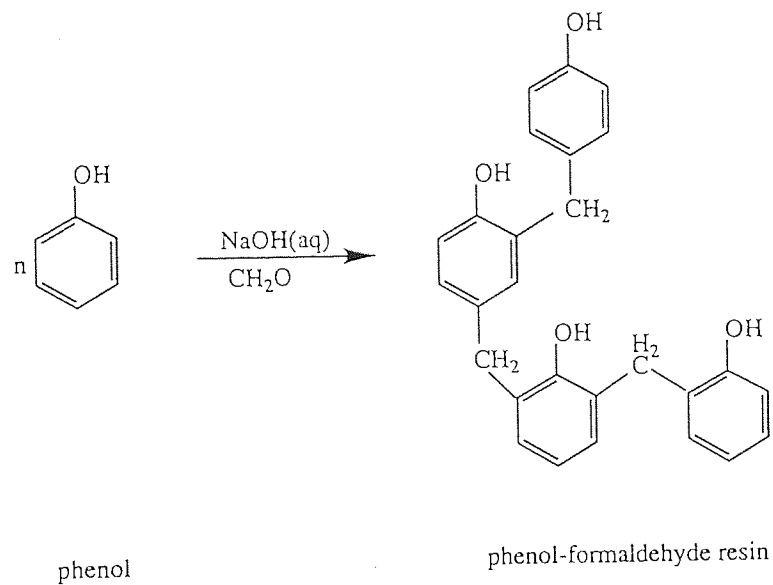


Figure 7.3 The synthesis of phenol-formaldehyde resin

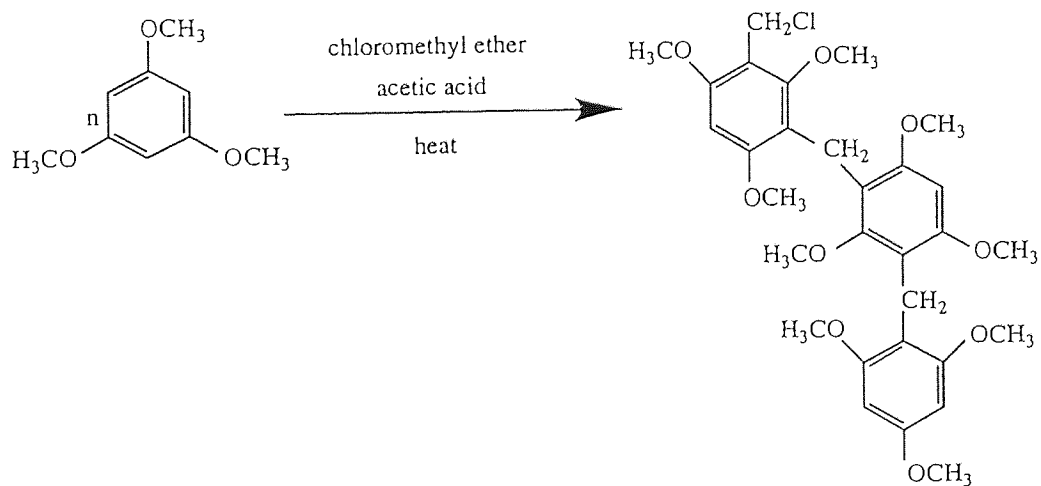


Figure 7.4 Possible mechanism in the synthesis of 1,3,5-trimethoxybenzene oligomer formed on reaction with chloromethyl methyl ether.

7.3 Electron Donor-Acceptor complexes between 2,4,6-trichlorophenol and triethyl-2,4,6-trimethylbenzylammonium chloride

Successful synthesis of triethyl-2,4,6-trimethylbenzylammonium chloride (Section 7.2.2) led to the study of EDA complex formation with 2,4,6-trichlorophenol. The results are detailed below in Section 7.3.1 and 7.3.2.

7.3.1 Ultraviolet/Visible solution spectrophotometric investigations

Formation of an EDA complex between the acceptor molecule (2,4,6-trichlorophenol) and the donor molecule (triethyl-2,4,6-trimethylbenzylammonium chloride) was attempted by making up solutions, with iso-propanol as the solvent, of each compound and mixing the solutions in varying proportions to firstly obtain the charge transfer spectrum and secondly the ratio in which the EDA or charge transfer complex is formed. The Table 7.1 below shows the solutions used.

Table 7.1 Experiments for the UV study of EDA complexes formed between 2,4,6-trichlorophenol and triethyl-2,4,6-trimethylbenzylammonium chloride

Experiment	0.001M donor cm ³	0.001M acceptor cm ³
1	50	0
2	40	10
3	30	20
4	20	30
5	10	40
6	0	50

Colour changes were not observed on mixing the components.

Each experimental mixture was analysed by UV-Vis spectrophotometry in the region 700-190 nm. The spectra arising from each of these mixtures were simply additions of the two components of the mixtures.

UV studies suggest that EDA complexes were not formed between 2,4,6-trichlorophenol and triethyl-2,4,6-trimethylbenzylammonium chloride.

7.3.2 ^1H NMR spectroscopic investigations

Though UV-Vis studies suggested that no complex between the acceptor molecule (2,4,6-trichlorophenol) and donor molecule (triethyl-2,4,6-trimethylbenzylammonium chloride) was present, the system was studied by ^1H NMR. The complex formed can be detected by determining the change in the chemical environment of a hydrogen atom, of either the donor or acceptor, by the controlled addition of one to the other. The complex, if formed, will have a resonance unique to itself.

Solutions were made up as described in Table 7.2. The solvent used was CCl_4 as this does not mask any region of the ^1H NMR and all the materials used in this experiment are CCl_4 soluble. Cyclohexane was also examined as a possible solvent but the 2,4,6-trichlorophenol was found to be insoluble.

Table 7.2 Experiments for the preliminary ^1H NMR study of EDA complexes formed between 2,4,6-trichlorophenol and triethyl-2,4,6-trimethylbenzylammonium chloride

Experiment	Donor mole fraction	Acceptor mole fraction	CCl_4 mole fraction
1	0.024	/	0.976
2	0.024	0.218	0.757
3	0.048	0.194	0.757
4	0.073	0.170	0.757

These samples were shaken overnight on a mechanical shaker and submitted directly for ^1H NMR analysis. The results of the ^1H NMR analysis were too complex to extract meaningful results.

A study of EDA complex formation between the 4-methoxybenzyl alcohol mixture, resulting from the synthesis described in Section 7.2.3, and 2,4,6-trichlorophenol was

also attempted but, as for the triethyl-2,4,6-trimethylbenzylammonium chloride/2,4,6-trichlorophenol solutions, the mixtures proved too complex to extract meaningful results.

7.4 Exchange of triethyl-2,4,6-trimethylbenzylammonium chloride onto montmorillonite

Having successfully synthesised triethyl-2,4,6-trimethylbenzylammonium chloride the ability of the salt to undergo exchange reactions was examined.

Bentonite (2.3 g) was dispersed in 67 cm³ of a 3:2 iso-propanol/water solution by placing on a mechanical shaker overnight. The mixture was allowed to settle for a short time to achieve maximum montmorillonite concentration in the dispersion and decanted quickly. The slurry was heated and kept at 60 °C for 30 minutes. The triethyl-2,4,6-trimethylbenzylammonium chloride was added (to satisfy the c.e.c. of montmorillonite) to the minimum amount of iso-propanol/water solution to form a thick paste. The paste was added to the montmorillonite solution and the mixture was stirred at 60 °C for an hour. The solution was then cooled, filtered, washed with 500 cm³ iso-propanol/water solution, the filtrate and the washings kept for analysis, air dried, ground and stored.

Analysis by Na⁺ atomic absorption showed that 85% exchange occurred.

The basal spacing was found to increase from 12.62 Å (montmorillonite) to a range of basal spacings between 15.8 Å and 13.8 Å (triethyl-2,4,6-trimethylbenzylammonium-montmorillonite). The basal spacings quoted were the two equal intensity maxima of the broad peaks obtained. Figure 7.5 shows the diffractogram. This increase in basal spacing is comparable with and lies either side of that found when trimethylphenylammonium is exchanged with montmorillonite (TMPA-montmorillonite = 14.24 Å, Chapter 3). The higher of the two values, 15.8 Å, may correspond to the exchange of the triethyl-2,4,6-trimethylbenzylammonium chloride into the interlayer region. The magnitude of the increase in basal spacing suggests that the ammonium cations are arranged in a monolayer in the interlayer region. The triethyl-2,4,6-trimethylbenzylammonium cation lies with the benzene ring flat or slightly angled in the interlamellar region, parallel to the silicate layers of the montmorillonite. The lower basal spacing value, 13.8 Å, may correspond to exchange of triethylamine salt present as impurity in the triethyl-2,4,6-trimethylbenzylammonium chloride. The detection of a range of basal spacings suggests that the impurity of the cation has led to exchange

and intercalation of various species. Thus as well as exchange of the triethyl-2,4,6-trimethylbenzylammonium cation, and the triethylamine salt, intercalation or sorption of any starting material present, products of side reactions and of iso-propanol may also have occurred.

7.5 Adsorption of 2,4,6-trichlorophenol and phenol by triethyl-2,4,6-trimethylbenzylammonium-montmorillonite

Though the primary focus of this chapter was the study of EDA complexes between 2,4,6-trichlorophenol and triethyl benzyl ammonium chlorides, adsorption of phenol was also measured. Unsuccessful synthesis of triethyl-4-methoxybenzylammonium chloride and triethyl-2,4,6-trimethoxybenzylammonium chloride resulted in only the triethyl-2,4,6-trimethylbenzylammonium being studied with respect to exchange and adsorption experiments.

The results in Section 7.3 suggested that the EDA complexes were not formed between the triethyl-2,4,6-trimethylbenzylammonium chloride and 2,4,6-trichlorophenol, but adsorption was measured nonetheless.

Adsorption isotherms were measured as described in Section 3.6

The adsorption isotherms obtained for triethyl-2,4,6-trimethylbenzylammonium-montmorillonite are shown in Figure 7.6. It can be seen that triethyl-2,4,6-trimethylbenzylammonium-montmorillonite adsorbs 2,4,6-trichlorophenol by a partitioning process which is characterised by linearity of the adsorption isotherm. In the studies described in Chapter 3, the adsorption of 2,4,6-trichlorophenol by TMPA-montmorillonite was not found to occur, adsorption of 2,4,6-trichlorophenol appeared to be enhanced by the presence of long chained alkylammonium compounds. This was thought to be due to 2,4,6-trichlorophenol preferentially interacting with the organic media over the aqueous media. Here it would appear that adsorption of 2,4,6-trichlorophenol has occurred via interactions with the benzene ring of the cation in the interlayer region, which does not occur when TMPA-smectite is used as an adsorbent. This suggests that benzene - benzene interactions are occurring, which may or may not be due to EDA interactions.

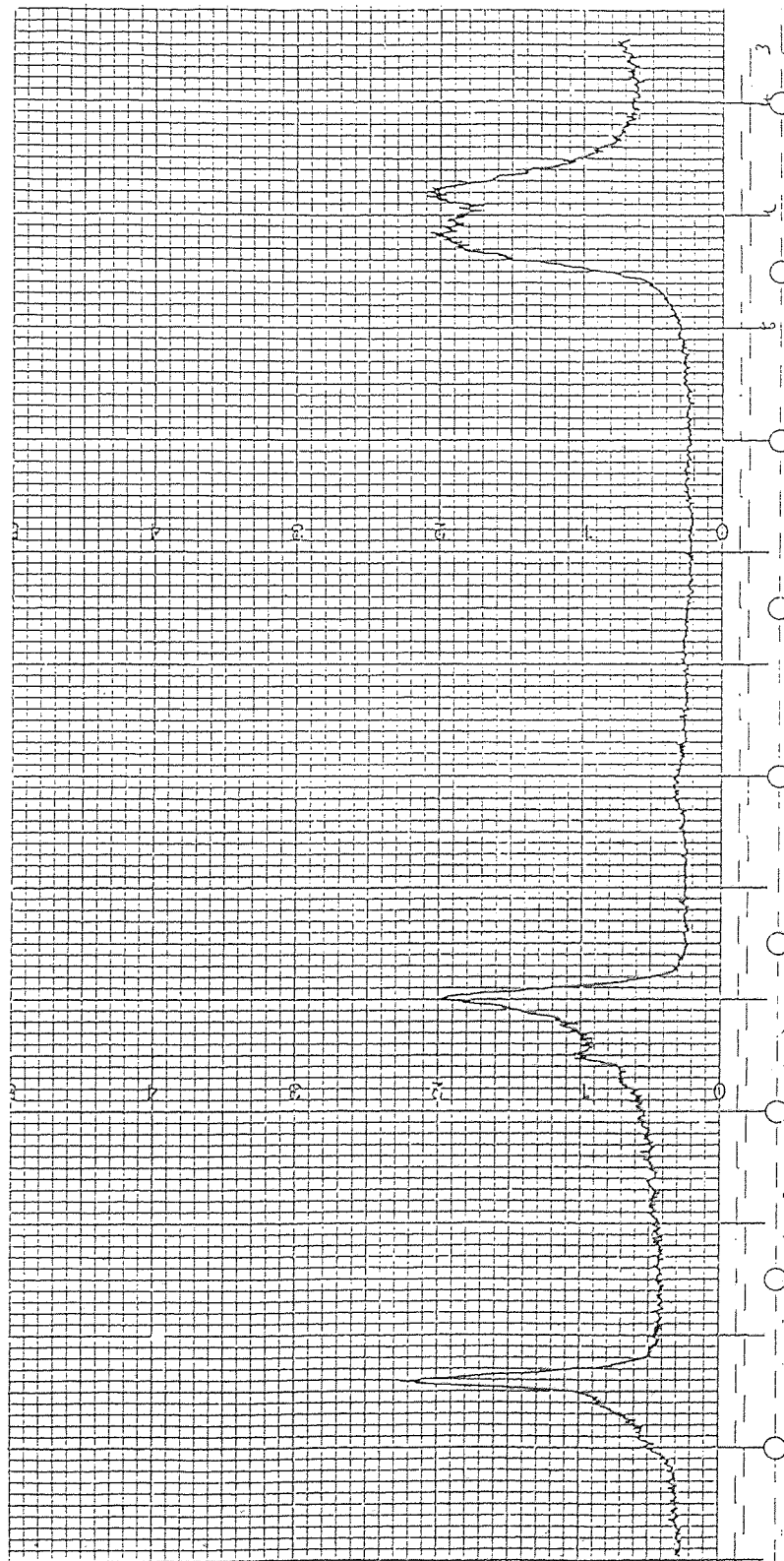


Figure 7.5 XRD spectrum of triethyl-2,4,6-trimethylbenzylammonium exchanged montmorillonite

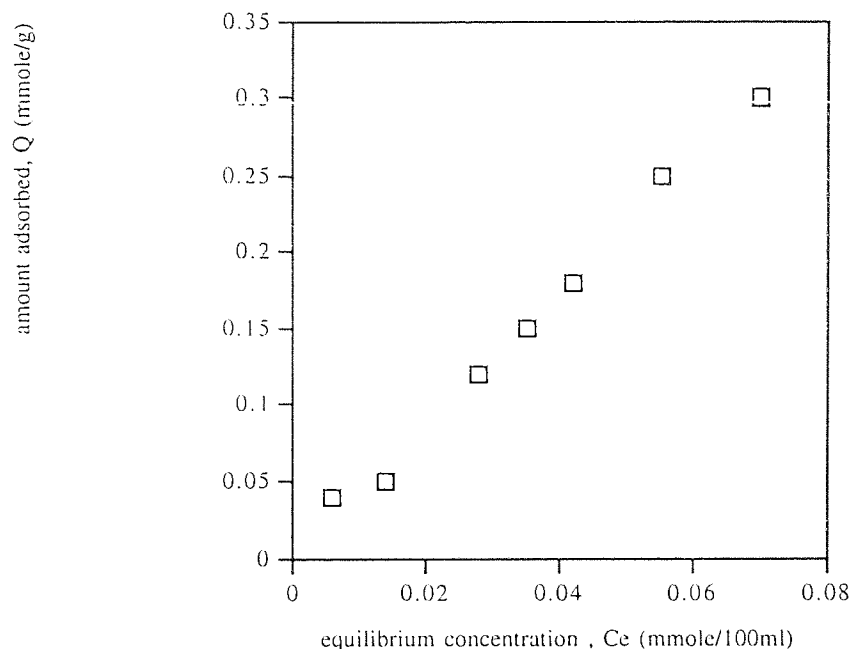


Figure 7.6 Adsorption of 2,4,6-trichlorophenol by triethyl-2,4,6-trimethylbenzylammonium-montmorillonite

When the TMPA cation is present in the interlayer region of the clay, part of the silicate layer is exposed. This exposure may repel molecules such as 2,4,6-trichlorophenol from the exchanged clay. The presence of three ethyl groups and the larger 2,4,6-trimethylbenzyl group in the triethyl-2,4,6-trimethylbenzyl-ammonium exchanged clay may shield the 2,4,6-trichlorophenol from the silicate layer, facilitating adsorption.

Phenol is not adsorbed by triethyl-2,4,6-trimethylbenzylammonium-montmorillonite. Phenol is very soluble in water and it is possible that the triethyl-2,4,6-trimethylbenzylammonium-montmorillonite is too hydrophobic to allow for interaction with the phenol, thus phenol preferentially partitions itself into the aqueous phase. If the adsorption had some dependency on EDA or benzene - benzene interactions it may well be that the phenol molecule is not sufficiently depleted of electrons to enable an interaction to occur. Another possibility relates to the presence of two different cations in the interlayer region - triethyl-2,4,6-trimethylbenzylammonium and triethylammonium cations (Section 7.4). It has been shown that phenol is adsorbed by Quats with short alkyl chains (Chapter 3) and it is therefore surprising that no phenol adsorption (due to the presence of triethylammonium cations) is observed. It is possible that, as observed in Chapter 3, interactions between the cations has lead to high adsorbent-adsorbent, Quat-Quat, interactions and little phenol-adsorbent interaction.

Thus 2,4,6-trichlorophenol can, contrary to previous observations, be adsorbed by compact quaternary ammonium compounds from aqueous media via benzene - benzene interactions where the size of the Quat is thought to be large enough to shield the 2,4,6-trichlorophenol from silicate layer. In the case of phenol adsorption, adsorbate-solvent or adsorbent-adsorbent interactions appear to compete with benzene-benzene, adsorbate-adsorbent, interactions such that phenol is not adsorbed by the exchanged montmorillonite.

7.6 Conclusions and Further work

Conclusions

Triethyl-2,4,6-trimethylbenzylammonium chloride can be prepared by the reaction of 2,4,6-trimethylbenzyl chloride with triethylamine when iso-propanol is used as the solvent. The impurities are 2,4,6-trimethylbenzyl chloride and amine salt which are not removed on recrystallisation. Excess iso-propanol solvent is present.

Triethyl-4-methoxybenzylammonium chloride was unable to be synthesised via methods using the tertiary amine route.

Synthesis of 2,4,6-trimethoxybenzyl chloride as a precursor to synthesis of triethyl-2,4,6-trimethoxybenzylammonium chloride was not successful. The presence of three methoxy groups on the benzene ring renders the starting material, 1,3,5-trimethoxybenzene, susceptible to attack and it is possible that the glassy, purple product obtained was an oligomer resulting from polymerisation via peroxides.

Evidence of triethyl-2,4,6-trimethylbenzylammonium chloride/2,4,6-trichlorophenol EDA complex formation was not observed by UV studies in iso-propanol or by ^1H NMR studies in CCl_4 . Both cyclohexane and carbon tetrachloride proved to be unsuitable solvents for the study of EDA complex formation between the triethyl-2,4,6-trimethylbenzylammonium chloride and 2,4,6-trichlorophenol.

Studies of EDA complex formation between 4-methoxybenzyl alcohol and 2,4,6-trichlorophenol were attempted but meaningful results were not obtained.

Triethyl-2,4,6-trimethylbenzylammonium chloride took part in the exchange reactions with montmorillonite, the percentage exchange being 85%. The basal spacings

suggest that the cations lie with the benzene ring flat in the interlayer region and are arranged in a monolayer. The range of basal spacings observed may have resulted from exchange with the triethyl-2,4,6-trimethylbenzylammonium chloride and the triethylammonium salt. Sorption or intercalation of impurities present may have occurred.

In the adsorption of phenol and 2,4,6-trichlorophenol by triethyl-2,4,6-trimethylbenzylammonium-montmorillonite, only 2,4,6-trichlorophenol was adsorbed. 2,4,6-trichlorophenol adsorption is facilitated by silicate surface coverage and benzene - benzene interactions which may or may not be EDA interactions. The combination of the presence of the substituted benzene ring, ethyl chains and relatively high clay layer charge was thought to reduce silicate surface exposure and result in adsorption.

Further work

In the synthesis of triethyl-2,4,6-trimethylbenzylammonium chloride, purification of the product may have been improved by recrystallisation from benzene, in which the triethyl-2,4,6-trimethylbenzylammonium chloride is assumed to be insoluble.

The alternative methods for synthesis of quaternary ammonium compounds listed in Section 7.2.1 may prove more successful in the synthesis of triethyl-4-methoxybenzylammonium chloride.

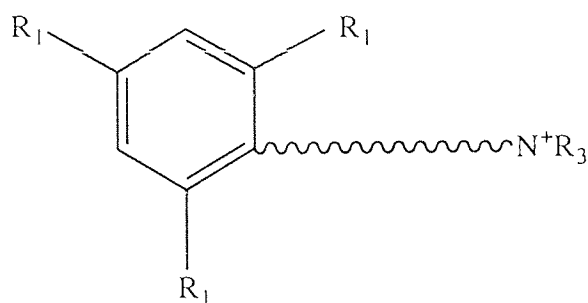
Both cyclohexane and carbon tetrachloride proved to be unsuitable solvents for the ^1H NMR study of EDA complex formation between the triethyl-2,4,6-trimethylbenzylammonium chloride and 2,4,6-trichlorophenol. For further studies a suitable solvent must be sought.

In the reaction of triethyl-2,4,6-trimethylbenzylammonium chloride with montmorillonite clay the $d(001)$ low angle reflection was broad due to exchange with triethyl-2,4,6-trimethylbenzylammonium chloride and triethylammonium salt; and sorption of the other components of the reaction product. Improved purification methods should limit the extent of such exchange and sorption occurring.

Triethyl-2,4,6-trimethylbenzylammonium exchanged montmorillonite adsorbed 2,4,6-trichlorophenol via a partitioning process but did not adsorb phenol, thus adsorption properties are unexpectedly similar to hexadecyltrimethylammonium exchanged montmorillonite, rather than to trimethylphenylammonium exchanged montmorillonite.

Detailed studies of the adsorption properties of this adsorbent will show whether the selectivity of this adsorbent is significantly different and superior to other quaternary ammonium compounds.

Other types of compounds that may participate in exchange reactions with clays and form EDA complexes with 2,4,6-trichlorophenol include compounds containing alkyl benzene derivatives and alkyl pyridine derivatives including 4,4'-bipyridyl amine. It is possible that the combination of a long alkyl chain with an good electron donor group on the end of the chain may further enhance adsorption of 2,4,6-trichlorophenol. An example of this is shown in Figure 7.7



R₁ = Me, MeO

Figure 7.7 Diagram representing structures of compounds that may further facilitate 2,4,6-trichlorophenol adsorption

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