CHEMICAL MODIFICATION OF SMECTITE CLAYS

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Today, speciality use organoclays are being developed for an increasingly large number of specific applications. Many of these, including use in cosmetics, polishes, greases and paints, require that the material be free from abrasive impurities so that the product retains a smooth 'feel'. The traditional 'wet' method preparation of organoclays inherently removes abrasives naturally present in the parent mineral clay, but it is time-consuming and expensive. The primary objective of this thesis was to explore the alternative 'dry' method (which is both quicker and cheaper but which provides no refining of the parent clay) as a process, and to examine the nature of the organoclays produced, for the production of a wide range of commercially usable organophilic clays in a facile way.

Natural Wyoming bentonite contains two quite different types of silicate surface (that of the clay mineral montmorillonite and that of a quartz impurity) that may interact with the cationic surfactant added in the 'dry' process production of organoclays. However, it is oil shale, and not the quartz, that is chiefly responsible for the abrasive nature of the material, although air refinement in combination with the controlled milling of the bentonite as a pretreatment may offer a route to its removal.

Ion exchange of Wyoming bentonite with a long chain quaternary ammonium salt using the 'dry' process affords a partially exchanged, 69-78%, organoclay, with a monolayer formation of ammonium ions in the interlayer. Excess ion pairs are sorbed on the silicate surfaces of both the clay mineral and the quartz impurity phases. Such surface sorption is enhanced by the presence of very finely divided, super paramagnetic, Fe_2O_3 or Fe(O)(OH) contaminating the surfaces of the major mineral components. The sorbed material is labile to washing, and induces a measurable shielding of the ^{29}Si nuclei in both clay and quartz phases in the MAS NMR experiment, due to an anisotropic magnetic susceptibility effect. XRD data for humidified samples reveal the interlamellar regions to be strongly hydrophobic, with the by-product sodium chloride being expelled to the external surfaces.

Many organic cations will exchange onto a clay. The tetracationic cyclophane, and multipurpose receptor, cyclobis(paraquat-*p*-phenylene) undergoes ion exchange onto Wyoming bentonite to form a pillared clay with a very regular gallery height. The major plane of the cyclophane is normal to the silicate surfaces, thus allowing the cavity to remain available for complexation. A series of group VI substituted *o*-dimethoxybenzenes were introduced, and shown to participate in host/guest interactions with the cyclophane. Evidence is given which suggests that the binding of the host structure to a clay substrate offers advantages, not only of transportability and usability but of stability, to the charge-transfer complex which may prove useful in a variety of commercial applications.

The fundamental relationship between particle size, cation exchange capacity and chemical composition of clays was also examined. For Wyoming bentonite the extent of isomorphous substitution increases with decreasing particle size, causing the CEC to similarly increase, although the isomorphous substitution site: edge site ratio remains invarient throughout the particle size range studied.

Keywords: Bentonite, Organoclays, Host/guest, Cyclobis(paraquat-*p*-phenylene), Alkyl quaternary ammonium salts

To Dawn

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Chapter One

AN INTRODUCTION TO
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Chapter One

AN INTRODUCTION TO CLAYS AND CLAY MINERALS

1.1 Clays and Clay Minerals

Clay is many things to many people. It is an abundant natural raw material, and it has an amazing variety of properties and uses, many of which will be discussed later in the chapter. However, the term 'clay' is somewhat ambiguous, each definition being orientational to the discipline in which it is used.

In ancient times clays were included under the rather wider term of 'earths', defined in 1546 as [1] "a simple mineral body which can be worked in the hands when it is moistened and from which mud can be made when it is saturated with water". Today clays are studied by geologists, agronomists, chemists, engineers and others, and although each would offer a definition influenced by their own area of interest, there is fundamentally much in common among the materials visualized. Even so, the term 'clay' is still used in at least three distinct ways.

In the first instance, it may be used simply for any fine-grained, natural, earthy, argillaceous material.[2] When used this way, the term includes clay, shale, or argillite, and some argillaceous soils.

Secondly, 'clay' may be used specifically as a rock term. Again, the definition here must be fairly general, because of the wide variety of materials that may still compose it, but in this usage clay is now composed largely of a group of crystalline minerals known as the clay minerals. Many definitions state the plasticity of clays when wet, and the American Ceramic Society definition [3] is typical. It states that "clay is a fine-grained rock which, when suitably crushed and pulverised, becomes plastic when wet, leather-hard when dried and on firing is converted to a permanent rock-like mass".

Further complications arise from the use of 'clay' in a third way, this time as a specific particle size term. However, these complications may be alleviated by talking instead of the 'clay fraction', that fraction of the material the particles of which are below a specific equivalent spherical diameter (e.s.d.). The size generally agreed upon as the upper limit of e.s.d. for the clay fraction of soils is 2μm but many inconsistencies still persist in the published literature.

It is clear from the above discussion that when defining clay in general, one must be aware of its plasticity, small particle size, and ability to harden on firing, and that chemical composition is too variable a property to be of use here. However, in the following pages of this work 'natural clays' will be taken to be heterogeneous mixtures of finely divided minerals, such as quartz, feldspars, calcite, pyrites, etc, with the most colloidally active components being one or more species of the clay minerals.

In this instance then, it is not adequate to define a clay mineral simply as "any mineral which occurs in a clay", and instead the definition offered by Mackenzie [4] will be taken. It states that "crystalline clay minerals are hydrated silicates with layer or chain lattices consisting of sheets of silica tetrahedra arranged in hexagonal form, condensed with octahedral sheets; they are usually of small particle size".

1.2 The Silicate Minerals

1.2.1 The siloxane linkage

The silicate minerals have been intimately connected with the evolution of mankind from prehistoric times. The name itself is derived from the Latin 'silex', meaning flint, and serves as a reminder of the simple tools developed in paleolithic times, some 500,000 years ago, and of the increasingly sophisticated knives and arrowheads of later ages.[5]

The earth's crustal rocks and their breakdown products, soils, sands, silts, and clays, are composed almost entirely of silicate minerals. This predominance of silicates and aluminosilicates is reflected in the abundance of O (45.5 wt %), Si (27.2%), and Al (8.3%), which are the commonest elements in the crust. Together, silicon and oxygen comprise three out of every four atoms available near the surface of the globe. Despite the great profusion of structural types, and the widely varying stoichiometries, which are present among the silicate minerals, it is possible to classify them on the basis of a few simple principles. Almost invariably silicon is coordinated tetrahedrally by four oxygen atoms, and these $\{SiO_4\}^{4-}$ units can exist either as discrete structural entities, or can combine by corner sharing of oxygen atoms into larger units. Clearly, the Si-O-Si linkage, the siloxane linkage [6] is of fundamental importance.

A comparison of the energies of formation of a range of cation-oxygen bonds likely to be present in clay minerals shows that no other M-O bond is as strong as Si-O, see Table 1.1. Al-O bonds are the next strongest, while the bonds between the other metal ions and oxygen are much weaker. It is the strength of the Si-O bond that is responsible for the marked resistance to weathering that is characteristic of the majority of the silicate minerals. However, the energy requirements of weathering may be considerably less than the energy requirements for formation, as the weakest bonds are subject first to attack. Consequently, it is incorrect to assume that all the silicate minerals are extremely resistant to weathering, and indeed many weather rapidly.[7]

Cation	Energy of formation (kg cal / mol)
Si^{4+} (discrete tetrahedra)	3142
Si^{4+} (framework)	3110
Al^{3+} (framework)	1878
Al^{3+} (non-framework)	1793
Fe^{3+}	919
Mg^{2+}	912
H^{+}	515
Na^{+}	322

Table 1.1 Energies of formation of cation-oxygen bonds
(from Huggins and Sun [8])

It is possible to evaluate the approximate percentage of ionic character in a bond between two atoms by considering the difference in electronegativity between them, their dipole moments, and bond lengths.[9] It is interesting to note that the Si-O bond has approximately 50% ionic character, hence both ionic and covalent effects must be considered when investigating the silicate minerals.

1.2.2 The silicate minerals

As discussed previously, the fundamental units of silicate minerals are $\{SiO_4\}^{4-}$ tetrahedra. These can be joined together in several ways, and it is upon the arrangement of the tetrahedra within the structure that the characterization of silicates is based, see Table 1.2.

	Shared vertex	Description	Structural unit	Examples
Neosilicates	0	discrete tetrahedra	$[SiO_4]^{4-}$	Garnet, Zircon Olivine, Topaz
Sorosilicates	1 or 2	discrete isolated groups	$[Si_2O_7]^{6-}$ $[Si_3O_{10}]^{8-}$	Thortveitite, Kinoite
Cyclosilicates	2	closed rings	$[SiO_3]_n{}^{2n-}$	Emerald, Beryl
Inosilicates	2	continuous chains or ribbons	$[SiO_3]_n{}^{2n-}$ $[Si_4O_{11}]_n{}^{6n-}$	Pyroxenes, Amphiboles
Phyllosilicates	3	continuous sheets	$[Si_2O_5]_n{}^{2n-}$	Clay minerals
Tectosilicates	4	continuous 3D framework	$[SiO_2]_n$	Silica, Zeolites Feldspars

Table 1.2 The six groups of silicates recognized on the basis of the arrangement of the SiO_4 tetrahedra in their structure

1.2.2.1 Neosilicates

The minerals in this group are composed of single tetrahedra linked together by external cations, which may be three, four, six, eight or twelve coordinate with oxygen, so that the overall structure is electrically neutral. Important members include zircon, $ZrSiO_4$, olivine, $(Mg, Fe, Mn)_2SiO_4$, and the garnets, $[M_3{}^{II}\ M_2{}^{III}\ (SiO_4)_3]$ where M^{II} may be Ca Mg or Fe, and M^{III} is Al, Cr or Fe.

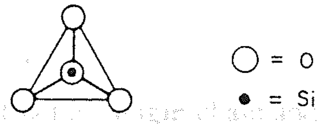

Figure 1.1 Diagrammatic representation of the neosilicate structure

1.2.2.2 Sorosilicates

Two or more linked tetrahedra formed by sharing a common vertex, introducing a siloxane linkage, are the basis for the structure of this group. Disilicates, containing the discrete $\{Si_2O_7\}^{6-}$ unit, are rare, but structures having three tetrahedra, discrete $\{Si_3O_{10}\}^{8-}$ units, are more so. Thortveitite, $Sc_2Si_2O_7$, is an example of a disilicate and kinoite, $Cu_2Ca_2Si_3O_{10}.2H_2O$, is one of the few trisilicates. The first tetrasilicate, $Ag_{10}Si_4O_{13}$, was not synthesized until 1979.[10]

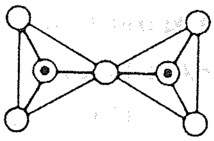

Figure 1.2 Diagrammatic representation of the sorosilicate structure.

1.2.2.3 Cyclosilicates

The structure of this group is characterized by three, four, six or eight membered rings of silica tetrahedra, linked together by cations such as Na, Mg and/or Fe, although three or six membered rings are the most common. Examples of such cyclic silicates include the mineral benitoite, $BaTiSi_3O_9$, and beryl, $Be_3Al_2Si_6O_{18}$. Interestingly, emerald has essentially the same composition as beryl, the only difference between them being that emerald also contains approximately two percent chromium, the source of its green colour.

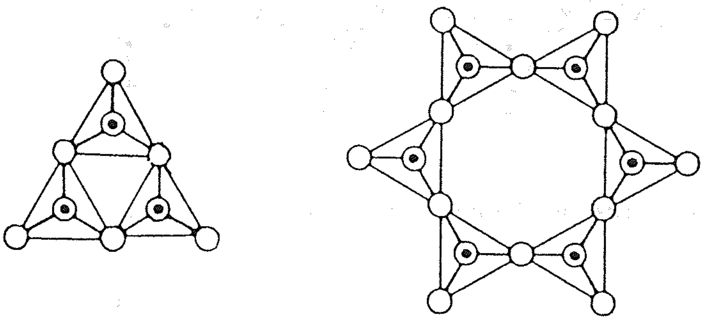

Figure 1.3 Diagrammatic representation of the cyclosilicate structure

1.2.2.4 Inosilicates

This group has in its structure single-chain and double-chain silica tetrahedra linked together by Ca, Mg and/or Fe. Such structures are capable of indefinite extension in the form of parallel chains, and are particularly prevalent in nature. Many differing conformations may be adopted by the linked tetrahedra, but the most common one is a repeat after every second tetrahedron, (2T), as exemplified by the pyroxene minerals enstatite, $Mg_2Si_2O_6$, and spodumene, $LiAlSi_2O_6$.

Alternatively two identical chains may polymerize further by linking laterally to form double chains or ribbons. Chains with a 2T repeat unit would have to combine by sharing an oxygen atom in every alternate tetrahedron, forming a

$\{Si_4O_{11}\}^{6-}$ ribbon. This is the structure of the amphiboles or asbestos minerals, perhaps the best known of the fibrous silicates, but examples of infinite one-dimensional structures consisting of linked triple, quadruple and sextuple chains have also recently been discovered.[11]

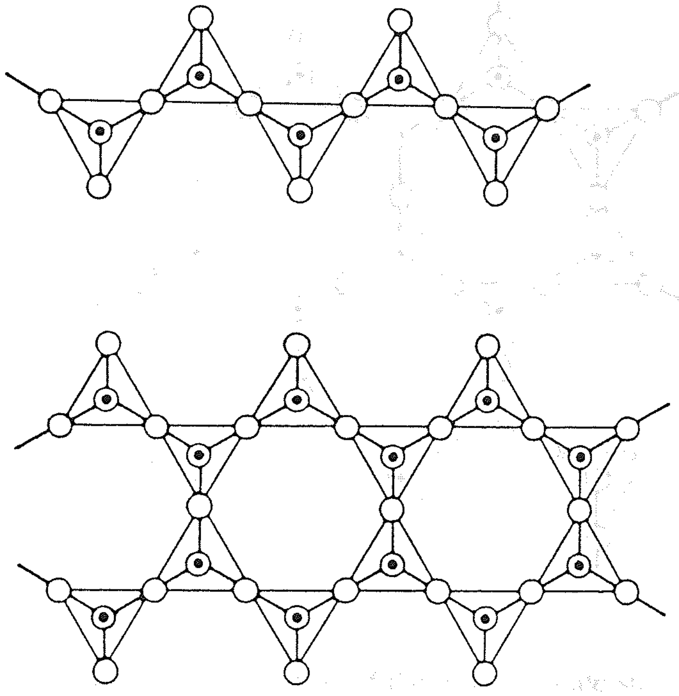

Figure 1.4 Diagrammatic representation of the inosilicate structure

1.2.2.5 Phyllosilicates

The simplest structures within this group can be thought of as being formed either by extension of the horizontal cross-linking of the 2T chains of the inosilicates, or by the planar condensation of the $\{Si_6O_{18}\}^{12-}$ rings of the cyclosilicates. The result is a planar network, or layer structure, of composition $\{Si_2O_5\}^{2-}$ in which three of the four oxygen atoms in each tetrahedron are vertex shared, and the fourth, apical, oxygen is located at right angles to the sheet. This structure is capable of indefinite extension in two dimensions, by further condensation of $\{Si_6O_{18}\}^{12-}$ rings, or extension into a third dimension, via sharing of the apical oxygen between pairs of tetrahedra, to form double layers of SiO_2 stoichiometry.

Layered structures can also occur when the apical oxygen links with a cation other than silicon to form a layer above the silicate sheet. This is the case when double layers are built up by the interleaving of layers of gibbsite, $Al(OH)_3$, or brucite, $Mg(OH)_2$, which have similar unit dimensions and can thus share oxygen atoms with the silicate network. Repetition of the process on the other side of the gibbsite or brucite layers leads to the formation of three layer minerals. Condensation in this manner affords the clay minerals, an important class of phyllosilicates that will be discussed in greater detail later in this chapter.

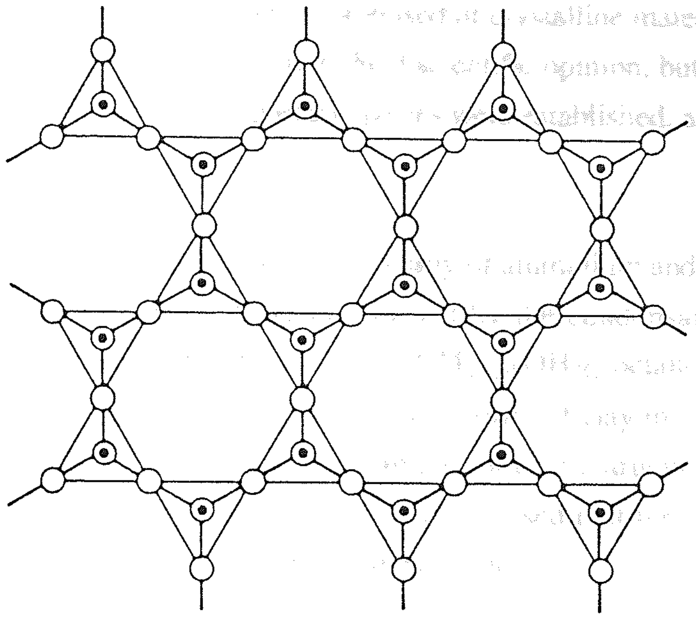

Figure 1.5 Diagrammatic representation of the phyllosilicate structure

1.2.2.6 Tectosilicates

The minerals of this group are considered solid solution minerals with a framework of silica tetrahedra capable of extension in three dimensions. This structure represents the end of the series, with each oxygen atom shared by two tetrahedra, and is obviously epitomized by the various forms of SiO_2 itself, tridymite, cristobalite, and quartz.

Within this framework, up to half of the silicon atoms may be replaced by aluminium, thus requiring the addition of further cations for charge balance. These ions, usually Na, K, and/or Ca, sit in the cavities within the framework, and the composition becomes that of a feldspar. Feldspars are the most abundant of all minerals, and comprise approximately sixty percent of the earth's crust. Most can be classified chemically as members of the ternary system albite-orthoclase-anorthite, $NaAlSi_3O_8$ - $KAlSi_3O_8$ - $CaAl_2Si_2O_8$. Zeolites too are based on the $\{AlSiO_4\}_n^{n-}$ framework structure, but the lattice is more open than that of the feldspars, with larger cavities and a network of channels being present.

1.3 Structure of the Clay Minerals

The successful classification of clays only became possible with the application of X-Ray powder Diffraction techniques to the elucidation of their structure, in the early 1920's. Within a short space of time evidence had been accumulated to indicate that clays, in the main, were composed of crystalline materials. At the time this conclusion ran counter to generally held scientific opinion, but in the 1930's the crystal structures of the more important species were established, and the concept of the 'clay mineral' was born.[12]

Generally, they are hydrous silicates, principally of aluminium and magnesium, and principally based on composite layers formed by the condensation of sheets of linked SiO_4 tetrahedra with those of linked $M_{2-3}(OH)_6$ octahedra, where M is either a divalent or trivalent cation. The vast majority of clay minerals thus belong to the phyllosilicate group,[13] although examples of chain-structured clay minerals can also be found.[14] However it should be recognised that the converse, that all phyllosilicates are clay minerals, is by no means true.

Condensation of the layers in different proportions leads to the subdivision of the clay minerals into several main groups. The most important of these are: kandites (kaolinite group); illites (mica group); smectites (montmorillonite group); vermiculites and chlorites. Condensation in a 1:1 proportion gives rise to the dimorphic minerals that constitute the kandites, with a general formula of $M_{2-3}Si_2O_5(OH)_4$. Similarly, the trimorphic clays are formed by a 2:1 condensation, with the octahedral sheet being sandwiched between two sheets of inward-pointing tetrahedra, giving a layer formula of $M_{2-3}Si_4O_{10}(OH)_2$. This is the mica-type structure and is characteristic of the illites, smectites and vermiculites. Differences in chemical composition, swelling properties, and the magnitude of the layer charge, are also used to classify clays into one or other of these groups. Finally, tetramorphic types also occur in which trimorphic units alternate with $M(OH)_{2-3}$ sheets of octahedrally coordinated M^{2+} or M^{3+} ions, giving rise to the chlorites. A schematic representation of these structures, each of which will be discussed more fully in the following sections, is given in figure 1.6.

There is scope in all these structures for isomorphous substitution, that is, for replacement of tetrahedral Si^{4+} and/or octahedral $M^{2+/3+}$ by cations of similar ionic radius but different, usually lower, valency. If substitution is simply on a one for one basis, the resultant layers gain a net, usually negative, charge. When this occurs the positive charge deficiency is for the most part balanced by sorption of extraneous cations, which may or may not be exchangeable.

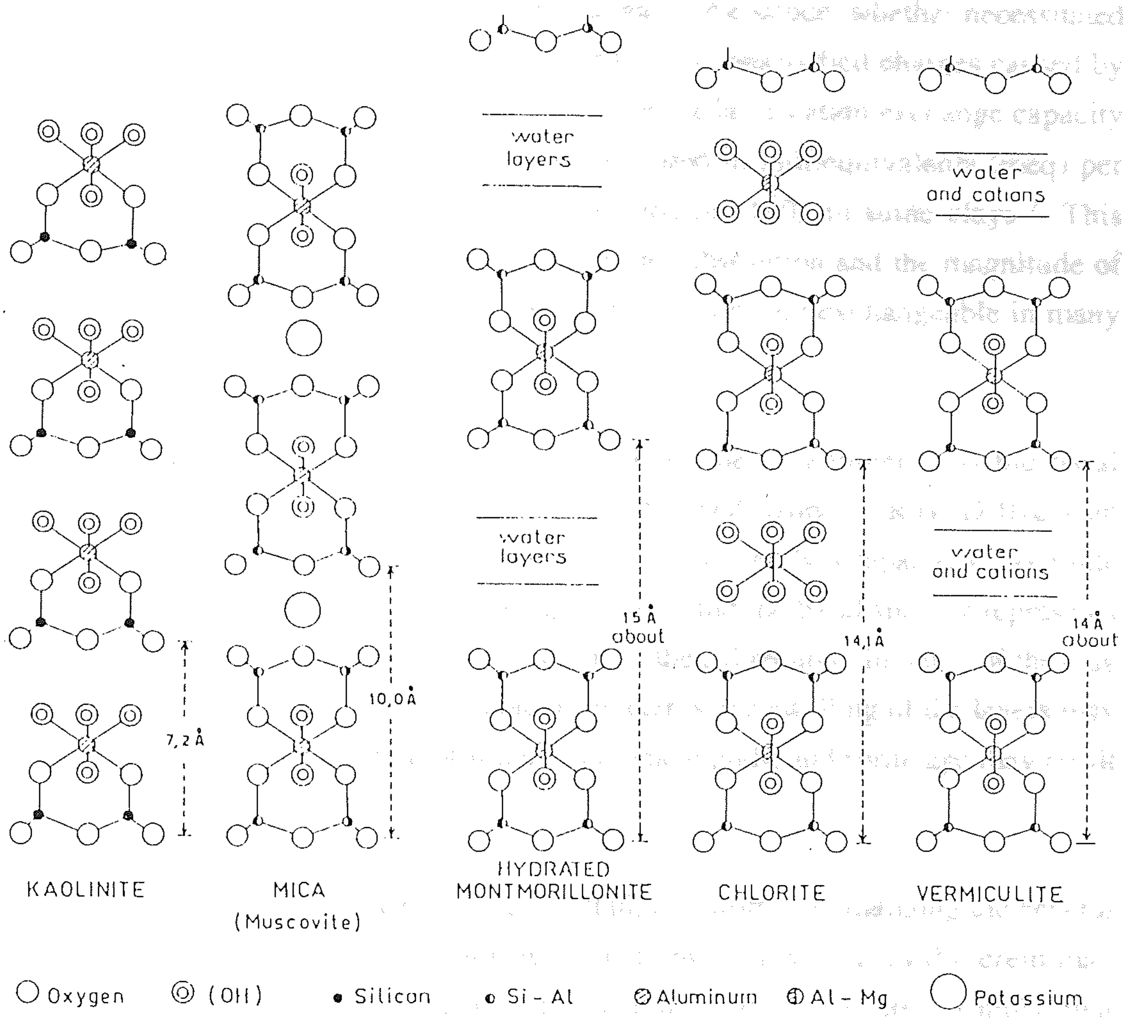

Figure 1.6 Schematic representation of the structures of the main groups of clay minerals (after Brindley [13])

However, one for one substitution is not the only form allowable. Three Mg^{2+} ions may replace two Al^{3+} ions in the octahedral layer of a sheet silicate and the structure will remain electrically neutral without the need for external cations. This is possible because only two-thirds of the octahedral sites need to be filled initially, if the cation is Al^{3+}, in order to obtain electrical neutrality. Minerals of this type, with two-thirds occupancy of the octahedral sites, such as gibbsite, $Al_2(OH)_6$, are termed dioctahedral, and have site vacancies within the lattice available to accommodate extra cations. Minerals such as brucite, $Mg_3(OH)_6$, with all the octahedral sites filled, are termed trioctahedral, have no vacant sites, and must charge balance by the use of external cations. Substitution of Al^{3+} ions for Si^{4+}

ions within the tetrahedral layer is also common, and also leads to a positive charge deficiency within the lattice.

The presence in the structure of cations external to the lattice, whether necessitated by isomorphous substitution or to a lesser extent by unsatisfied charges caused by broken bonds at the crystal edge, is the cause of the large cation exchange capacity (C.E.C.) displayed by many clays. It is measured in milliequivalents (meq) per 100g of clay, and may be as much as 150 meq per 100g in some clays.[2] This though does not always reflect the extent of the substitution and the magnitude of the layer charge, as far from all the extraneous cations are exchangeable in many clays, especially the micas.

One final property used to identify and classify the clay minerals is the basal spacing. This is the d(001) reflection obtained from X-Ray Diffraction experiments. The sheet silicate structure of the clay minerals is capable of indefinite extension along the a and b crystallographic axes, and the basal spacing represents the repeat distance between successive sheets in the c direction. In many of the clay minerals the basal spacing is a variable parameter, since swelling of the layers may occur through the intercalation of water or organic liquids, and shrinkage may result from dehydration.

Before going on to discuss each group in detail, it is worth summarizing the general structure of the clay minerals, not least so as terms that will be used therein may first be precisely defined. Clay particles, as mined, are aggregates of individual flakes held together, not by a cementitious substance, but by the interlocking of the flakes alone. The flakes are composed of tiny crystal platelets, normally stacked together face-to-face. A single platelet is one unit layer, and consists of an octahedral sheet and one or two tetrahedral sheets.

1.3.1 The kandite group

The kandite group of clay minerals are characterized by their 1:1 type layer structure. Probably the best known mineral of this group is kaolinite, the main constituent of kaolin, or china clay. The name probably originates from the mountain Kao-ling in China, where this product was extracted for centuries and used in the manufacture of chinese porcelain.[15] Kaolinite has the general formula $Al_4Si_4O_{10}(OH)_8$, and is shown schematically in figure 1.7.

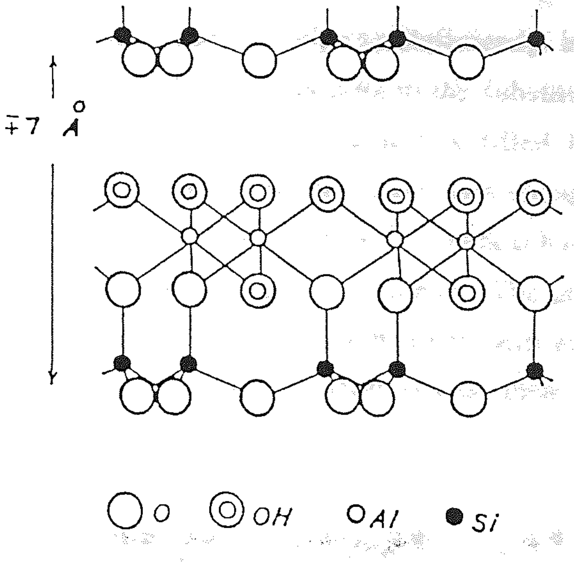

Figure 1.7 Schematic representation of the structure of kaolinite (after Grüner [16])

Electron microscopy shows generally well defined hexagonal crystal flakes, with ordered stacking. The unit layers are held together by hydrogen bonding, yielding an invariant basal spacing of 7.14Å, and a second order 3.57Å diffraction in oriented samples. There is little isomorphous substitution in kaolinite and consequently the permanent charge per unit cell, if not zero, is very small. However, due to the presence of exposed hydroxyl groups, it does have a variable, or pH dependent, negative charge, giving it a small C.E.C. in the range 3-15 meq per 100g.[2] As a result of this, kaolinite exhibits low plasticity, shrinkage, and swelling properties.

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 10Å. Halloysite is expandable in water, but most other members of the group, such as dickite and nacrite are, like kaolinite, nonexpandable.

1.3.2 The illite group

Clay minerals of this group are characterised by a 2:1 type layer structure. The unit layers are usually held together strongly by charge balancing cations, introducing a link between successive sheets, and distinguishing minerals of this group from those of the smectite group. The illite group can be divided into several sub-groups or divisions on the grounds of their chemical composition.

1.3.2.1 The micas

The micas have a large positive charge deficiency in the tetrahedral sheets, approximately one per unit, corresponding to the substitution of one in every four silicon atoms by aluminium. This deficit is filled by large ions, generally potassium, which occur between the unit layers and strengthen their bonding. As a result the charge balancing cations in micas are nonexchangeable, and the C.E.C. is approximately zero, despite a large layer charge. The unit layers, now connected by potassium ions, cannot slip past each other, and are unable to swell. The bonding is weak enough, however, to allow an easy cleavage.

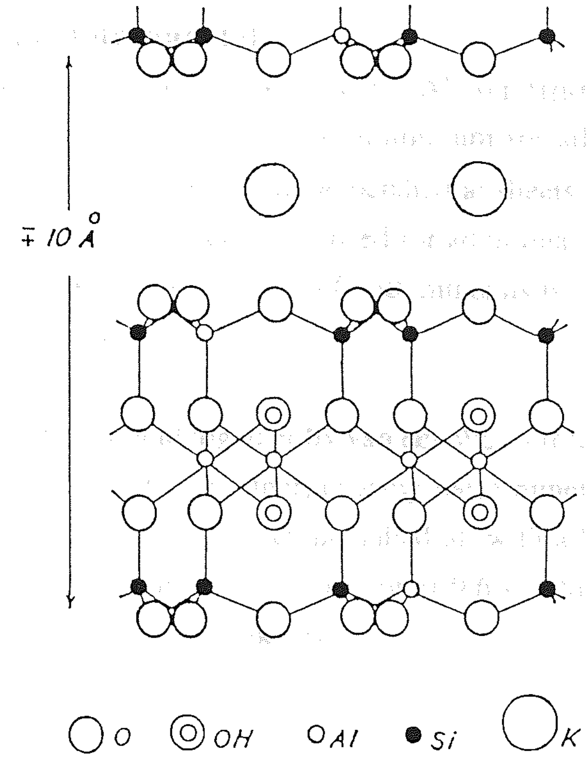

Figure 1.8 Schematic representation of the structure of Muscovite mica (after Pauling [17])

The octahedral sheet contains varied cations which determine the diversity of micas. Muscovite mica, $KAl_2(AlSi_3)O_{10}(OH)_2$, is a true dioctahedral mica, and is shown schematically in figure 1.8. The basal spacing is approximately 10Å, which is the basic periodicity of all the minerals which are constructed according to the mica type. The biotite micas are true trioctahedral micas, having their octahedral layers populated mostly by Mg^{2+} and/or Fe^{2+}. Examples include phlogopite, $KMg_3(AlSi_3)O_{10}(OH)_2$, and biotite itself, $K(MgFe)_3(AlSi_3)O_{10}(OH)_2$.

Although the charge balancing cation is predominantly potassium, sodium micas such as paragonite, $NaAl_2(AlSi_3)O_{10}(OH)_2$, are known. They do not form as easily as potassium micas and are more readily decomposed. This is a consequence of sodium's smaller ionic radius causing it to not fit the hexagonal ring of basal oxygens as well as potassium, and therefore to not be held as strongly.

The linking cation may also be calcium or magnesium, in which case the charge deficiency per unit has to be doubled, causing every alternate tetrahedral silicon to be replaced by aluminium. These minerals are termed brittle micas, an example of which is margarite, $CaAl_2(Al_2Si_2)O_{10}(OH)_2$.

1.3.2.2 Pyrophyllite and talc

In these two particular minerals, pyrophyllite, $Al_2Si_4O_{10}(OH)_2$, and talc, $Mg_3Si_4O_{10}(OH)_2$, there is no substitution of aluminium for silicon in the tetrahedral sheets. No substitution is present in the octahedral sheets either, so the structures are electrically neutral, and there is no need for additional alkali ions between the unit layers. It follows that the C.E.C. of both minerals is approximately zero, and that neither swell in water.

The unit layers are only held together by van der Waals forces, hence the ease with which the layers slip past each other, causing these minerals to have superb dry lubricant properties. Pyrophyllite is dioctahedral, with a basal spacing of 9.3 Å, and talc is trioctahedral,with a basal spacing of 9.6Å.[2] Structurally, they are the parents of all illite and smectite minerals.

1.3.2.3 The illites

Illites are the most common clay minerals in nature. They are structurally similar to the micas, except that now less than one silicon in four in the tetrahedral sheet is replaced by an aluminium ion. This in turn means a proportionate diminution of alkali ions between the layers. The resulting structural formula is a variable one, $K_xAl_2(Al_xSi_{4-x})O_{10}(OH)_2$, where $0.5 < x < 0.75$. A partial replacement of octahedral aluminium by Mg^{2+}, Fe^{2+} and Fe^{3+} is also frequent. Glauconite, an important isotype of illite, is formed when the octahedral aluminium is largely replaced by ferric iron.

Often, as well, potassium is not the sole charge balancing cation present, with sodium, calcium, and the hydroxonium ion, H_3O^+, being common alternatives. For example, if potassium is largely replaced by sodium, the mineral is brammalite.

If, instead, hydroxonium ions are present, the unit layers are more weakly bound and may expand slightly. However, the physical properties of the illites are closer to kaolinite than to the expanding, smectite clays. Illites have a C.E.C. in the range of 10-40 meq per 100g of clay.[2]

1.3.3 The smectite group

The clay minerals of the smectite group have a 2:1 layer, mica-type structure, but the bonds between the unit layers are considerably weaker. This is due in part to the absence of potassium as the dominant exchange ion, but is predominantly due to the location of the charge deficient site. In most smectites the majority of substitution occurs in the octahedral layer, and the resultant negative layer charge is evenly distributed across the unit layer. This is not so in the micas, where electrical imbalance arises instead through tetrahedral substitution, and the negative charge remains localized at the site of substitution. Interlayer, charge balancing cations are thus held less strongly in smectites than in micas, resulting in weaker bonds between the unit layers.

Due to these weaker bonds varying amounts of water can enter between the layers, and the stacking of successive layers becomes random. The basal spacing can thus vary over a wide range, the minimum, 9.6Å, corresponding to the fully dehydrated state. Highly hydrated smectites can have basal spacings of up to 20Å, and in dilute aqueous suspension the unit layers may completely disperse, but frequently a value of approximately 14Å is found. Another consequence of the smeared out layer charge is that smectites tend to be turbostratic, that is, the layers are randomly stacked with respect to the in-plane a and b axes of adjoining layers.

As mentioned earlier, pyrophyllite and talc are the prototype minerals for the smectite group. The principle members may then be differentiated on the basis of the relative amounts of substitution in the octahedral or tetrahedral layer, and on the species of atoms substituted. The average extent of such substitution requires about 0.33 additional monovalent cations, or their equivalent, per formula unit, and these ions are in general exchangeable. Consequently, smectites have relatively high cation exchange capacities, in the range 80-150 meq per 100g of clay.[2]

The five principal members of the smectite group are montmorillonite, $Na_{0.33}(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$, beidellite, $Na_{0.33}Al_2(Al_{0.33}Si_{3.67})O_{10}(OH)_2$, nontronite, $Na_{0.33}(Fe^{3+}_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$, hectorite, $Na_{0.33}(Mg_{2.67}$

$Li_{0.33})Si_4O_{10}(OH)_2$, and saponite, $Na_{0.33}Mg_3(Al_{0.33}Si_{3.67})O_{10}(OH)_2$. The first three are dioctahedral smectites, and are based on the formula and structure of pyrophyllite, and the latter two are trioctahedral, and based on talc.

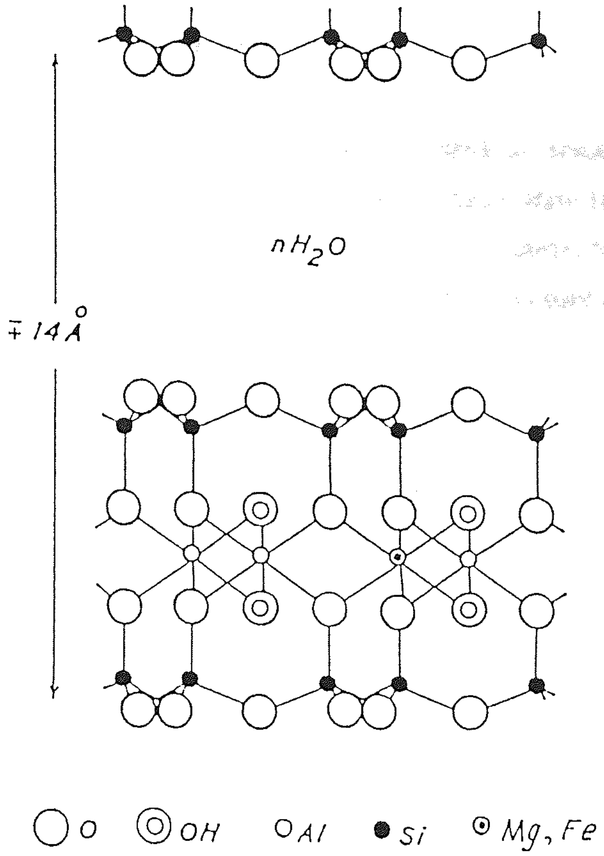

Figure 1.9 Schematic representation of the structure of montmorillonite (after Hofmann [19])

There are many parallels that can be drawn between these two series. Montmorillonite, a dioctahedral smectite, and hectorite, a trioctahedral smectite, both have substitution almost entirely in the octahedral sheet. Analogously in beidellite and saponite it takes place principally in the tetrahedral sheets. Combinations of both types of substitution can occur, and there is a continuous solid solution series between the principle members of the dioctahedral minerals, montmorillonite-beidellite-nontronite. Likewise, there is a similar series between the trioctahedral minerals, hectorite-saponite. However, there does not appear to be a solid solution series between the di and trioctahedral members.[18]

Sodium is the most common counterion associated with the smectite minerals, whereas potassium is the cation preferred by the micas. Its predominance is by no means universal, however, and in nature calcium, magnesium, and potassium are also commonly found. Copper, nickel, chromium, vanadium, and zinc too may occasionally substitute in major amounts into the octahedral layer, forming volkhonskoite (Cr), sauconite (Zn) and pimelite (Ni).

1.3.4 The vermiculite group

This group of minerals could well be regarded as trioctahedral members of the smectite group. They have a 2:1 type layer structure, with a C.E.C. of 100-150 meq per 100g of clay,[2] due mainly to considerable substitution of aluminium for silicon in the tetrahedral layer. The structure is shown schematically in Figure 1.10.

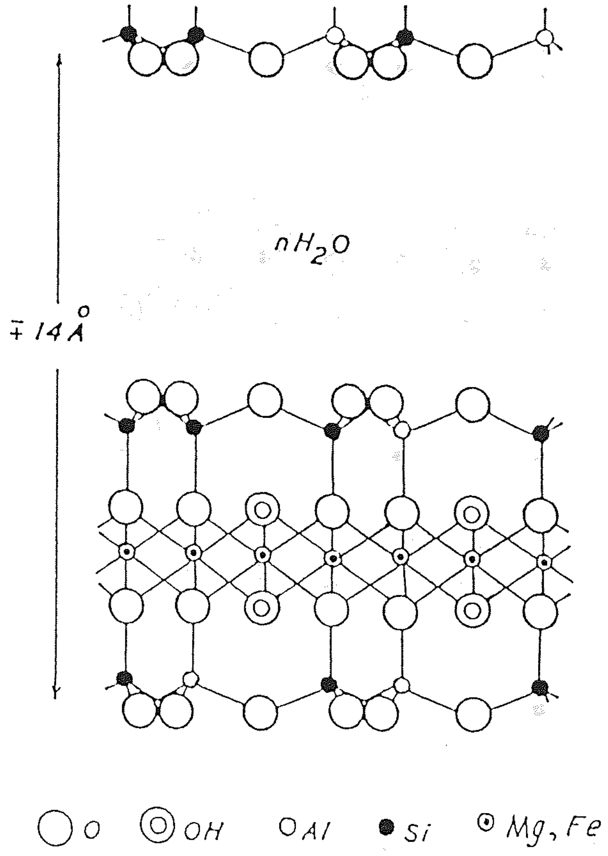

Figure 1.10 Schematic representation of the structure of vermiculite
(after Grüner [20])

The interlayer cation is usually magnesium or calcium and the unit layers are separated by either one or two layers of water molecules, so the basal spacing is variable. However, any expansion is limited to about 5Å, giving a basal spacing of approximately 14Å. For this reason the vermiculites are considered as a group separate from the smectites, or swelling clays. Particle size is also larger among the vermiculite minerals, and stacking is less random than in the smectites. The general structural formula may be written $(Mg,Ca)_{0.5x}(Mg,Fe^{2+})_3(Al_xSi_{4-x})O_{10}(OH)_2$.

1.3.5 The chlorite group

The chlorite structure consists of 2:1 mica type layers, with a further octahedral layer situated in the interlayer region. Thus chlorite, so named because of the green colour of many of the specimens, due to the presence of ferrous iron, are designated 2:1:1 layer structures. The basal spacing is generally 14Å, but in contrast to the smectites and vermiculites, it is not variable.

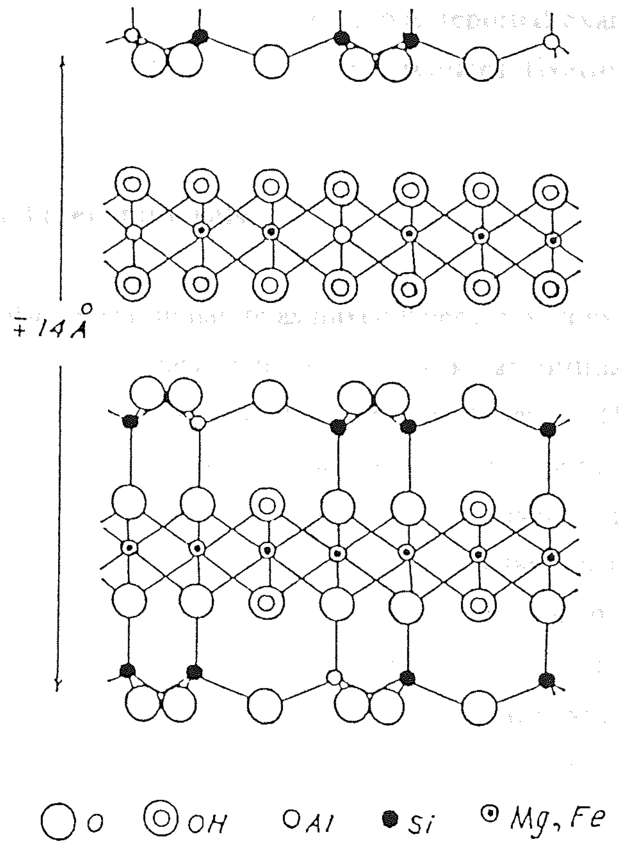

Figure 1.11 Schematic representation of the structure of chlorite (after Pauling [21])

True chlorites are trioctahedral in both the octahedral layers, their structure consisting of alternate sheets of trioctahedral mica bonded by sheets with a brucite

$Mg_3(OH)_6$, structure. Such chlorites are by far the most common, although dioctahedral chlorites, layers of dioctahedral mica condensed with gibbsite-like, $Al_2(OH)_6$, sheets, are known. So too are di-,trioctahedral chlorites, chlorites that are dioctahedral in their 2:1 layer and trioctahedral in the interlayer sheet, but no natural chlorites of the reverse structure have been found. The general formula for the chlorite group may thus be written $(Mg,Fe,Al)_6(AlSi)_4O_{10}(OH)_8$. The structure is shown schematically in Figure 1.11.

Substitutions in the tetrahedral and octahedral micaceous sheets, as well as in the interlayer sheet, are extremely varied. The replacement of magnesium by aluminium in the brucite sheet accounts for the development of a positive charge, which practically neutralizes the negative charge of the substituted 2:1 layer. Therefore chlorites have only a very small unit layer charge, and consequently a small C.E.C. of 10-40 meq per 100g of clay.[2] The hydroxy interlayers are sites for anion retention, with phosphorous being one reported example.[22] On the other hand, the presence of these interlayers reduces fixation of potassium and ammonium ions.

1.3.6 Mixed layer minerals

Clay minerals also appear in nature as mixed layer clays, consisting of interstratified layers of two or more types of mineral. Unlike an ordinary mixture of clays, interstratified clays cannot be separated by physical means. There are three types of mixed-layer structure, the most common being irregular layers, randomly interstratified. No law governs the alteration of the layers in this type, and they are given no particular mineral names, being described instead in terms of the proportions and types of the layers. The second type of mixed layer structure is that of regular layers of different minerals, alternating according to a specific law, the simplest being of the form ABABAB... The final type is of 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 layers. The most common of all is illite-montmorillonite. The mixed-layering of these two minerals comes about as a result of the continuous series of illite species that exists between muscovite mica and montmorillonite as the end members. Muscovite is considered to be the prototype of illite,[23] and illite in turn, and in soils affected by high precipitation, is in time altered into montmorillonite.

1.4 Genesis of the Clay Minerals

The nascence of clay minerals is a subject of much debate. It is presumably true that the first clay mineral to form on earth received a definitive thermodynamic message that directed materials in the environment to crystallize in a profoundly elegant manner to a phyllosilicate, by action of the environment that was operative. The result was a 1:1 or 2:1 layer mineral, or possibly a less well-organized precursor of them, such as allophane.[24]

One way or another, over the course of geologic time, the earth's crust came to contain a large array of different silicate minerals. Each may become thermodynamically unstable due to a change in environment, thus each may be altered, and each, directly or indirectly, may play a part in the genesis of the clay minerals.

There are three principle processes, detrital inheritance, transformation, and neoformations, by which the genesis of clay minerals may come about.[25] Before these may be studied in any detail a superficial knowledge of the materials of the earth's crust is necessary.

1.4.1 The materials of the earth's crust

As a whole, the earth may be considered to be a stony shell some 2000 miles thick, resting on a core of molten iron 4000 miles in diameter. The shell itself is not uniform, but is to some extent layered. The top layer is known as the earth's crust, is on average approximately 30 miles thick, and is composed of granitic material rich in silicates of alkalis, lime, and aluminium near the surface, and a somewhat denser basaltic zone richer in silicates of magnesium and iron further down.[26] Below this is the mantle, believed to be composed of olivine- or garnet-bearing minerals, which extends right down to the molten core.

During the course of galactic evolution, the first solid rocks on earth formed about 4.5×10^9 years ago.[27] Rock, as defined by the geologist, is merely an aggregate of mineral particles. It may be a mass of associated grains or crystals all of one single mineral species, but more usually consists of two, three, or half a dozen or more kinds of minerals assembled by a series of natural processes. Thus the term encompasses plastic clays, unconsolidated sands, crystallized salts, and river sediments, as well as blocks of granite. Even so, all may be classified as either high-temperature, low-temperature, or metamorphic rocks.

1.4.1.1 High-temperature rocks

Any rocks that are formed by crystallization, or simply solidification, of molten magma are high-temperature, or igneous, rocks. The magma may either crystallize slowly at various levels within the crust of the earth, or solidify rapidly upon breaking the surface as lava-flow. It is this variety of possible physical conditions under which the magma may cool that is responsible for the diversity of rock formed, just as much as is the magma's chemical composition. On this basis igneous rocks may be classified into three distinct types.

The plutonic or abyssal rocks are slow-cooled at depth, and are usually continuous through several cubic miles. Temperatures are not much below the freezing point of the magma, and crystal growth is slow and only about a few scattered centres. The liquid-solid equilibrium is metastable, and the resulting rock is coarse-grained and completely crystalline.

The volcanic rocks result from the chilling of magma poured out on the earth's surface. The quickly cooled magma passes rapidly through the metastable region, and crystallizes principally in the labile region, where the number of centres is immeasurably larger. A fine-grained texture is the result, often containing some natural glass as a consequence of especially rapid cooling that takes the magma right through both the metastable and labile regions, and causes solidification without crystallization. The third class of igneous rock is the hypabyssal rock, which is intermediate in character, and in origin, between the other two.

1.4.1.2 Low-temperature rocks

To a greater or lesser extent all igneous rocks at the surface of the earth are breaking down. The changes which set in, conditioned by the low-temperature instability of all high temperature minerals, is the ultimate source of all low temperature, or sedimentary, rocks. Although they are more difficult to classify than igneous rocks, having more varied origins and a wider range of composition, again three principal types are recognised.

Fragmental, or clastic, rocks are sediments such as gravels and sands which consist predominantly of the solid rock fragments formed from the waste of pre-existing, igneous or sedimentary, rocks, and the secondary products of chemical weathering such as the clay minerals. Such rocks may have accumulated under fresh or salt water, or on land, and may have been transported by water, ice, or wind.

Organic deposits are equally varied, covering all rocks which are predominantly composed of the remains of animals or plants. Those of vegetable origin are generally carbonaceous, like coal and peat, and those of animal origin are usually phosphatic or calcareous, like limestone, although they may occasionally be siliceous.

Chemical deposits in the main result from the precipitation of substances in solution, but may also be organic, fragmental or volcanic in origin. Rocks in this group include rock-salt, gypsum, calcium carbonate, and dolomite, all the result of chemical precipitation in shallow seas, and potash and magnesia salts, nitrates, iodates and borates.

1.4.1.3 Metamorphic rocks

If low-temperature rocks then become deeply buried, compressed, and subjected to high temperatures themselves, they become unstable, and new minerals characteristic of the new conditions form or re-form as the result of a new series of physico-chemical processes. Such rocks are termed metamorphic rocks. They are not identical to igneous rocks because the process of metamorphism is not a simple reversal of the weathering processes that produce the sedimentary rocks. Mechanical sorting and segregation of constituent minerals is inevitable during transport and sedimentation, and so metamorphic rock identical in mineral constitution to a normal igneous rock can only occur when an igneous rock is itself metamorphosed. All metamorphic rock is crystalline, granular, and composed of high-density minerals such as garnet.

1.4.2 The mechanisms of genesis

The geological environments which form clay minerals can be basically divided into five types, weathering, sedimentation, burial, diagenetic, and hydrothermal.[28] It is within these environments that the mechanisms of genesis act.

The first of these is detrital, or mechanical, inheritance. It is nothing more, nor less, than the breaking, wearing or rubbing off of mineral grains from pre-existing, igneous or sedimentary rocks. As a result, clay minerals are inherited by one environment from another, without modification. This can only happen when the new environment can offer conditions of stability and, therefore, of survival to the clay particles. The importance of this mechanism decreases only when the environments are capable of degrading the inherited clay particles, or using them in constructions. As soon as the environments act on the inherited material, it is modified, and the mechanism becomes that of transformation.

Transformation of clay minerals can take place during any of the geological environments mentioned earlier, but primarily take place during weathering or sedimentation. Transformations may either be negative, termed degradation, meaning decomposition and loss of substance, or positive, termed aggradation, and meaning construction and gain of substance. Common to both modes of transformation, however, is that the clay mineral is modified without alteration of its 1:1 or 2:1 layer structure. At every stage of the modification the inherent 2D sheet framework must be maintained, so virtually restricting transformations to being between clays of closely related families. The most frequent and the best known cases are the transformations within the 2:1 layer clay minerals, such as illite-montmorillonite, illite-vermiculite, and vermiculite-montmorillonite.

If, on the other hand, the process of modification passes through solutions, and the new minerals are built from the ashes of the former ones, the mechanism is neoformation. This commonly occurs only in the domains of weathering, sedimentation and diagenesis. The well-leached environment, which is acidic and free of cations, determines the formation of kaolinite, whereas the insufficiently renewed environment, which is alkaline and rich in cations, determines the formation of the 2:1 type layer minerals.[25] It is then the proportions of the elements present that govern whether it be an illite, montmorillonite or chlorite.

It is worth noting that the neoformation, or neosynthesis, of clays in nature is very similar to, and may yield much information on, the experimental low temperature synthesis of clay minerals in the laboratory. Natural neoformation demonstrates that laboratory synthesis can adopt one or other of two opposing routes. Neoformation by subtraction is the dissolution of a crystal, glass, or gel in situ, until the disordered residue within comes to the conditions and the proportions favourable to the growth of new crystals. By contrast, neoformation by addition is the concentration and organization of chemicals gathered in solution, and may take place far from the parent rocks.

Until recently, only a few investigators attempted such syntheses without the use of elevated temperatures. Of the successful ones, minerals of the kaolin group have been reported from studies on the manipulation and ageing of gels,[29] and montmorillonites have been obtained by concentration and evaporation of drainage water from experimental weathering compartments.[30] The latter method, whilst only allowing synthesis to take place very slowly, has confirmed earlier conclusions [31] that the formation of clay minerals depends more on the conditions of pH than on the ratio of the constituents in the natural medium. By contrast, syntheses of clay minerals at high temperature may be accomplished with ease, and is the work of numerous research groups. Even so, the synthetic neoformations furnished in this manner are in many instances exact copies of natural minerals, indicating that both methods of preparation obey strict rules imposed by thermodynamics, and that the composition of natural clays really corresponds to the greatest lattice stability.[32]

1.5 Montmorillonite

Montmorillonite is classified structurally as a 2:1 layer silicate, more specifically a dioctahedral member of the smectite group of clay minerals. It has an idealized formula of $Na_{0.33}(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2.nH_2O$, although calcium and magnesium, as well as sodium, are commonly found as charge balancing cations. Isomorphous substitution differing from that recorded by the idealized formula is often found in the octahedral layer, and permitted too in the tetrahedral layers. A wide variety of materials result, often with quite differing properties, and this can lead to confusion over attempts to classify these minerals further. Variations in origin or occurrence have also been used extensively to this aim, as have the uses for which they are sold, and so it becomes necessary to further define here the materials used in the work of the following chapters.

1.5.1 Modes of origin

The clay minerals in general may be formed in a variety of geological environments, by one or other of the three principal processes of detrital inheritance, transformation, and neoformation. Montmorillonite is no exception, having also been shown to arise from a variety of origins. Its small particle size, combined with its ability to readily disperse in water, facilitates its easy migration from the upper horizons of profiles to pastures new. Indeed, the migration of clay minerals in such a manner is in the following order: montmorillonite> vermiculite> mixed layers> chlorite> illite> kaolinite.[25]

However, it is far more common to find that a montmorillonite formation is the result of a transformation. Obviously many types exist, but these are usually discussed under the broader headings of alteration of volcanic ash or tuff essentially in situ, hydrothermal alteration generally of igneous rocks, and other miscellaneous modes of origin.

Alteration of volcanic ash or tuff in situ is by far the commonest mode of origin of montmorillonite, and is established by the presence of microscopic shards of the parent ash or tuff, by the character of the non-clay minerals, and, at times, by transition to associated beds of ash or tuff. Alteration in situ is indicated by the high concentration of clay minerals, by the absence of detrital minerals, and by the association with adjacent beds. The alteration process is essentially devitrification and hydration of the ash. This generally takes place in water, with a shallow marine environment being most common, although many formations appear to have formed in fresh water.[33] However, alteration only occurs if the drainage is moderate enough to maintain an alkaline environment. Only a few instances are known in which ash falling on land has altered to montmorillonite, but there appears to be no reason why a particularly wet ash falling on land should not alter to a smectite clay.

The second type of transformation commonly responsible for the formation of montmorillonite is that of hydrothermal alteration. In such instances the character of the parent rock may show wide variations, being either metamorphic, igneous, or sedimentary in nature. Usually alteration of this kind produces a suite of clay minerals in any given occurrence, but occasionally a single clay mineral may develop in place of a large mass of host rock, and in many cases the sole alteration product is montmorillonite. The depth of alteration, the absence of vertical variations in composition, and the absence of any suggestion of a soil profile are definite evidences for this type of transformation.

Of the miscellaneous transformations applicable to the formation of montmorillonite, simple weathering is perhaps the best known example. However, most of the evidence for these alternative modes of origin is negative evidence, the absence of evidence necessary to prove the other modes of formation to have been active. Very few examples exist where weathering seems definitely to have played a role in the origin of montmorillonite.

The montmorillonite fraction in montmorillonite-bearing soils is also commonly the product of a series of transformations. By an attack on the connecting links between the layers, the two most commonly inherited clay minerals, chlorite and illite, are weathered to vermiculite, and then in the extreme to a vermiculite-montmorillonite mixed layer, and then to montmorillonite itself. At the same time allophanes appear in the soils, which correspond to complete disintegration, and the end of the silicate cycle.

The direct formation, or neoformation, of montmorillonite is also possible in certain sedimentary environments. Occurrences formed in this manner are most commonly found in chalks, where there is no trace of volcanic heritage, in association with neoformed cristobalite.

1.5.2 Definition and classification

Prior to the use of X-Ray Diffraction techniques to the elucidation of clay mineral structures, considerable confusion existed over the naming of species. This much is evidenced by the history of montmorillonite.[34] The original material was from Montmorillon, France, and named 'montmorilloniste' by Manduyt in 1847.[35] At that time it could only be stated that it contained silica, alumina, and water, and it took almost a further one hundred years before it was to be unquestionably recognised as a new mineral. During these intervening years the name was used sporadically, and newly discovered beds were incorrectly assigned a variety of other minerals' names. Worse, montmorillonite became industrially desirable around the turn of the century, and the mineral was soon sold under a range of names, based either on the location of the mined formation or the end use. Some of these terms now hold widespread usage, as the following definition [36] of montmorillonite indicates. It states that montmorillonite is "a clay mineral, probably originating in the devitrifiction of volcanic glass. The rock 'bentonite' is formed almost entirely of this mineral, and 'fuller's earth' is generally largely composed of it".

Bentonite was first described by Knight in 1898, as "a peculiar variety of clay found in Wyoming, U.S.A." [37] This was under the name of 'taylorite', after the Taylor ranch, the site of the first mine, near Rock River in the south of the state.

Finding that the name was preoccupied, Knight then proposed the name 'bentonite',[38] from its occurrence in the Benton formation, itself named after Fort Benton, Montana, located more than four hundred miles north of Rock River.[39]

Early in the twentieth century, several geologists [40,41] established that this particular clay is an alteration product of volcanic ash. This recognition led to definitions based on origin, the one most widely quoted and generally accepted being the following one by Ross and Shannon [42] : "Bentonite is a rock composed essentially of a crystalline, clay like mineral formed by the devitrification and accompanying chemical alteration of a glassy igneous material, usually a tuff or volcanic ash". They further stated that "it is usually the mineral montmorillonite, but less often beidellite".

However, there are many clays now designated as bentonite which have not originated by the alteration of volcanic ash or tuff, and the term is now well established for any clay which is composed dominantly of a smectite clay mineral, and whose physical properties are dictated by this clay mineral.

Finally, bentonite may be further classified on the basis of its swelling capacities when wet or added to water. Bentonite in which exchangeable calcium is more abundant than other ions has much lower swelling capacities than sodium varieties. Geographically, the low-swelling calcium type occurs in states bordering the Gulf of Mexico, and so is commonly called 'Southern bentonite'. On the other hand, the largest high-swelling sodium bentonite deposits, and the major producing districts, are in Wyoming and adjacent states. Therefore, this bentonite, capable of gel formation when added to water, is commonly called 'Wyoming' or 'Western bentonite'.

The term 'fuller's earth' is perhaps even harder to define, as the origin of the term dates back into antiquity, when it was first applied to material used in cleansing and fulling wool, thereby removing the lanolin and dirt from it. The name itself is derived from the latin word 'fullo', meaning fuller, a person whose trade is that of scouring and felting cloth.[43]

Today it is more or less a catchall for clay or other fine-grained earthy material mined and sold for its low plasticity and strong decolourizing and degreasing properties. This is exemplified by the definition given by the U.S. Bureau of Mines when asked for a precise definition.[43] It states that "fuller's earth is that kind of material which is used in applications where fuller's earth is traditionally used". Efforts have been made to find a more restrictive definition, with many workers noting that[44] "fuller's earths particularly rich in montmorillonite approach the rock bentonite in nature". Taking this idea further, Robertson, in tracing the history of the material back to antiquity,[43] defines fuller's earth simply as calcium montmorillonite. In keeping with this straight forward definition, hereafter fuller's earth shall be considered to be calcium montmorillonite, and Wyoming bentonite to be sodium montmorillonite.

1.5.3 Occurrence

The various species of clay minerals are not distributed evenly throughout the sedimentary sequence. Chlorite and illite are the most abundant clay minerals, and although they are found in sediments of all ages, they predominate in ancient sediments. Conversely, montmorillonites are abundant in tertiary sediments, less common in Mesozoic, and rare below that.[45] They are particularly abundant in formations of Middle Tertiary and Upper Cretaceous.[46] Kaolinite too has been found to be less abundant in very ancient sediments, specifically those deposited before the Carboniferous.[2]

Cainozoic (Tertiary and Quaternary)	Pleistocene
	Pliocene
	Miocene
	Oligocene
	Eocene
Mesozoic	Cretaceous
	Jurassic
	Triassic
Upper Palaeozoic	Permian
	Carboniferous
	Devonian
Lower Palaeozoic	Silurian
	Ordovician
	Cambrian
	Precambrian

Table 1.3 The stratigraphical system[36]

One can interpret this relationship between clay mineral type and geologic age once again in terms of the stability of the structures of the ensuing environments. In the course of geologic time burial will occur, and it seems likely that metamorphic processes would then cause the alteration of montmorillonite and kaolinite to a mica type mineral. Compaction, causing complete dehydration of the structure, would be accompanied by the adsorption of alkalies and alkaline earths from ground waters, resulting eventually in the disappearance of montmorillonite and kaolinite in more ancient sediments. This would be expected to be a much slower process for kaolinite than montmorillonite, hence the continuing presence of the former in formations of greater geologic age than the latter. Finally, it follows that very ancient sediments must be composed largely of the illite and chlorite types of clay minerals, and this indeed is the case.

Montmorillonite occurs in its purest form in primary deposits of bentonite, but montmorillonites of varying degrees of purity have been found in many places all over the world. Perhaps the best known deposits are in North America, where they are extensively produced commercially in about half a dozen areas. The principal producing district is in the Black Hills region of South Dakota, Wyoming, and Montana, in the general area where bentonite was first described, named, and mined. Bentonites are also commercially developed on a large scale in the Gulf Coast area, the Rocky Mountain states, and California. See Figure 1.12.

Other major producing districts in the Western Hemisphere include the Prairie Provinces of Canada, Mendoza and San Juan Provinces of Argentina, and a host of small sites, principally in Brazil and Mexico. Valuable montmorillonite deposits are also located in many parts of Africa, with important commercial production in Morocco, Algeria, South Africa, and Mozambique, and in Asia, with India, Phillipines, and Japan engaged in active commercial production. Deposits are also widely distributed in Europe, with the important producers being the Soviet Union, Italy, Spain, Czechoslovakia, Yugoslavia, and the United Kingdom.[33,39]

Bentonites have been reported associated with all types of sediments, however they are most often found associated with beds which are marine in origin. It follows that the strata immediately overlying and underlying bentonites in a sedimentary sequence may be of any type. In general, the basal contact of bentonite with underlying beds is sharp, whereas there is a gradational contact with the overlying beds of shale, sand, etc. The bentonite beds themselves may vary in thickness from an inch or less to twenty feet or more, and tend to be lenticular, that is, they tend to thin out horizontally and merge with the enclosing formations.[33]

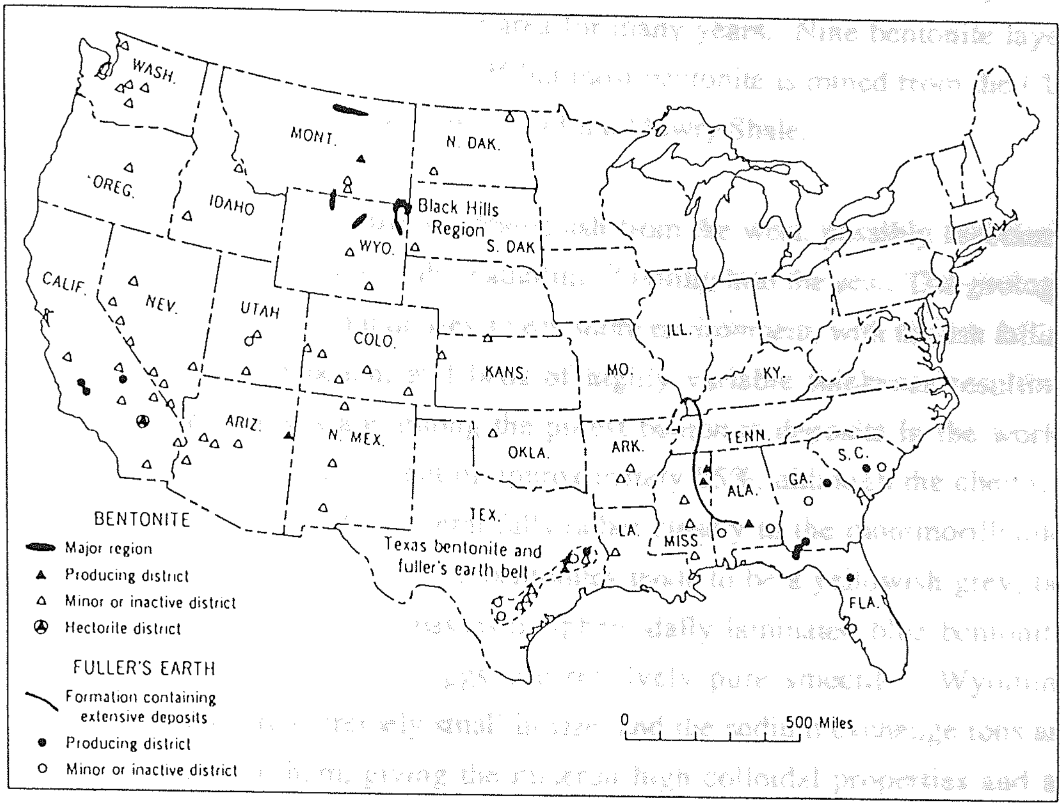

Figure 1.12 Principal bentonite and fuller's earth districts of the United States [39]

Bentonites vary in colour from black to white, and may be of any colour in between, but most are grey, blueish grey, light yellow or green. Frequently the bentonite is blue-green when fresh and becomes yellow upon weathering. The weathering is caused by continual expansion and contraction upon wetting and drying, and results in the outcrops frequently having a 'popcorn' appearance, and increased colloidal properties.

1.5.4 Wyoming bentonite

Wyoming bentonite is mined exclusively from deposits in the Northern Rocky Mountains-High Plains region of Wyoming and South Dakota, U.S.A.[47] Virtually all the bentonite produced from these deposits occurs in sedimentary formations of Cretaceous age, composed of shales, marls, and agrillaceous sandstones. They all have a shale overburden, and the underlying beds are silicified downwards for a distance of one to three feet, apparently by downward movement of silica from the bentonite. The Cretaceous formations of Wyoming are an example of the multiplicity of bentonite layers, sometimes up to twenty individual beds, separated by non-bentonite materials. The Black Hills district in the northeast of Wyoming has represented the major producing area for many years. Nine bentonite layers may be recognised in this formation,[48] but most bentonite is mined from the Clay Spur Bentonite Bed in the uppermost part of the Mowry Shale.

Wyoming bentonites result from volcanic ash from the west, possibly associated with the emplacement of the Idaho batholith,[49] falling into the sea. The geologic framework of the formation indicates a near-shore environment, with the ash falling into lagoons near the beach, and beds of highly variable thickness resulting. However, these deposits are among the purest bentonite deposits in the world, having a montmorillonite content of approximately 85%, although the chemical composition is such that the mineral falls rather closely to the montmorillonite-beidellite boundary line. Wyoming bentonites tends to be a yellowish grey, but they contain distinct modular masses of spheroidally laminated blue bentonite, although these so-called 'blue eggs' are relatively pure smectite. Wyoming bentonite platelets are extremely small in size, and the sodium exchange ions are held only loosely to them, giving the material high colloidal properties and an equally high specific surface area.

1.6 Physicochemical Properties of Smectite Clays

The structure, chemical composition, exchangeable ion type, and small crystal size of smectite clays are responsible for several unique properties that are most important in their industrial and chemical uses. These include a large and chemically active surface area, a cation exchange capacity, strong colloidal behaviour, and the ability to interact with organic and inorganic molecules. Many of these properties are interrelated, but as far as possible the following discussion focuses on only those that are vital to the majority of their industrial and chemical applications.

1.6.1 Crystal size and surface area

Crystal size, crystal shape, and aggregate characteristics have an important influence on colloidal and rheological properties, and a high surface area is a pre-requisite of high catalytic activity. Smectite crystals may be as large as 2μm or considerably smaller than 0.2μm, with an average size of about 0.5μm.[33] Their total, internal and external, surface area is usually approximately 700-800 m^2/g, which is very close to the theoretical surface area on dispersion to near unit-cell dimensions.[2]

Individual crystal morphologies may be rhombic, hexagonal, lamellar, lath, or fibre-like in shape, leading to a variety of aggregate types that tend to remain intact even when dispersed in water.[50] This phenomenon exists because during the growth of smectite clays by either transformation or neoformation, crystals become interlocked and difficult to separate, except by a strong shearing force. This causes the effective particle size and surface area of smectite clays to often be considerably less than the actual particle size and surface area, and has important consequences for industrial rheological applications. Natural sodium smectites, such as Wyoming bentonite yield the smallest effective crystal size and the largest surface area in clay-water systems because their natural crystal size tends to be small, and their high swelling pressure also acts to disrupt interlocked crystals.

Small crystal size obviously dictates a large external surface area, but the smectite clays, by virtue of their expansion characteristics, also have very considerable internal surfaces. External surface area is most commonly determined by measuring the amount of adsorbed nitrogen at monolayer coverage from a B.E.T. plot of adsorption isotherm data.[51,52] Inert gases in general do not penetrate between layers of an expanding clay, so only the external surface area may be determined, but this is not so with small polar molecules such as water or ethylene glycol. In this case the molecule is adsorbed on both external and internal surfaces, and a value for the total surface area is obtained.[53] Combining both methods thus affords reliable values for the total surface, the external surface, and by difference, the internal surface area of smectite clays. Typical values reported for hydrogen exchanged Wyoming bentonite are 810 m^2/g for the total surface and 43.9 m^2/g for the external surface.[54]

All three values may be obtained, however, from adsorption reactions with polar molecules alone. Total surface area is determined in the usual way, but if all traces of interlayer water are first removed from the sample by preheating, then even the organic molecule does not penetrate between the unit layers, and values for retention on external surfaces alone are obtained.[54]

1.6.2 Hydration, dehydration and dehydroxylation

The relative weakness of the van der Waals forces between successive unit layers of smectite clays allows hydration and dehydration of the interlamellar surfaces to occur. The main driving force is electrostatic attraction between the dipole of the water molecule and the charge of the exchangeable charge balancing cation. The hydration process itself occurs in a series of steps, with between one and four layers of water molecules being formed in the interlayer region, depending on the relative humidity level. The principal factors that are responsible for controlling hydration, and determining the extent and rate of adsorption, are the magnitude and location of the layer charge, the species of exchange ion, and the interaction of the water molecules with the cations and the silicate surface.[13]

The magnitude of the negative layer charge and its location, whether it is derived predominantly from octahedral or tetrahedral substitution, strongly influence the point localization of the interlayer cations. This in turn influences the ordering of the water layers. When only one or two layers are adsorbed, the molecules are arranged in a highly ordered, quasicrystalline manner, regardless of the degree of point localization. Additional water layers, however, may be disrupted if the cation is held strongly to the silicate surface.

The type of exchange ion present also helps determine the extent of disruption in highly hydrated samples. Multivalent cations enhance the rigidity of the first water layer, but as additional layers are adsorbed they promote disorder, and act to make the water more fluid. By contrast, monovalent ions tend to reinforce a rigid structure of water layers because they dissociate from the layer surface and so are, in effect, dissolved in the water structure.

Hydration in this manner continues until four water layers have been adsorbed, and a basal spacing of approximately 20Å is reached. This is the limit of type one swelling. Beyond this point electrostatic and van der Waals forces are balanced by the osmotic pressure of the interlamellar ions, and type two swelling is observed. The transition is sharp, with the basal spacing jumping from 20Å to 40Å, and increasing steadily thereafter. Eventually, the individual layers dissociate completely as the water content is increased. However, only lithium and sodium smectites display type two swelling, because multivalent cations provide a bridge between the facing silicate surfaces, so inhibiting unlimited swelling.

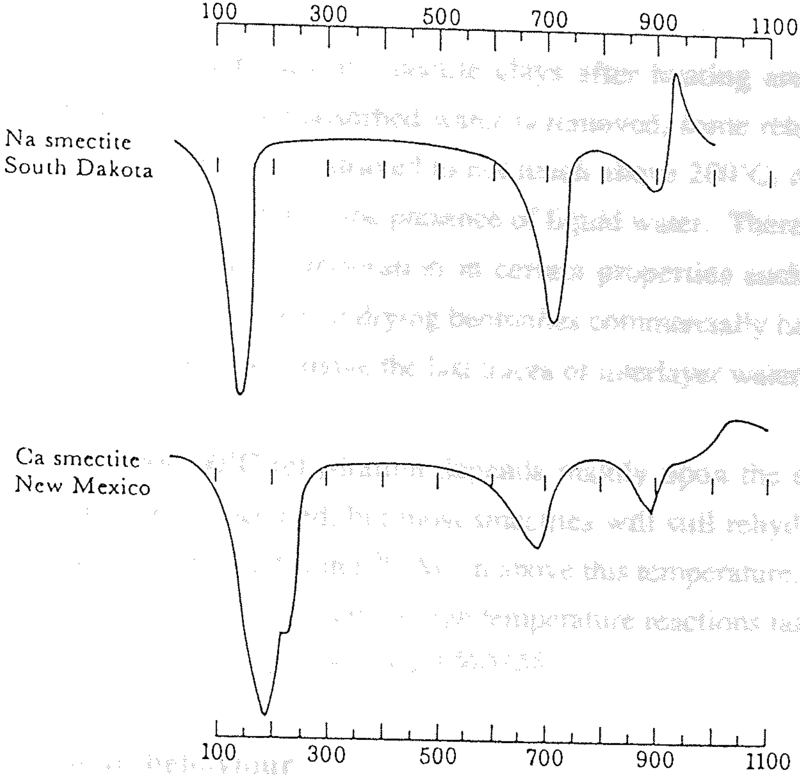

Figure 1.13 D.T.A. patterns illustrating adsorbed and lattice water loss for a typical sodium smectite and a typical calcium smectite [50]

When smectite clays are heated, water is lost in two distinct temperature ranges, as shown in Figure 1.13. At low temperatures, 100-200°C, dehydration occurs, as adsorbed water is lost from the interlayer region, and a 'collapsed' structure results. This process, being simply the reverse of hydration, is, like hydration, primarily dependant upon the type of exchange ion present.[55] When this is sodium, dehydration occurs in a single stage, but when calcium and magnesium are predominant, dehydration often proceeds in two stages. Further, such two-stage dehydration occurs at a higher temperature than does the dehydration of sodium smectites, although both retain much adsorbed water at temperatures well in excess of 100°C.

At higher temperatures, 500-700°C, there is a further loss of water. This is dehydroxylation, as water is now lost from the octahedral metal hydroxide sheet of the silicate structure. Dehydroxylation involves the breakdown of the silicate structure itself, and so variations are due mainly to differences in crystalline structure, chemical composition, and ultimately the strength of the metal hydroxide bonds.[56]

The rehydration characteristics of smectite clays after heating are not so well understood. Even if all of the adsorbed water is removed, some rehydration will always occur, but if heating is restricted to not much above 200°C, most smectite clays will rehydrate completely in the presence of liquid water. There is, however, generally an accompanying deterioration in certain properties such as swelling and/or dispersion and experience in drying bentonites commercially has shown that for this reason, it is unwise to remove the last traces of interlayer water.

After heating to 500-700°C rehydration depends mainly upon the extent of the dehydroxylation that has occured, but most smectites will still rehydrate to some extent in the presence of liquid water.[50] Much above this temperature, and the clay structure is completely lost. A variety of high temperature reactions take place, and a series of new silicate minerals are formed.[56,57,58]

1.6.3 Colloidal behaviour

When certain smectite clays are added in small amounts to water, rapid hydration occurs, with type two swelling causing eventual dissociation of the individual layers and complete dispersion of the platelets within the system. In addition, their electric potential causes the platelets to repel each other, and because they are so small they may remain suspended in the liquid indefinitely, so that a colloidal state is obtained. The smectite clay-water system goes through three states as the concentration of clay in the system is increased. These are the opalescent suspension, the thixotropic gel, and the stiff paste that resembles the highly hydrated solid.[59]

Within the dilute pre-gel suspension complete, random dispersion is possible. This has been confirmed by direct studies of the structure of clay particles in situ using small angle X-ray scattering techniques. They conclude that most of the particles are individual platelets,[60] separated by over 100Å.[61] However, an equally recent small angle neutron scattering study has suggested that many small stacks, each of only a few platelets separated by a double layer of interlayer water, are present in some dilute clay suspensions, depending on the type of exchangeable ion present.[62] It has even been suggested that most smectite particles are actually associated in tactoids, or non-spherical aggregates,when in dilute aqueous suspension.[63] These apparent discrepancies, however, are overcome by considering a fractal aggregation model.[64]

As the concentration of the dispersion increases, to between two and six percent by weight, so gellation occurs. The exchange cations diffuse into the bulk and an ion atmosphere around the clay platelets results. The ability to impart high viscosity and to develop thixotropy are unique properties of naturally occuring montmorillonite, hectorite, and high sodium saponite, and due mainly to small particle size, large surface area, and high dispersability.[50]

Until recently it had been believed that this phenomenon resulted from layer positive-edge to negative-face interactions, which generated a 'house of cards' structure that extends throughout the available volume, forming a solid gel.[65] However more recent work [59,61,63] has generated evidence that is irreconcilable with this model.

All conclude that the main feature of a gel is face-to-face, rather than edge-to-face, association. Data generated by the study of spin-lattice relaxation times of water molecules in the system indicated that the size of the tactoid does not change significantly as the clay concentration increases.[59] This suggests a micellization approach to tactoid formation, and that gellation occurs only once a critical tactoid concentration is reached. Complementing this work, a small angle X-ray study has shown that once the gel has formed, any further increase in concentration does result in an increase in the number of layers per stack.

The stability of a clay-water system may be altered very greatly by the addition of a small amount of electrolyte.[65] Less than one percent by weight of an inorganic salt will make a clay dispersion colloidally unstable, and coagulation of the particles, or flocculation, will occur. Interestingly, the same concentration of salt, when added to a gel, which is merely a special type of floc, has the effect of breaking down the structure, or causing deflocculation.

In the first case, the salt-free sol is stable because the van der Waals attractive forces between one particle and another are successfully counteracted by an electrical repulsive force between the particles. However, as the salt concentration is increased the magnitude of the electrical repulsion diminishes, while the particle attraction remains virtually unaffected. Consequently the attraction begins to dominate, and the sol flocculates.

Within a gel the situation is quite different. The structure is dependant upon electrical, edge-to-face attractions, whether or not they, or face-to-face interactions, occur in the gel in greater number. The inorganic salts now act to cause charge reversal of the positive edge sites, by anion adsorption, thus disrupting edge-to-face interactions and initiating breakdown of the gel.

This is known as peptization, and is used in a number of technologies to control viscosity and yield stress of clay-water suspensions. One of the more common commercial peptizing agents is tetrasodium pyrophosphate, TSPP or Tetron, an anionic peptizer. Peptization can also be achieved by reversal of the negative face charge of the clay platelet, using a cationic peptizer. Long chain quaternary ammonium ions may be used, but much greater quantities are required to achieve a comparable effect, although the accompanying increase in hydrophobicity may often be desirable. The viscosity of organic dispersions of alkylammonium montmorillonites can also be controlled by inorganic salts.[66]

1.6.4 Clay-organic/inorganic interactions

There are an almost endless number of organic compounds that interact in a variety of ways with smectite clays. The list is so large because of the many types of bonding that are possible [67] between the oxygen surfaces and the organic molecules. Indeed, an immense literature has developed on the subject, that is far in excess of that available on clay-inorganic interactions. Nevertheless, it is both convenient and correct to consider them both simultaneously, because of the many similarities that exist in the ways in which interaction may occur.

Clay minerals interact with organic materials by adsorption, intercalation, and cation exchange.[68] However, the lack of a universally accepted definition for each of these terms with respect to clay minerals still leads to confusion as to the exact nature of the modified smectite. Therefore, each is defined precisely in the following classification of clay-organic/inorganic interactions, in accordance with the way in which each will be used herein. In addition to the mechanisms of interaction already mentioned, pillaring is also included as it has become an increasingly important method for the modification of clays in recent years, particularly in the field of catalysis. Classification in this manner leads one naturally to the three principal types of chemically modified clays, intercalates, ion exchanged clays, and pillared clays.

Classification	Mechanism of interaction
Adsorption	External surface uptake only
Intercalation	Interlamellar uptake with retention of natural exchange ions (i) uncharged polar organic molecules (ii) metal ion complexes (iii) cation-anion pairs
Ion exchange	Surface and/or interlamellar uptake by replacement of natural exchange ions
Pillaring	The proping open of the silicate layers by either intercalation or ion exchange to overt interlayer collapse in the absence of a swelling solvent

Table 1.4 Classification of the mechanisms of clay-organic/inorganic interactions

1.6.4.1 Adsorption

Interaction with expanding clays by adsorption alone, defined here as being restrictive to external surface sorption only, is shown exclusively by non-polar molecules. These may be inorganic gases, such as nitrogen, oxygen, argon, and sulphur dioxide,[51, 52] or organic molecules such as n-paraffins.[69]

In all cases the sorption isotherms are of the Sigmoid type-2 form,[70] that is, S-shaped. The low pressure portion is concave to the pressure axis, the high pressure region is convex, and the intermediate region is approximately linear. The point at which this approximately linear portion begins corresponds to the covering of the surface of the adsorbent by a complete unimolecular layer of sorbate, and forms the basis of the B.E.T. external surface area determination mentioned in Section 1.6.1. Hysteresis loops have been observed between sorption and desorption branches with some organic sorbents.[71]

1.6.4.2 Intercalation

Intercalation refers to the reversible insertion of atoms, ions, or neutral molecules into the interlamellar regions of clays, or other layer structures such as graphite, TaS_2, or MoS_2.[72] Some or all of the interlayer water may be lost to accommodate the intercalating species, but should ion exchange take place to remove the resident interlayer cation, the reaction is considered here to be one of ion exchange, rather than intercalation, and will be considered in the following section.

The structural features of the host lattice are maintained, although some perturbation, varying from subtle to extreme, often occurs. This is also true of the hosts chemical, optical, and electrical properties, so providing scope to custom-build materials with predetermined characteristics. Intercalation complexes can themselves be divided into those that incorporate uncharged polar organic molecules, those containing metal ion complexes, and those containing cation-anion pairs.

(i) Intercalation of uncharged polar molecules

At air temperature and humidity water is the most common polar compound present in the interlayer space of smectites. However, many uncharged polar organic molecules may easily be intercalated by reacting air-dried smectites with the appropriate organic liquid,[68] and some may successfully intercalate from aqueous solution.[73] If the latter procedure is adopted though, a chain length of at least five units is required for appreciable intercalation to take place.[74]

In both cases though, water is still intimately involved in the overall modification. The organic compound must successfully compete with water for essentially the same ligand positions around the exchangeable cation for intercalation to occur. Small molecules are unable to do this and so require the clay to be fairly well dehydrated initially, but molecules with more than five units, both aliphatic and aromatic, may be intercalated to an appreciable extent in the presence of excess water because of the increased contribution of van der Waals forces to the adsorption energy. If, in addition, the uptake of one organic molecule is accompanied by the removal of a number of water molecules initially coordinated to the cation, the system gains an appreciable amount of entropy, further favouring intercalation.

The clay surface also makes a contribution to the intercalation process, through hydrogen bonding between its oxygens or hydroxyl groups and the functional group of the organic molecule. Thus the ease and extent of intercalation depends on the water content of the system, the properties of the clay mineral structure, the properties of the organic molecule itself, and the nature of the exchangeable ion.

If the exchangeable ion is only weakly polarizing, such as sodium or barium, all the interlayer water including the cations primary hydration shell, may be displaced. The cation then becomes completely solvated by the organic liquid, having organic molecules between itself and the oxygen atoms of the silicate surface. Displacement of water directly linked to strongly polarizing cations, such as magnesium or aluminium, is more difficult, although it can be achieved by special treatments which dehydrate the cation.[75]

Ion-dipole interactions between the organic molecule and the cation are influenced by the basicity of the organic molecule, and its mode of packing in the interlayer space, discussed above. Direct coordination to the interlayer cation is possible, with exchangeable transition metal cations, having unfilled d orbitals, forming stable coordination complexes with bases capable of donating electrons.[75] This is, however, tantamount to intercalating a transition metal complex, and so will be discussed in the following section. More usually, such bases are predominantly bound to the interlayer cations by water bridges.[76]

Both the degree of hydration and the type of exchangeable cation also determine the extent of surface acidity, and therefore the possibility of protonation of the bound organic molecule. Protonation of organic compounds at a clay mineral surface is either involved or implicated in the initiation of colour,[77] polymerization,[78] and decomposition [79] reactions catalysed by layer silicates.

(ii) Intercalation of metal ion complexes

The formation of an interlamellar complex by the interaction of electrons from an organic system with the empty orbitals of a metal may be achieved via two fundamentally different methods. The first, most obvious, method is to pre-synthesize a stable complex, add this to the smectite in the presence of an organic solvent, and stir the mixture until significant uptake has occured. If the complex is neutral, uptake will be via intercalation, but if the clay contacts a solution containing a complex ion, then an ion exchange mechanism may operate.[80,81] Beyond the exchange capacity of the clays a third mechanism, that of intersalation, or the intercalation of salts, may occur.[82] Both intercalated and ion exchanged transition metal complexes have been shown to be efficient catalysts for the ring opening reactions of phenols [83] and the reduction of nitrobenzene to aniline [84] respectively.

Alternatively, the desired complex may be formed in situ in the interlayer region. The appropriate metal ion is first exchanged into the clay, replacing the charge balancing interlayer cation, and then the desired ligand is introduced into the system. Many complex forming ligands such as thiourea,[85] bipyridyl,[82] and acetylacetone,[75] readily intercalate and coordinate to interlayer cations to form complexes identical with, or similar to, those in solution. Indeed, smectite clays exchanged with transition metals can be used to remove amine pollutants from aqueous solutions by complex formation in the interlayer of the clay.[86]

Interlamellar π-arene complexes between transition metals and benzene,[87] and methyl-substituted benzenes [88] have also be observed. Partial replacement of the interlamellar water by benzene leads to the formation of a type I complex, in which the benzene ring is planar and retains its aromaticity. However, further controlled dehydration yields the type II complex, in which the ring becomes greatly distorted, the π electrons are localized, and aromaticity is lost. Interestingly, the methyl-substituted benzenes appear only to form the type I complex, perhaps because steric factors hinder the necessary ring distortions.

(iii) Intercalation of cation-anion pairs

Inorganic salts, such a potassium acetate,[89] and ammonium chloride,[90] may be intercalated with clays of neutral layer charge, such as kaolinite. This phenomenon is called intersalation, but the term has since been used to denote the presence of cation-anion pairs in smectite clay interlayers. These may indeed be simple inorganic salts, or either salts of transition metal complex ions [91] or salts of organic ions, such as alkylammonium halide salts.[92]

1.6.4.3 Ion exchange

Smectite clays also have the property of sorbing certain anions and cations, in addition to neutral molecules or complexes. These ions are in general exchangeable for other anions or cations by treatment with ions in aqueous solution. The exchange reaction is stoichiometric, causing each clay type to have a particular cation exchange capacity (CEC). This is measured in milliequivalents (meq) per 100g of clay, and determined at neutrality, ie., pH 7.

(i) Cation exchange

Vastly more information is available regarding cation exchange than anion exchange, primarily due to the significantly larger capacity for cations than anions that is a feature of the great majority of the clay minerals. The first systematic studies of cation exchange were carried out in the middle of the last century,[93] when the phenomenon was known as base exchange. This terminology persisted for many years, even long after it was established that the hydrogen ion may also participate in exchange. Today, however, the term cation exchange is universally accepted and used.

A range of cation exchange capacities must be given for each group of clay minerals, as no single capacity value is characteristic of any given group. This follows from a consideration of the factors that influence exchange, and the nature of the three different causes of cation exchange capacity in smectite clays.

Substitutions within the lattice, of either aluminium for silicon in the tetrahedral sheet, or magnesium for aluminium in the octahedral sheet, cause about 80% of the total CEC in montmorillonite.[2] Each positive charge deficiency brought about in this way has to be balanced. Sometimes this is done by other lattice changes, such as substituting hydroxyl groups for lattice oxygens, or by filling more than two thirds of the octahedral positions, but frequently it is done by the introduction of cations into the interlamellar region of the clay. Exchangeable cations resulting from lattice substitutions are mainly found at the basal surface. Those arising through tetrahedral sheet substitution are therefore closer to the site of substitution than those arising through octahedral sheet substitution, and are consequently held by a stronger force than their octahedrally derived couterparts. They are even frequently found to be substantially nonexchangeable, but the contribution to the overall CEC from cations resulting from replacements in the octahedral sheet is essentially invariant.

In contrast, the other 20% of the overall CEC of montmorillonite stems from broken bonds around the edges of the platelets, giving rise to further unsatisfied charges, balanced by exchangeable cations. The number of broken bonds, and hence the exchange capacity from this source, increases as the particle size decreases. For montmorillonite however, it has generally been considered that the CEC does not change substantially with particle size,[94] although conflicting data have been reported in the literature.[95]

The CEC of montmorillonite is reduced to a considerable extent though by heating, even to temperatures below that at which the swelling property is lost.[96] The amount of reduction is large for lithium montmorillonite and much smaller for sodium montmorillonite, due probably to the comparative ease with which the lithium ion can move into the lattice.

The number of broken bonds increases too as the degree of crystallinity falls, thus working the clay by grinding serves to increase the exchange capacity.[97] pH is another factor affecting the exchange capacity derived from edge site broken bonds, with attack of acids and alkalies on the clay mineral structure controlling the contribution to the exchange capacity in this instance.[98] At low pH the exchange reaction is slow, as hydrogen ions and metal ions compete for the exchange sites, but at high pH it is changes in the solution chemistry of the metal ion that determine the reaction rate. Other factors, such as the clay concentration,[99] and the particular base used,[100,101] also affect the magnitude of the CEC at neutral pH.

The third contributing cause of exchange capacity in smectite clays is the hydrogen of exposed hydroxyl groups around the broken edges of the crystal. Replacement of this hydrogen by a cation is possible, which would then become exchangeable.

There are also many factors that influence the rate of the exchange reaction, their effect being different for different groups of minerals. pH has already been mentioned, but the type of clay mineral, the type and concentration of the cation, the degree of hydration, and the nature of the anion are all important determinants. Generally the reaction for kaolinite is the most rapid, being almost instantaneous. It is slower for montmorillonite, but requires an even longer time to reach completion for illites, chlorites and vermiculites.

Not all cations are equally replaceable or have the same replacing power. Moreover, there is not a single replaceability series characteristic of all clay minerals, but separate series for the various minerals types. For montmorillonites the series is $Li^+<Na^+<K^+<Ca^{2+}<Mg^{2+}<Al^{3+}$. Evidently, divalent ions will replace monovalent ions more readily than the other way around, however hydrogen is an exception since for the most part it behaves likes a divalent or trivalent ion. Amongst ions of the same valence, replacing power increases qualitatively with atomic number, or as the size of the nonhydrated ion increases.[102]

The cation concentration also plays a part in the exchange reaction, as it is a stoichiometric one and so the laws of mass action hold. Thus in general, an increase in the concentration of the replacing cation causes greater ion exchange by that cation.[102] Similarly, the concentration of the replacing ions already filling exchange sites, or the degree to which ion exchange has already occured, influences the ease of release of those original cations still remaining.[103] Interestingly, as calcium ions are removed from a clay those remaining become more tenaciously held, whereas sodium ions become easier to replace as the degree of saturation with sodium ions becomes less.

Smectite clays are able to remove ions from aqueous suspensions of very insoluble substances, and ion exchange will also proceed in the presence of relatively little water, but usually the environment is a dilute aqueous one, in which the ions have considerable solubility. In partially hydrated smectites the cations at the crystal edges are held directly, or very closely, to the silicate surface, and those located interlamellarly are held midway between successive basal surfaces. As the degree of hydration increases the cations become separated from the clay surfaces by increasing layers of water molecules. Consequently ion exchange becomes easier, and is at its most rapid in dilute aqueous suspension.

Finally, the nature of the anion in the replacing solution has to be considered. Not only will this affect the rate of exchange, but the CEC is generally dependant as well.[104]

Cationic surfactants may also take part in ion exchange, many being able to easily replace exchangeable inorganic ions. The metal ion replaceability series appropriate to the clay mineral under study still holds, so that for montmorillonite sodium ions are more readily replaced than calcium ions by organic cations.

The affinity for alkylammonium cations for various clay minerals has been particularly thoroughly studied. For a series of straight chain monoalkylammonium salts exchanging onto sodium montmorillonite, the associated free energy change increases linearly with chain length.[105] Generally the affinity of alkylammonium cations for the clay is linearly related to the molecular weight.

Within a group of primary, secondary, and tertiary amine salts of identical molecular weight, the ease of ion exchange decreases in the series $R_3NH^+ > R_2NH_2^+ > RNH_3^+$.[106] Thus the increased contribution of van der Waals forces to the bonding energy, due to an increased substitution of hydrogen by alkyl groups, more than compensates for the reduction in affinity due to any decrease in the number or strength of hydrogen bonds between the amine cation and the basal oxygens.

Exceptions to this series are the small methylammonium cation, which bonds more strongly than would be expected, and the bulky quaternary ammonium ions, R_4N^+. These are less strongly bonded than would be expected, with symmetrical ions such as the tetra-n-butyl ammonium ion ranking behind the secondary ammonium ions, and asymmetric ions such as the dimethyl-di-n-octadecylammonium ion having to be classified among the primary ammonium ions.[107] This may be explained in terms of the shape of the ion, and the degree of van der Waals contact between it and the silicate surface, or neighbouring alkylammonium ions on the surface, that is consequently permissible. The behaviour of sulfonium and oxonium ions is similar to that of R_3NH^+.[107]

Van der Waals forces, hydrogen bonding, and in addition, ion-dipole interactions and experimental conditions such as pH and surfactant concentration, all affect the ease of exchange of organic cations. So too, in many cases, does the layer charge, because with large exchange cations the extent of ion replacement may be size-limited. In a montmorillonite with a CEC of 100 meq per 100g and a unit cell mass of 720g mol^{-1}, and assuming that 80 percent of the exchange positions are on basal plane surfaces, there would be 1 equivalent exchange site for every 1.75 unit cells. Assuming a basal surface area of 92.26Å^2 per unit cell, there would be a total surface area of about 160Å^2 per exchange position, or an area of about 80Å^2 on each basal plane surface.[2] If the organic cation takes up an area greater than this value, then complete exchange with a monolayer interlayer is impossible, and if an area of 160Å^2 per exchange site is exceeded then even complete ion exchange with a double layer interlayer is unachievable.

An increasing layer charge also serves to confer selectivity upon the clay.[68] Smectites bind a great many different kinds of surfactants whereas vermiculites are more discriminating, and high-charge vermiculites particularly so, being able to select distinct surfactants from mixtures in solution.

Lastly, it should be noted that a pseudo ion exchange reaction may be brought about by the protonation of intercalated molecules such as ammonia, amines and pyridine, by protons occupying the exchange sites. Similarly, such molecules may be protonated as a result of the dissociation of water molecules coordinated to strongly polarizing exchangeable metal cations, and they may then undergo genuine ion exchange onto the clay.

(ii) Anion exchange

The smectite clay minerals, and indeed all the other clay minerals considered in section 1.3, exhibit anion exchange behaviour to a limited extent. In such clays there are two different causes of an anion exchange capacity, both resulting in exchange occurring around the edges of the platelets. The first is the replacement of the accessible hydroxyl ions present at the edges of the platelets.[108] The second is the fitting of anions such as phosphate, arsenate and borate, onto the edges of the tetrahedral sheets. These anions are about the same size and possess the same geometry as the silica tetrahedron, so extending the sheets.[2]

This is in contrast to cation exchange, which in montmorillonite is due mostly to lattice substitutions, and only in a minor way to edge sites. Thus the cation exchange capacity far exceeds the anionic exchange capacity, but for kaolinite, in which cation exchange is due solely to broken bonds, the cation and anion exchange capacities are substantially equal.

However, clays can be found in nature that have a positive charge surplus, rather than a positive charge deficiency, and consequently also possess an appropriate number of charge balancing anions, usually carbonate, located interstitially. These are the anionic clay minerals,[109] many of which are based on double hydroxides of main group and transition metal hydroxides. An example is hydrotalcite, $Mg_6Al_2(OH)_{16}(CO_3^{2-}).4H_2O$.[110] The structure is similar to that of brucite, $Mg(OH)_2$, with substitution of magnesium for aluminium gaining the lattice a positive charge. The charge balancing anions are generally exchangeable. For the hyrotalcites, that have an exchange capacity of 100-150 meq per 100g, the replaceability series is approximately $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$ and $CO_3^{2-} > SO_4^{2-}$.[111]

1.6.4.4 Pillaring

Interlamellar reactions in metal ion exchange forms of smectite clays are precluded at temperatures in excess of around 200°C by the dehydration and associated collapse of the interlayer region. This limitation may be removed by propping open the silicate layers with thermally robust molecules, so that the layers remain separated even in the absence of a swelling solvent. This technique is known as pillaring, and has opened up many possible new applications, especially in the field of heterogeneous catalysis.

The concept of pillaring smectite clays was first demonstrated by utilizing tetraalkylammonium ions to introduce interlayer porosity into montmorillonite.[112] However these, and bicyclic amine cations,[113] thermally decompose below 250°C. Large transition metal complexes such as $[Fe(phen)_3]^{2+}$ also serve to pillar smectites, but themselves degrade below 450°C.[114] Pillared clays based on polynuclear hydroxymetal cations, that are stable above 500°C, are now well known.[115] Aluminium, chromium, iron, magnesium, nickel, niobium, silicon, tin and zirconium have all be successfully used to this end.

The dominant species in aluminium pillared clays is an Al_{13} oligomer, based on the known cation $[Al_{13}O_4(OH)_{28}]^{3+}$. The high thermal stability of these clays is accounted for by the dehydroxylation of the oligomer to Al_2O_3 clusters at elevated temperatures. Aluminium pillared clays provide an interlayer spacing, or gallery, of up to 10Å, but zirconium pillared clays have been reported with galleries up to 13Å high.[116] Chromium pillared clays exhibit exceptionally large basal spacings of up to 28Å, giving a gallery height of approximately 19Å.[117] Here, the pillaring species is $[Cr_4(OH)_2(H_2O)]^{10+}$ which forms the mixed oxide $Cr_2^{III}Cr_3^{IV}O_{12}$ upon heating.[118]

The complete range of gallery sizes currently attainable with polynuclear hydroymetal cations is 2-25Å This is considerably greater that the range of 2-8Å provided by the zeolites, and already provides much scope for tailoring the catalyst to the application. In addition, the spacing between the pillars should be dependant upon the layer charge, and therefore also controllable, although other factors complicate this relationship considerably.[119]

1.7 Surface Active Agents (Surfactants)

Surfactants are amphiphilic molecules, consisting of a hydrophilic head group and a hydrophobic hydrocarbon tail, that consequently possess the property of interfacial activity. This sets them apart from organic compounds in general, and is the reason for their widespread commercial importance today, both in the domestic product area and in a myriad of industrial production and processing applications.

1.7.1 Structure and classification

Surfactants are primarily applied in aqueous solution, so that classification by type of hydrophilic group is appropriate. Classification in this way differentiates anionic, cationic, nonionic, and amphoteric surfactants.

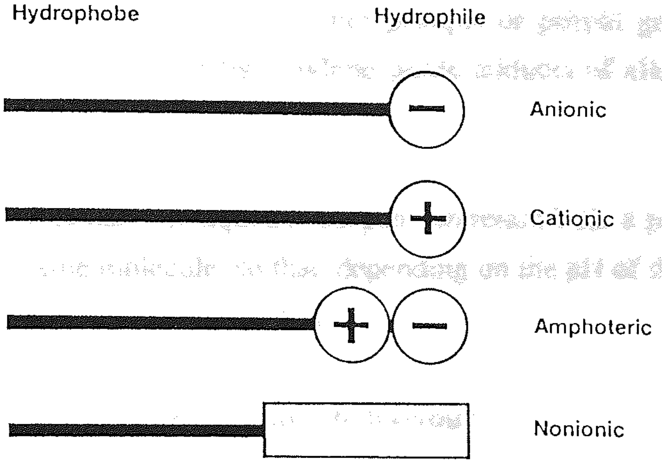

Figure 1.14 Schematic representation of surfactant types

Both anionic and cationic surfactants are surface active substances in which generally one or two hydrophobic hydrocarbon groups are connected to one hydrophilic group. In aqueous suspension, dissociation of the hydrophile occurs into an anion and cation pair. The anion is the carrier of the surface active properties in the case of the anionic surfactants, and the cation is the carrier in the case of the cationics.

Of the anionic surfactants, alkylbenzene sulphonates are the major product, although fatty alcohol sulphates and fatty alcohol ether sulphates are gaining market share.[120]

In principle, cationic surfactants may be synthesized from any combination of elements capable of forming an 'onium' structure, $R_nX^+Y^-$.[121] This could in practice include compounds of nitrogen, phosphorus, sulfur, arsenic, selenium, tellurium, antimony, and bismuth. In actuality, the field is dominated by nitrogen-containing structures, either protonated amino- or quaternary- ammonium compounds. Other materials are either too toxic or too expensive.

In the case of the nitrogen containing surfactants, the alkyl chain may either be attached directly or indirectly to the nitrogen atom, and the nitrogen atom itself may even be part of a heterocyclic ring.[122] However, the quaternary ammonium salts of the distearyl dimethyl ammonium chloride type are still by far the commercially most important class.

Nonionic surfactants are surface active substances which, in aqueous solutions, do not dissociate into ions. The aqueous solubility of these compounds is provided by polar groups such as polyglycol ether groups, or polyol groups. This market continues to be dominated by ethylene oxide adducts of alkylphenols and fatty alcohols.[120]

Amphoteric surfactants in aqueous suspension retain both a positive and negative charge in the same molecule, so that, depending on the pH of the medium, they can display anionic or cationic properties.

1.7.2 Interfacial and solution behaviour

In solutions such as water the surfactant molecules distribute in such a manner as to place their hydrophobic groups in a hydrophobic environment, causing the concentration at the interfaces to be much higher than in the bulk solution. Hence, at the phase borders, the formation of an orientated absorbed layer occurs. This results in a lowering of interfacial tension between the adjacent phases, a change of wetting properties, and the formation of an electrical double layer at the interface. Then, when a certain surfactant concentration, the critical micelle concentration (c.m.c.), has been exceeded, the surfactant molecules begin to agglomerate in the inner regions of the solution, into spherical, cylindrical or lamellar micelles. This behaviour is again attributable to their amphiphilic structure.

Several commercially important surface active properties can be identified as resulting from the interfacial and solution behaviour of surfactants. These may be categorized [120] as emulsification/ demulsification, wetting/ re-wetting, foaming, dispersing, defoaming, detergency, and solubilizing. In many applications a combination of several of these properties is required, and in many instances two or more surfactants must be formulated to afford the desired effect.

1.8 Applications of Clay Minerals and Surfactants

1.8.1 Industrial importance of the clay minerals

Clay minerals are an essential component of soils, to which we owe our survival, and they are also the raw materials for some of mankind's most ancient and essential artefacts, such as pottery, bricks and tiles. In acknowledging this, one must not overlook or underestimate their continued importance in the more technical industries of today.

China clay or kaolin, which is predominantly kaolinite, is particularly valuable because it is essentially free from iron impurities, and therefore white. Almost half the world production is used for paper filling or paper coating. China, crockery and earthenware are now more usually produced from ball clay, a very fine grained, highly plastic material which is a combination of kaolinite, mica and quartz.

Block mica itself is particularly tough, usually transparent, chemically inert, has high dielectric strength, and is stable to 500°C. Perfect basal cleavage as well thus makes it ideal for use in furnace windows, in electrical insulation, and in vacuum tubes. Ground mica is used as a filler for, amongst other things, rubber, plastics, and insulating boards.

Talc too is valued for its chemical inertness and, like kaolinite, can be obtained pure white. It is soft, smooth, and is a good dry lubricant. Its most important applications are in ceramics, insecticides, paints, and paper manufacture, with its more familiar use in cosmetics and toiletries accounting for only a few percent of world production.

It is the smectite group of clay minerals however that has perhaps the greatest diversity of uses, many of which will be discussed in the following section.

1.8.2 Smectite clays in the service of man

Smectite clays were in the service of man long before their industrial importance was recognised. In ancient times, when pure soft water was known to have some detergent properties, some river muds were found to be more effective. Consequently the washing of woollen cloth with fuller's earth was practiced in Cyprus as long ago as about 5000 BC. This is not much more than a thousand years since sheep were fully domesticated.[43] The Romans too would clean woollen cloth by first soaking it in an alkaline solution, often stale urine, and then trampling it underfoot in a vat containing a slurry of fuller's earth. The cloth would then be thoroughly rinsed to remove the earth, which would carry away with it much of the grease and dirt present in the wool.

As fulling has been practiced for nearly 7000 years there can be no doubt that fuller's earth and other clays have been used also for cosmetic and medicinal purposes for a similarly long period of time. Pliny the Elder, in his writings entitled Natural History, which he began about 77 AD, gives many pharmaceutical recipes requiring the use of a variety of medicinal clays. Most of these are in actuality either kaolinite or calcium montmorillonite, but when combined with other ingredients such as vinegar and wax they have the effect of dissipating swellings, checking discharges, cleansing wounds and removing toxins. When applied to the body in a form of mud pack the complexion is improved and pimples removed. Many of these applications are based on the strong absorptive properties of the smectite clay minerals, and demonstrate the considerable expertise that had evolved at this time. Indeed, similar treatments are still in existence today, particularly in the cosmetics market, with only a refinement of the ingredients being a significant development.

Geophagy, the practice of earth eating, has also been widespread throughout the world for thousands of years. In many tribes, clay, usually montmorillonitic, is eaten by almost everyone and held to be a remedy for stomach complaints or a tonic for nursing mothers. It is often baked or smoked and is even used as sustaining 'food' for long journeys. Even in the early part of this century sailors would eat fuller's earth as protection against dysentery and diarrhoea while at sea.

Earths have also been used for clarifying wines since classical times. The use of fullers' earth, hectorite and bentonite have been reported, both on their own and in combination with carbon, lime and flocculants such as gelatine and egg white.[43] The negative layer charge of the clay coagulates the positively charged organic species that form the colloidal impurities in the wine. Smectites are now used to clarify beer, cider, vinegar and fruit juices, with acid treated smectites being used to filter and decolourize vegetable and mineral oils.[50]

The firework art, although not practiced in Europe until it spread through Asia to Italy at the beginning of the Renaissance, is another skill that has been known for thousands of years. The first fireworks originated in China and clay was an essential construction material, plugging the end of the case at the base of the firework.[123] By using a small consolidated quantity of powdered clay it was ensured that should the firework explode accidentally, the plug would shatter to a fine powder and so not act as a dangerous missile. Much the same construction is still in use today even though fireworks are now used for smoke screening and signalling, line-carrying, bird-scaring, rain-production and a variety of engineering applications as well as for entertainment and religious purposes.

Despite these examples of the uses made of smectite clays by the ancients, man has felt the benefit of their presence in agricultural soils for far longer. Ever since man first grew crops in those soils that proved to be the most fertile, he has relied upon many of the properties unique to the expanding clays. Such minerals are of special importance in soil chemistry, having a surface chemistry and bulk physical properties very different from that of the larger mineral grains, gravel, sand and salt. Adsorption and cation exchange are of great practical significance in nutrient uptake by plants, soil fertility, nutrient retention and now in fertilizer application.[22]

The exchangeable cations are generally available to plants by exchange with H^+ ions generated by the respiration of plant roots. Nutrients added to the soil, in the form of fertilizers, or brought via rain and river waters, will be retained by the colloidal surfaces and are temporarily prevented from leaking. Similarly pollutants may effectively be removed from the soil by undergoing exchange reactions with the clay. In effect, the cation exchange properties of the smectite minerals provides the soil with a storage and buffering capacity for cations, thus aiding sustained plant growth. The beneficial effect of the addition of calcium clays, or marls, to soils was known in antiquity and claying, or marling, the land has been carried out ever since. During the eighteenth and nineteenth centuries particularly huge areas of soil were improved in this way. The twentieth century has now seen the arrival of synthetic soils, made up solely of silica sand and pure calcium montmorillonite that are used in the scientific study of plant growth.

These early applications of smectite minerals though, if specific to the nature of the exchange cation, are for calcium montmorillonite, fuller's earth.

Sodium montmorillonite, if used to clay the land, would cause the soil to become impermeable and incapable of sustaining crops. However the tremendous swelling ability associated with the sodium form, directly responsible for the development of this imperviousness, is the very property desired in the majority of its uses today. Indeed, water impedance itself, whether to prevent seepage from ponds, dam walls, canals and irrigation ditches, or to protect the outsides of basement walls, is one such area of use. Even so, the history of sodium montmorillonite is not nearly so illustrious as that of its calcium analogue.

The first commercial shipments of sodium montmorillonite, from Rock Creek, Albany County, Wyoming, were not made until 1888.[37] Shipments went to New York, Philadelphia, Chicago, Milwaukee, Boston, Denver and San Fransciso, but the quarry was unable to ascertain for what purpose it was being used. To this effect, in 1898 W.C. Knight stated [38] "The most singular feature connected with it (sodium montmorillonite) is that no one seems able to find out the use of this clay".

Many uses were found though and within ten years the Wyoming montmorillonite, or bentonite, was being used in the manufacture of soap, as a packing for a special kind of horseshoe, as a diluent for powerful drugs, and as an adulterant of candy.[124] Soon after this it gained commercial value as a water softening agent, exchanging its alkali for the lime of hard water.[40] In addition to the cation exchange mechanism, as a colloidal electrolyte the bentonite also served to precipitate out salts from solution, so aiding the softening process.[33]

Modern applications are today so numerous that they are best subdivided into large tonnage and small tonnage uses. Of the large tonnage applications, filtration and clarification, water impedance, and general absorbent uses have already been discussed, and oil well drilling fluids, being a major application for clay/organic cation complexes as well as for the mineral clays, will be discussed in the following section. It has been however, along with the foundry and iron ore pelletizing industries, one the of largest users of smectite clays of the past three decades.

Several million tonnes of smectite clays are used annually in foundrys for the preparation of moulding sands. The clay must give the sand mould sufficient strength to maintain the cavity, formed by the removal of a pattern, before, during and after the pouring of the hot metal. The mould itself may be made of sand, clay and tempering water, as in greensand practice, or of sand bonded by clay, after the tempering water has been dried out, as in drysand. Thus, both green and dry strength, as well as flowability and hot strength are important properties of moulding sands. The process was invented in the fourteenth century as an improvement upon the lost wax process, but for hundreds of years only natural sands, containing a high proportion of clay, were used. The first synthetic moulding sands were not made until the early part of the twentieth century, when a mixture of pure silica sand and Wyoming bentonite was used.

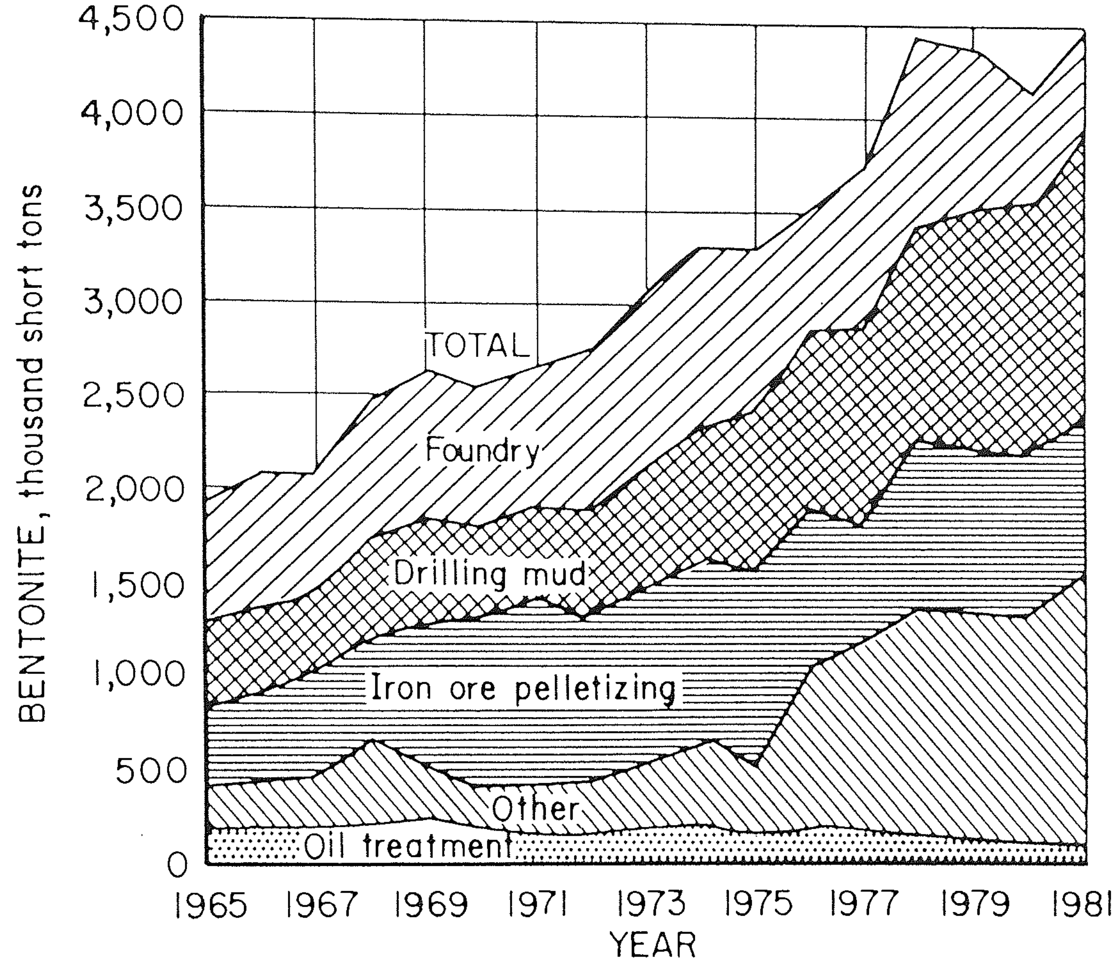

Figure 1.15 Bentonite sold or used for specified uses [39]

At the beginning of the last quarter of this century, pelletization of iron ore had not only overtaken foundry use in terms of tonnage used, but was the largest single use of smectite clays. This is despite the fact that it was not used for this purpose until just twenty years previously. Low grade ore is ground to a fine particle size so that impurities can be separated from the iron. The fine grained ore concentrate is then pelletized into units of the order of one inch or more, using smectite clays as a binder, prior to drying and packaging, so that it can be used as blast furnace feed. Only natural sodium or sodium exchanged smectite clays are suitable for this application, as they are the only clays to provide the required pellet development and binding strength.

Of the two other uses that may be classed as large tonnage ones, the first, as animal bedding or pet litter, is really just the largest of the absorbent based applications. Granular grades of clay about 10-30 mesh are heated to between 400°C and 1000°C to develop their absorbent capacity and deodorizing activity.

The second is as a carrier or diluent in the pesticide industry. The clay is important in attaining a uniform dispersion of the toxicant, in helping the plant to retain the pesticide in the wind and rain, and preserving the pesticides toxicity. Various types of clays are used but bentonites have the capacity to stick well to the leaves and so are components of many pesticide formulations.

There is an ever increasing number of miscellaneous small tonnage and speciality uses of smectite clays. Some of these have been developed from centuries old uses of clay materials, whilst others are genuinely new applications.

Smectite clays have long been used to make bricks for housebuilding. They are also now added to cements and mortars, to enhance impermeability and overall workability, and to structural clay products generally, to increase the plasticity required for extrusion. The ceramics industry too now uses small amounts of low iron smectites, both to impart strength and vitrification properties to ceramic bodies, and to provide slips with good suspension characteristics.

The high purity with which such minerals can now be obtained has increased their value in many of the areas where clays first found application. Soap manufacturers are now showing renewed interest in sodium smectites, because of the environmental problems connected with phosphates, and the pharmaceutical and cosmetics industries are now using more than ever before. Smectites are also still used in food production, though primarily as a binding agent in pelletized animal feed. The printing and paper industries too use small quantities of smectite clays, both within the inks themselves, to control consistency, and as a surface coating to, or filler within, the paper, to increase both the quality of the paper and the quality of electrographic printing.[125]

Arguably the most modern application for smectite minerals is in the field of radioactive waste disposal. Waste streams carrying radioactive materials of high biological activity, are treated with sodium montmorillonite, which absorbs these isotopes, so decontaminating the waste water. Once the radioisotope is bound to the clay it is made inaccessible by calcining the clay to vitrification point, so collapsing the structure. More recently sodium smectites have been used as barrier materials, packed around buried canisters in waste repositories, ready to store up any slow leakage.[126]

Catalysis though is perhaps the most important of the rapidly growing number of new applications. Montmorillonites and acid treated montmorillonites have been used as catalysts for only the last fifty years or so, but already many classes of reactions have been shown to give better yields, in shorter times or at lower temperatures, when carried out over clay catalysts. In most cases the clay acts purely as a solid source of protons, which derive from the dissociation of interlayer water molecules coordinated to the exchange cations.[127] Thus, due to their greater polarizing power, trivalent exchange cations such as A1, Fe or Cr confer greater catalytic activity upon the exchanged clay than do monovalent or divalent cations. The acidity of the interlamellar water also depends upon the amount of such water present,[128] and thus the reaction temperature. Below 100°C the interlayer cations are fully hydrated and the clays behave only as weak acids, whereas between 150-180°C, when the cations are no longer fully hydrated, the clays behave as much stronger acids.[129]

By far the largest market for acid catalysts is as cracking catalysts, however synthetic zeolites have largely replaced clays in this field because they have superior thermal stability and suffer much less from the formation of surface coke deposits which reduce the catalytic activity. Acid catalysed reactions abound though, and clays and pillared clays have been shown to catalyse many of them. The published literature now contains an array of examples, such as the condensation of methanol to olefins,[130] the hydration of olefins to ether,[131] the esterification of aliphatic alcohols with aliphatic acids,[132] and the selective alkylation of 1, 2, 4- trimethylbenzene to durene.[133] The polymerization of styrene to solid polymers in the presence of montmorillonite and other clays has also received attention. Here though the clay behaves primarily as a chemical initiator, forming the reactive intermediate, a carbonium ion, by proton transfer to the monomer.[134, 135]

There are also several industrial scale syntheses involving the use of montmorillonites, for example the dimerization of unsaturated fatty acids to dicarboxylic acids.[27] It is thought that in this reaction the activation of the double bond is brought about by interaction with an empty 3d orbital on silicon, once the alkyl chain is lying flat on the silicate surface. Other reactions catalysed by smectite clays include the dehydrogenation of cyclohexane to benzene [136] and a variety of isomerizations and redox reactions.

1.8.3 The industrial history of surfactants

Today the domestic product area is by far the largest consumer of surfactants, and indeed the oldest man-made surfactant is soap. The Sumerians, who inhabited the region between the Tigris and Euphrates rivers, were producing soap from a mixture of oil and wood ash in 2500 BC. Their detailed account of the process, that has survived along with some of the product, constitutes the oldest known record of a chemical reaction.[137]

Soap manufacture was also known to other ancient cultures. The Egyptians utilized soap formulations with special additives for medicinal purposes, and the Gauls applied it as hair pomade. The development of commercial soap production had spread from the Mediterranean region, with the development of a technical process for soda ash manufacture and an improved transportation network for the import of large quantities of low cost tropical vegetable oils, to all the other European countries by the second half of the eighteenth century.

By the early part of this century though, the continual search for improved detergents meant turning away from soaps. Their alkaline reaction and sensitivity towards water hardness provided insurmountable problems. The first synthetic soap substitutes proved to be excellent wetting agents, but showed poor detergency performance. However, in 1928, with the sulfation of fatty alcohols, the first synthetic washing active substances had been discovered.[138] With the development of an economically feasible route to their large scale manufacture a few years later, the first synthetic detergent was brought onto the market by the German company Henkel in 1932. The surfactants from natural fatty alcohols were quickly followed by other groups of synthetic surface active substances, and in 1953 for the first time the total tonnage of 'as sold' synthetic detergents exceeded that of soap.[139] By the end of the decade soap had almost completely been replaced as the surface active ingredient in detergents. In practice, tetrapropylenebenzene sulphonate (TPS) was most often used, but it too was soon replaced as biologically 'soft' surfactants began to dominate the market, with linear alkylbenzene sulphonate (LAS) initially commanding the largest market share.

Today applications of surfactants can be found in an enormously diverse range of industries, from agriculture to textiles, as antistatic agents or viscosity modifiers, and a complete review would be inappropriate here. A much more complete overview of modern industrial applications has been written recently by Karsa.[120] It is generally true however that, with few exceptions, industrial surfactants are used either as essential additives or processing aids. In many cases they are only a minor part of a particular system or formulation, and so may be regarded as a true 'performance' chemical. Detailed knowledge of a surfactant's composition and surface active properties is necessary for selection of the optimum product for a particular end use, thus it is not easy to generalize about the distribution of surfactants by chemical type.

This said, the first synthetic detergents were anionic, and this class of surfactants continues to dominate the field in terms of total tonnage. Of the anionics, alkylbenzene sulphonates continue to be the major product, offering low cost and great versatility. Anionics also offer high foaming power, but this is becoming increasingly undesirable in a number of applications. Consequently, the sale of nonionics is increasing in these markets as they offer both superior cleaning power and low foaming power. This class continues to be dominated by ethylene oxide adducts of alkyl phenols and fatty alcohols. The cationics, like the nonionics, have a small but rising percentage of the total surfactant market, and will be discussed in greater detail in the following section.

1.8.4 Application of cationics

In most of their applications the cationics do not compete with other surfactants. They compete with non-surface active products such as the phenolic germicides and the tallow textile softeners. Consequently their economic behaviour, as well as their areas of use, does not always mirror that of the anionic and nonionic surfactants.

The cationic surfactant market is still dominated by quaternary ammonium salts of the distearyl dimethyl ammonium chloride type which are used in domestic fabric conditioners. However, the alkyl group is either tallow-derived, so the supply is limited by mutton and beef consumption, or coconut-oil-derived, so the supply is limited by climatic restrictions to the Philippines, Indonesia and other tropical areas. The introduction of petrochemical alkylamines would appear to be inevitable if the market continues to grow rapidly, but for many applications they still do not provide the same performance as the naturally derived alkyl chains. Analogous compounds, derived from phosphorus, arsenic or sulfur, have virtually no commercial importance because they are either too toxic or too expensive.

Cationics are unsuitable as detergents and even tend to act as soil fixatives. However once the garment has been cleaned, cationics are used in the rinse as fabric conditioners. In fact fabric conditioning is the largest single application of cationic surfactants. Formulations are based on either dihydrogenatedtallow dimethyl ammonium chloride, or ditallow imidazolinium sulphate, in isopropanol solutions.[140]

The former is generally considered to give the better performance, but is inconvenient to process, being a low melting paste, and so the tallow based imidazoline, a liquid at ambient temperature, is preferred by some smaller manufacturers. There is good correlation between chemical structure and softening characteristics. Increasing the chain length of a mono long chain quaternary ammonium compound, from C12 to C18 and again to C22, results in increased softening, with the optimum number of alkyl chains per molecule being two. Interestingly a tallow derived alkyl group imparts better softening than a coconut oil derived one.[141]

Fabric conditioners must be capable of being preferentially absorbed from rinse water onto fabric relatively rapidly. During the wash cycle, which is usually conducted under alkaline conditions, fabric acquires a negative charge, causing the positively charged cationic micelles to be adsorbed almost quantitatively. If a concentration of 0.075% of softener, based on the weight of fabric, is used 85 to 95% will be exhausted onto the fabric within 1 to 3 minutes.[142]

Exhaustion is enhanced by using high molecular weight quaternaries with low water solubilities. This near quantitative adsorption gives the cationics an advantage over the anionics insofar as they are effective as much lower concentrations. A level of 0.1% based on fabric weight is sufficient to give a good 'hand' to the treated textile. This treatment results in a softer feel and greater fluffiness, an increased drying speed and ease of ironing, and a noticeable antistatic effect that causes the garments to stay cleaner for longer.

Although rarely used as detergents, cationics do have other textile applications. They are commonly used as dye fixatives for anionic dyes, tying up any excess dye adsorbed on the fibre, but as the resulting complex is not fixed directly to the fibre it is removed by washing with detergents.

Cationics are also used as antistatic agents in their own right during synthetic fibre manufacture, where the spinning and weaving processes would be impossible without them. Lastly, a variety of cationics, such as alkyl trimethyl ammonium chloride and cetyl pyridinium chloride, have been used as dry cleaning additives.

Quaternary ammonium salts with only one long alkyl group, C12-C18, or two somewhat shorter alkyl groups, C8-C10, are primarily utilized as antimicrobial active substances. Probably the best known among these are the benzalkonium chlorides.

In this application, the alkyl chain is usually coconut oil derived. Benzalkonium chlorides show a fairly broad spectrum of antimicrobial activity, but most cationics show some degree of activity.

Fatty amines, amine salts, and quaternary ammonium compounds are all employed as emulsifying agents. In this capacity they are most frequently used in the preparation of bitumen emulsions for road construction, although the general principles suggest that cationic emulsifiers offer good potential for a wide variety of o/w and w/o emulsion systems. During road building the bitumen is applied to the road surface in a molten state, and chippings are subsequently spread onto, and rolled into, the surface by the use of a road roller. The purpose of the emulsion is to improve the adhesion of the hydrophobic bitumen to the hydrophilic aggregate, so that the road becomes more resistant to water. Thus, bitumen emulsions can be poured even while it rains.

Cationic bitumen emulsions have a number of advantages [141] over anionic systems. They are tolerant of hard water to the extent that $CaCl_2$ is sometimes added when extreme long term stability is required. This makes them easier to produce, with dispersants and stabilizing additives being unnecessary. They also give good stone-coating results over a much wider range of aggregate types than do anionic systems, and are applicable to both wet and dry aggregates. The cationic most widely used for this purpose is the diamine derived from octadecylamine via cyanoethylation and hydrogenation.[140]

A few other specific uses of quaternary ammonium compounds exist, primarily as hair conditioning agents and manageability additives in shampoos, and occasionally as pigment dispersion agents in oil based paint formulations, but other cationics, mainly fatty amines, find applications in other fields. Among these is corrosion inhibition, where a mineral oil solution of fatty amines is used to provide a protective film on steel, or as an ingredient in cutting oil formulations. Cationics are also frequently added to crude petroleum in order to protect pumps, pipelines and storage tanks from corrosion.

The major area of use though is in ore benefaction, either as solvent extraction agents or flotation agents. Solvent extraction is a technique that is customarily used when the desirable element is present only in low concentrations but is extremely valuable. One example that illustrates this perfectly is the solvent extraction of uranium ores with kerosene.[141] Here the ore, typically containing 2kg of U_3O_8 per tonne, is leached with sulphuric acid, and the resulting aqueous solution of uranyl sulphate is extracted into kerosene as the uranyl amine complex, $(R_3NH)_2UO_2(SO_4)_2$. This is then stripped from the separated organic phase by extracting the kerosene fraction with 5% aqueous NaCl at pH1. The uranyl amine salt is converted to a water soluble form of the uranyl sulphate anion, $[UO_2(SO_4)_2]^{2-}$, and the amine is retained in the kerosene layer for recycling.

Finally, both cationics and anionics are employed as flotation agents in ore flotation processes. Cationics will form a monomolecular film on the surface of negatively charged ore particles, and anionics, analogously, will coat positively charged particles. Whichever surfactant type is chosen, the result is a hydrophobic coating of the ore particles. Then, during the flotation process, air bubbles are passed through the suspension and cause the hydrophobic components to float on the surface of the water. Cationic surfactants, usually fatty amines or amine salts, are used in the flotation of potash ore, phosphate rock, quartz and feldspars, and many other ores.[143] In the specific flotation process for iron ore, cationics find their greatest utility in the flotation of the siliceous constituents.[144]

1.8.5 Industrial applications of organoclays

Complex formation between clays and organic substances has been known since antiquity, being the basis of the wide use of clays for decolourizing edible oils, clarifying alcoholic beverages, and fulling earth. However, it was not until the 1930's that a systematic investigation began into the reactions of clays and defined organic cations and bases. This early work was undertaken by soil scientists, with the aim of understanding the mechanisms underlying the formation of clay humus complexes, because it had been supposed that the stability and resistance of organic matter in soils were, at least in part, due to such complex formation.[73] The focus of attention soon shifted to systems consisting of pure clay mineral species and well defined organic compounds because of the complexity of soil constituents. Workers in other areas soon became involved, as clay-organic systems began to find applications in a variety of industries.

Today that diversity of application is such that it is again desirable to subdivide uses into either small tonnage or large tonnage ones. Of the small tonnage applications, the use of organoclays in cosmetics and polishes is really just an extension of the use of mineral clays. Foundry technology too has begun to incorporate the use of organoclays as well as mineral clays. Foundry moulding sands utilizing organoclays, and oil instead of tempering water, have been found to be advantageous for small castings which are required to have an especially clean surface.

Organic exchanged smectites are used in some inks to control consistency, penetration and misting during rotary letterpress printing. By reducing misting, the release of very small droplets of ink into the atmosphere when the ink is pinched between the ink roller and the transfer roller, high printing speeds and clearer print room conditions are possible.[145]

Many applications in waste disposal also exist, with enhanced immobilization of organic toxicants present in leachate water being achieved by using organoclays as sorbents.[146,147,148] In general, the more hydrophobic the cation on the smectite the greater the uptake of the pollutant, chlorophenols, via non-polar interactions between it and the alkyl tails on the exchange cation. The construction of landfill liners, by exposing a portion of the subsurface material to hydrophobic organic cations during its installation, may be envisaged as a way of utilizing this process industrially, wherever the subsoil has a significant clay content.

Chlorophenols have also been efficiently bound to a novel type of modified clay adsorbent, an inorgano-organo-clay.[149] Such clays have their exchange sites blocked off by polycations, and a cationic surfactant apparently irreversibly bound to the surface.[150] The surfactant then acts as the source of surface organic carbon in the binding of the pollutants to the clay. Apart from chlorophenols, highly effective removal of benzene from water has also been demonstrated, in this case using tetramethylammonium exchanged Wyoming bentonite.[151]

In the laboratory organoclays may be used as stationary phases in gas-liquid chromatographic columns, with complete separation of problematic organic mixtures, such as the isomers of xylene and other C8 aromatic hydrocarbons,[152] being possible. The retention values appear to be related not only to the available pore space and steric factors, but also to the magnitude of the layer charge and the location of this charge in the silicate structure. More recently, quaternary ammonium exchanged smectites have been used successfully as phase transfer catalysts. Among those reactions studied using such a system are the preparation of symmetrical formaldehyde dialkyl acetals from dihalomethanes and primary alcohols,[153] and a range of organic nucleophilic displacement reactions.[154]

Greases, paints, fibreglass resins and drilling fluids constitute the large volume applications of organophilic clays. The simplest of these is the production of a grease, which is essentially a lubricating oil which has been gelled by the addition of between 5 and 12 percent w/w of an organoclay. This serves to increase the apparent viscosity of the oil, and to change it from a Newtonian fluid into a thixotropic fluid. When subjected to shear the grease will flow, and is thus able to lubricate the moving part to which is has been applied, but when the shear ceases, the grease gels rapidly, and is retained within the joint or bearing.

A recent development is the self activating organoclay grease gellent, which incorporates a polar activator attached directly to the clay platelets.[155] A conventional grease formulation requires the addition of a polar activator, usually methanol, acetone, or propylene carbonate, by the grease manufacturer. This then attaches to the silicate surface so lifting the hydrocarbon tail of the organic cation off the clay, and promoting partial dispersion via an increase in basal spacing between the platelets within an individual stack. Complete random dispersion, or the separation of platelet stacks into individual platelets, can then easily be achieved by mechanical shear. Gelation, the formation of a network of intermolecular hydrogen bonds between the platelet hydroxyls, will then occur, so long as a gel promoter, water, is also present.

Recent work [156] has clearly established that dispersion and gelation are two independent phenomena, and that water can only aid in the latter. Furthermore, the old polar activators such as methanol, also act as degellants, interfering with the hydrogen bonding network and lessening the overall strength of the final gel, possibly by withdrawing water from the hydroxyl network of the platelets. Since with the new self activating organoclays no added activator is present to lessen the strength of the gel structure, the new technology allows the grease manufacturer to achieve the maximum rheological benefits of the organoclay additive with a minimum of formulating adjustments.

The behaviour of organoclay rheological additives in grease systems is similar in many respects to their behaviour in paint and coatings systems. Paint is a loosely used word covering a whole variety of materials, such as enamels, lacquers and varnishes, as well as primers, undercoats and surfacers, but they are all formulations based on three principle ingredients. The pigment has both decorative and protective properties, but unless it is combined with a resin or binder, it rubs off. The third basic ingredient is the solvent or vehicle for the pigment, which enables good penetration into intricate crevices to be achieved. A whole range of additives, present in only small amounts, but having a profound influence on the paints physical and chemical properties, then complete the formulation.[157]

In oil-based paints, organoclays play a vital role in stabilizing the colloidal system, by preventing pigment settling, reducing separation of liquid components, and controlling absorption into porous substrates. Application benefits are also provided as sag is minimized, while brushwork imperfections are still able to smooth themselves out. Recent years have seen a rapid increase in the variety of paint systems available, from 'high solids' paints, essentially just pigment and a liquid resin, to aerosol paints, which require organophilic clays capable of ensuring that the heavy pigment particles settle only to a soft, voluminous, easily redispersible, sediment.

Fibreglass resin is a 50% w/w solution of low molecular weight unsaturated polyester in styrene. An organic peroxide initiator, and a metal soap catalyst, cause the styrene to cross-link the polyester to give a tough thermoset plastic.[158] The thixotropic properties needed by the liquid resin are similar to those required for paints. Additives and fillers must be suspended during prolonged storage, separation of the fibreglass, and consequent sagging of the composite, must be prevented while the resin is curing, and the apparent viscosity at high rates of shear must be low, to enable easy pumping and spraying onto the mould. It is generally accepted that the optimum time for full viscosity recovery after cessation of shear is approximately two minutes.

Oil well drilling fluids comprise the fourth and last major use of organoclays. High-swelling bentonites, in their natural form, are actually still used in far greater tonnages than organic clad smectites, but while the popularity of the former is quickly falling, organophilic clays are being used increasingly in drilling fluid formulations. The total market for organoclays is also very much smaller than that for mineral clays and so shows far greater dependence upon drilling mud use than does the wider, overall clay market.

If drilling fluid is defined as a material employed to aid tools in the creation of a borehole, the use of drilling fluids antedates the petroleum industry. Fresh water was the first drilling fluid, and its use can be traced back nearly two thousand years to the Egyptians, and almost three thousand years to the Chinese.[45] The percussion method of drilling was used, with water being poured into the hole and the cuttings removed by bailing. Circulating drilling fluids for the rotary drilling system have been in use since the mid 1800's,[159] but still the drilling fluid circulated was water.

It is probable that the advantage of having a mud present in the drilling fluid was discovered by accident. By the end of the last century it was well known that a natural water/clay suspension was often formed when the drilling bit passed through shale formations, and it was felt that this helped line the walls of the hole. So when in 1900, during the drilling of the famous Spindletop well in Texas, quicksand was penetrated and extensive fluid loss encountered, the drill crew introduced a clay/water suspension into the annulus, and the permeable sands were immediately sealed off and the hole prevented from caving in.[43]

Since that historic day the technique of drilling with bentonite muds has developed almost beyond recognition. The functional requirements placed on the mud have grown from one, cutting removal, to many, including gas pressure control and hole stability maintenance. Nevertheless, it was not until the use of weighting agents, particularly barytes, to help suspend the drill string, became established in the 1920's that an efficient, low-cost suspending agent became an absolute necessity, and bentonite was officially recognised as a drilling mud additive.

Only certain sodium and sodium exchanged calcium smectites had the potential to meet the American Petroleum Institute (A.P.I.) or the Oil Companies Materials Association (O.C.M.A.) standards covering the use of clays in drilling muds,[50] but the development period of rotary drilling had begun, and with it came great advances in mud technology. In the early 1940's the low-pH phosphate or red muds were simple and cheap, but could not tolerate severe contamination of high temperatures, and so were inadequate for deeper drilling. Their limitations led to the development of lime muds for deeper wells, but it was during this transition period that an advance took place, which is commonplace today, but which probably did more to alleviate difficult hole conditions than any other technique of its age, namely the use of oil in the mud.[160]

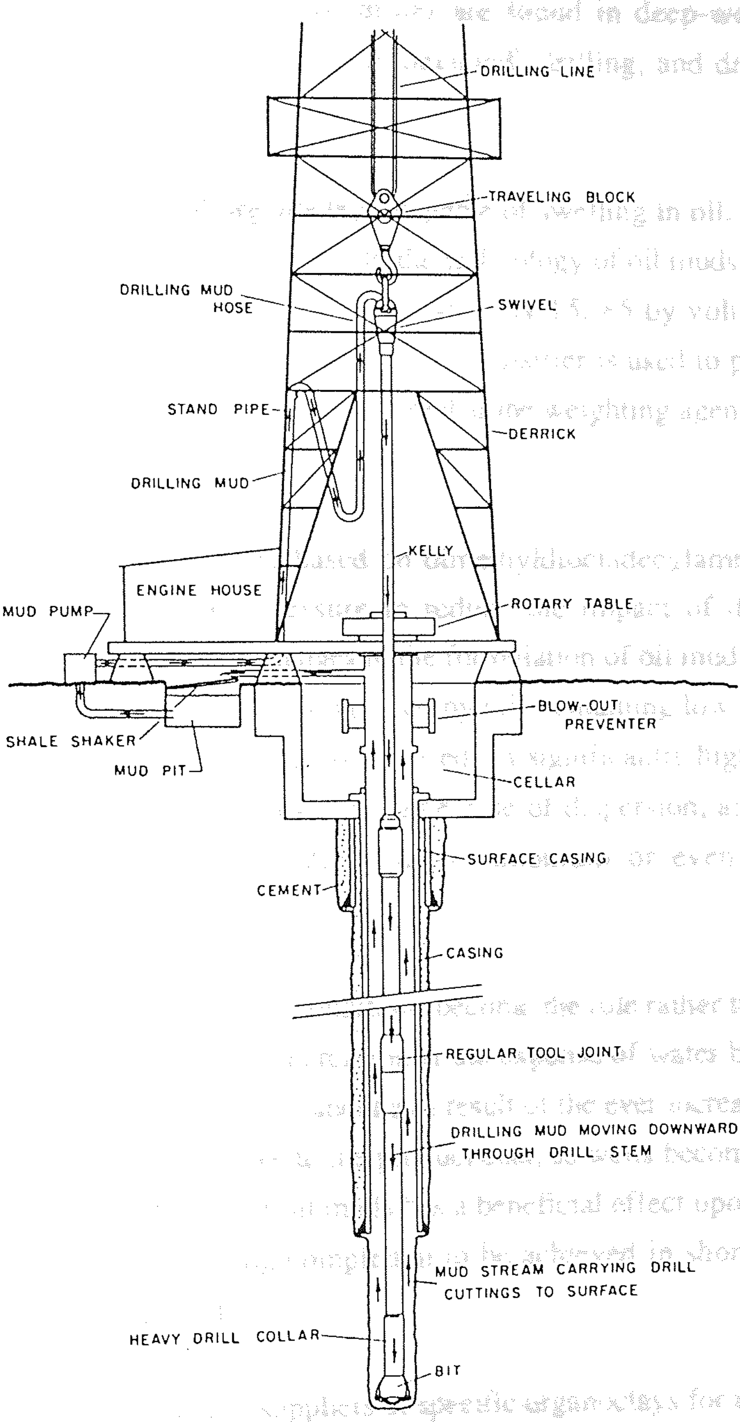

Figure 1.17 Circuit of drilling fluid through a well in rotary drilling [159]

Oil-based drilling fluids overcome certain undesirable characteristics of water-based muds that are primarily due to the properties of water itself,[45] such as its ability to dissolve salts, to interfere with the flow of oil and gas through porous rocks, to promote the disintegration and dispersion of clays, and to effect corrosion of iron. In addition, oil muds offer better lubricating qualities, high boiling points, and lower freezing points, but are always more expensive and so can be justified only if these particular advantages give superior performance under the particular conditions of use. Such conditions are found in deep-well (greater than four thousand metres) and curved, or 'deviated', drilling, and drilling through water-sensitive formations.[158]

The development of organoclays, capable of swelling in oil, as bentonite swells in water, was a major contribution to the technology of oil muds. An oil-based mud is an emulsion of water in diesel oil, typically 15: 85 by volume, with organoclay dispersed in the oil phase. A primary emulsifier is used to produce the emulsion, and a secondary one is used to ensure that the weighting agents and drill cutting are oil wet.

The early oil muds were based on dimethyldioctadecylammonium clays, but in recent years growing pressure to reduce the impact of drilling fluids on the environment has led to changes in the formulation of oil muds. In offshore drilling particularly, diesel has been replaced by oils containing low level of aromatics, so forcing a change in the organoclay used. A significantly higher organic content is required in order to achieve the same ease of dispersion, and consequently such muds use methylbenzyl dioctadecylammonium or even methyltrioctadecylammonium clays.[145]

Today, as 'special' drilling conditions become the rule rather than the exception, the use of oil-based muds is increasing at the expense of water based ones. One final advantage they have comes about as a result of the ever increasing contribution that actual drilling costs make to the product cost, as wells become deeper and drilling takes longer. The use of oil muds has a beneficial effect upon the penetration rate of the drill bit, allowing completion to be achieved in shorter times than would normally be expected.

Akzo, one of the major suppliers of specific organoclays for use in the formulation of oil-based drilling muds and other applications, sponsor this research. They were formed in 1969 as a result of a merger between AKU and KZO, and after several major acquisitions they are now one of the fifteen largest multinational chemical companies, with operations in over fifty countries, at more than two hundred and fifty locations world-wide.

Akzo's activities are organised into four divisions, fibres and polymers, coatings, pharmaceuticals, and chemicals. The chemical division traces its roots to the early stages of the industrial revolution, with the establishment of a sulphuric acid production site in Amsterdam in 1835, and to a flour mill in Deventer in 1838. Today, the chemical division has emerged as a leader in a number of speciality chemicals, including polymerization and cracking catalysts, insoluble sulphur for the tyre industry, and fabric softener bases for the detergent industry, as well as a range of speciality use organoclays.

1.9 Project Objectives

When the first systematic investigations into the formation of organoclays were carried out, in the 1930's, they were conducted from the viewpoint of the clay mineral itself. An organoclay was merely the product of a reaction between a clay mineral and an organic cation or base. Such reactions are important in soil chemistry, and were initially studied more than were the product organoclays themselves.

However, clay-organic systems soon began to find applications in a variety of industries, and today speciality use organoclays are now being developed for an increasingly large number of specific applications.

Commercially, organoclays have traditionally been prepared by contacting a dilute aqueous dispersion of sodium montmorillonite with, usually, a dialkyl dimethyl ammonium salt. A major advantage of this 'wet' method is the inherent removal of abrasives naturally present in the parent mineral clay, although the cost is measured in both time and money.

An alternative method, recently developed at Akzo, is the 'dry' method, which is essentially just the intimate dry mixing of the reagents. This is both quicker and cheaper than the 'wet' method, but no refining of the clay is achieved. Consequently the product is unsuitable for applications in which a smooth 'feel' is essential.

The major objective of this work is to explore the 'dry' method as a process, and to examine the nature of the organoclays produced, for the production of a wide range of commercially usable organophilic clays in a facile way.

The role, if any, of the natural impurities mined with the clay in determining the bulk properties of the 'dry' process product is examined in Chapter 3. An air classification treatment that resulted in the refinement of the Wyoming bentonite as received into 'coarse' (70%) and 'fine' (30%) fractions is also examined, with a view to producing a higher quality 'dry' process organoclay. It is also far from certain whether such solventless ion exchange goes all the way to completion, and so the distribution of quaternary ammonium compounds on the silicate surfaces of the product is also studied.

Many organic cations will exchange onto a clay, and in Chapter 4 a tetracationic cyclophane, a complex quaternary, is studied. In addition to its behaviour as a simple organic cation in undergoing ion exchange onto a clay, it is known to take part in charge-transfer chemistry with a variety of electron-rich molecules. This facilitates the study of host/guest chemistry on a bound surface as a possible route to robust and durable chemical sensors.

Finally, in Chapter 5, a more fundamental study of the types of exchange sites available within a smectite clay mineral lattice is conducted. The relationship between particle size, cation exchange capacity and chemical composition is examined, utilizing a number of physical techniques unavailable to the original workers in this area.

Chapter Two

STANDARD INSTRUMENTATION
AND METHODOLOGY
FOR
PREPARATION AND ANALYSIS

2.1 Materials and Chemicals used

2.1.1 Alkylammonium salts

Arquad 2HT-75 and Arquad 218-100 are Akzo trade names for quaternary alkylammonium salts used at their Littleborough site for the commercial production of organoclays.

Arquad 2HT-75 is a 75% solution, in 60% propan-1-ol/water, of dihydrogenated tallow dimethylammonium chloride, $R_2N^+(CH_3)_2Cl^-$, where R is hydrogenated tallow alkyl, predominantly stearic alkyl, $C_{18}H_{37}$-, but also containing C_{16}(31%), C_{14}(4%) and C_{12}(1%).[161]

Arquad 218-100 is a purer product, close to 100% dioctadecyl dimethylammonium chloride $(C_{18}H_{37})_2N^+(CH_3)Cl^-$, that is an off-white solid at room temperature.[162]

2.1.2 Clay minerals

The montmorillonite used for this work is supplied to Akzo by Steetley Minerals Ltd. as Wyoming bentonite G.G. grade. The raw mineral, originating from the Wyoming-South Dakota area of the United States, is a yellowish grey in colour, with a C.E.C. of 70 meq per 100g by ammonium ion exchange.[163] A sample of the mineral in its 'as mined' state has also been obtained direct from Steetley Minerals Ltd. for examination.

Laponite is a synthetic smectite clay, its natural analogue being hectorite. It is a white sodium clay, and is supplied by Laporte Industries Ltd. in several forms. The purest of these is Laponite RD, its idealized formula being $Na_{0.7}Si_8(Mg_{5.3}Li_{0.7})O_{20}(OH)_4$.[164]

2.1.3 Other reagents

Armeen M2HT, a ditallow methylamine, R_2NCH_3, where R is hydrogenated tallow alkyl, was obtained from Akzo, and di-n-decylamine, $(C_{10}H_{21})_2NH$, was obtained in low purity from Lancaster Synthesis Ltd. The pillaring agent aluminium chlorohydrate, ACH, was obtained from Reheis chemicals. All other reagents were of 'A.R.grade', or if not obtainable, then 'General purpose reagents' were used.

In view of the importance of the role of cations in clay chemistry, all aqueous chemical solutions were made up with distilled and deionized water.

2.2 Methods for the Modification of Clays

2.2.1 Modification via the 'wet' process

Organoclays have traditionally been prepared by contacting a dilute aqueous dispersion of sodium montmorillonite with, usually, a dialkyl dimethyl ammonium salt.

Commercially, the raw clay is first made up with water to a 4% slurry, to which a dispersant, sodium phosphate, is added in order to lower the viscosity. A degree of refining is now achieved through centrifugation of the slurry, resulting in the removal of the majority of the mineral impurities and abrasives in the sediment. To the clean clay slurry, the appropriate amount of organic cation necessary to achieve the desired degree of ion exchange, and 1% w/w of sodium carbonate, required [50] to improve fluid loss and viscosity of the product mud, is then added. The mixture is then stirred until exchange is complete, with the product organoclay finally being isolated by passing the reaction mixture through a press filter.

The major advantage of the process is the inherent removal of abrasives. This allows the product to be used in a wide range of applications, such as cosmetics, paints and polishes, in which a smooth 'feel' is essential. However, for physical reasons not all clay: organic ratios are filterable. Organoclays incorporating hydrophobic organic cations are only filterable near to the C.E.C. of the clay, and those incorporating hydrophilic organic cations will not filter at all, even at exact exchange. In addition to this problem, taking the dry clay into dilute dispersion and then removing all the water again after the reaction is complete, is both costly and time-consuming.

On a laboratory scale, previous work [165] has shown that complete cation exchange may be achieved by placing the reaction mixture in a sealed conical flask, and attaching this to a wrist-action mechanical shaker for one week. This procedure has been adopted to simulate the 'wet' process throughout this work, unless variations are specified.

2.2.2 Modification via the 'dry' process

'Dry' process organoclays are produced in approximately 1.3 Kg batches in the laboratory, using a high shear mixer, operating at 60°C to maintain the organic cation in its molten state. The raw clay and 1% w/w of sodium carbonate are initially dry blended for one minute, 100 cm^3 of water is then blended in for five minutes before the appropriate amount of organic cation is added. The mix is blended for a further thirty minutes, before being extruded, dried in a fluid bed drier, and milled.

This method is both quicker and cheaper than the 'wet' process, but the product organoclay is of inferior quality in that it still contains abrasives and impurities mixed with the clay, prohibiting its use in many applications. The role, if any, of these impurities in determining the bulk properties of the product is not known. It is also far from certain whether the reaction goes all the way to completion. All these points have been addressed during the course of this work.

2.2.3 Modification via microwave heating

Much recent interest has been shown in the potential of microwave heating in many branches of chemistry. Significant decreases in reaction completion time have been reported for the synthesis of both organic [166] and organometallic [167] products. The rapid synthesis of intercalation compounds [168] and the acceleration of organic reactions carried out on inorganic supports such as montmorillonite [169] have also recently been achieved utilizing microwave irradiation. Further, the process of ion exchange onto clay has been recently demonstrated to be greatly accelerated by the use of a conventional microwave oven.[170]

For all similar work here, a standard domestic microwave oven, Sharp Carousel IIR-84801, 650 W, is used together with 120 cm^3 screw top teflon pressure vessels. The tightly sealed vessels, containing not more than 10 cm^3 of reaction mixture, are then subjected to five one minute bursts of microwave energy.

2.2.4 Preparation of homoionic mineral clays

The type of exchangeable ion associated with the clay is very much dependant upon the environment in which the clay was originally formed. It is due to the marine environment present at the time of the formation of the South Dakota and Wyoming

Cretaceous bentonites that these minerals are predominantly associated with sodium counterions when mined today. However, in relatively recent times, groundwater leaching has led to a partial replacement of the sodium by calcium and magnesium, derived from overlying shales and limestones.[50]

The standard method recommended for the preparation of homoionic mineral clays involves washing the clay with a 1M solution of the appropriate metal chloride [171] or metal hydroxide,[172] followed by separation of the clay by decantation. Although a high salt concentration initially aids flocculation, and hence washing, as the electrolyte concentration is lowered the suspension becomes prone to gelling. Alternative methods have been proposed, including the use of an ion exchange column packed with Amberlite IR120 synthetic ion exchange resin.[105] However, a novel approach is used here, based on the classic method of Posner and Quirk,[171] which utilizes a semi-permeable membrane to facilitate ion exchange and the subsequent removal of excess electrolyte.

Wyoming bentonite (5 g) is first washed with a 1M solution of the appropriate alkali metal chloride, and then separated by decantation. This procedure is repeated five times, and then a further three times at pH 3, adjusted with 1M hydrochloric acid. The clay is finally resuspended in the alkali metal solution at pH 3 and stirred for 36 hours. After separation by settling, the clay is dialysed against deionized water until no chloride ion is observed in solution, using the silver nitrate test.

2.3 Analytical Techniques

2.3.1 Atomic Absorption spectrophotometry

The elemental concentrations of various cations in aqueous solution were measured on a Perkin Elmer 373 spectrophotometer, employing a hollow cathode lamp and an oxidizing, air/acetylene flame. Calibration was carried out using BDH atomic absorption standards. For the standard conditions used, the working range was linear up to concentrations of approximately 1 ppm* for sodium and 5 ppm for calcium, in aqueous solution.

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* 1ppm = 1μg cm^{-3}

2.3.2 Diffuse Reflectance Ultraviolet/Visible spectrophotometry

Diffuse reflectance UV/Vis spectrophotometry was carried out on a Pye Unicam SP800B UV spectrophotometer, with an SP890 diffuse reflectance attachment. The spectra were run over a wavelength range of 300-700 nm, with magnesium oxide as the reference material. Freshly prepared, powdered magnesium oxide, from the burning of cleaned magnesium ribbon over a bunsen flame, was used on every occasion.

2.3.3 Elemental Analysis

Carbon, hydrogen and nitrogen elemental analysis was carried out in duplicate by Elemental Microanalysis Ltd of Oakhampton, Devon.

2.3.4 Gouy balance

Magnetic susceptibilities were measured with standard Gouy equipment, incorporating a Newport Instruments electromagnet and a Stanton SM12 balance. The apparatus was calibrated against a paramagnetic standard, $Hg[Co(NCS)_4]$, and gramme magnetic susceptibilities, χ_g, were calculated in the usual way.[173]

2.3.5 Fourier Transform Infrared spectroscopy

Infrared spectra in the range 4000-600 cm^{-1} were recorded using a Perkin Elmer 1710 FT-IR instrument. Either KBr discs or caesium iodide plates were employed for analysis of organic materials.

Infrared spectroscopy has also recently found extensive applications in clay mineralogy studies, because amorphous as well as crystalline clays absorb infrared radiation, making such a technique complimentary to X-ray diffraction spectroscopy. For the analysis of clays, a diffuse reflectance attachment was employed.

2.3.6 Laser particle sizing

Particle size ranges for samples of Wyoming bentonite were calculated using a M3.0 series laser particle sizer from Malvern Instruments. The necessary calculations are made by applying the theories developed for light scattering, and thus are based on the assumption that all particles are spherical. While this is most definitely not true for clay platelets in aqueous suspension, the assumption is valid for clay aggregates. Consequently, only aggregate size was measured using this technique. Iodomethane was the chosen suspension medium, as it would not significantly swell the clay, and was dense enough to retain the larger aggregates in suspension.

2.3.7 Magic Angle Spinning Nuclear Magnetic Resonance spectroscopy

Solid samples were analysed on a Brucker AC300 instrument with a solid state probe. The magic angle of 54.74° was set by minimizing the Br resonance linewidth for a sample of KBr. Spinning rates were of the order of 5000 Hz. Operating frequencies were 75.469 MHz for ^{13}C, 59.628 MHz for ^{29}Si, and 78.206 MHz for ^{27}Al. All spectra were measured relative to tetramethylsilane, $(CH_3)_4Si$, or aluminium nitrate, $Al(NO_3)_3$.

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

The clay samples to be analysed, approximately 0.25 g on a dry (105°C) basis, were first made up with 30-40 cm^3 of distilled water to 0.5-1% slurry. The slurries were then acidified by the addition of 1 cm^3 of dilute sulphuric acid (14 cm^3 conc. H_2SO_4 diluted slowly to a total volume of 100 cm^3), to aid in sharpening the end point. The methylene blue dye adsorption capacity was then determined by titration with standard 0.01M methylene blue dye solution (3.74 g Basic Blue 9, $C_{16}H_{12}N_3SCl.3H_2O$, dissolved in 1 dm^3 of distilled water). Increments of 1 cm^3 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 became confirmatory as a true end point if the titrated slurry still showed excess dye upon re-running the spot test after a two minute waiting period.[174]

Minor modifications to this method were made during the course of this work and are fully described in section 5.2.2.

2.3.9 Mössbauer spectroscopy

Mössbauer spectra were kindly provided by Professor F. J. Berry, Chemistry Department, The Open University. All spectra were computer fitted, and all isomer shifts quoted are relative to iron metal.

2.3.10 Optical microscopy

Wyoming bentonite samples were examined using a Reichert microscope with a 12 V, 100 W lamp.

2.3.11 Powder X-Ray Diffraction

Diffraction traces were obtained from a Phillips X-ray diffractometer using the Cobalt K_α line (1.791Å). Traces were recorded at 1°2θ per minute in the range 1-4 x 10^3 counts per second, at 1°2θ per centimetre and 400 full scale deflection.

Meaningful analysis is sometimes difficult if the sample is poorly crystalline or of very small crystal size. In such instances, such as when studying laponite, orientated samples were produced when possible by first gelling the clay, and then laying the gel onto a glass slide. Drying the gel in a slow and controlled way caused a clay film, in which the clay platelets were similarly orientated parallel to the glass slide, to form on the slide. This resulted in stronger reflections, pulling the peaks clear of the baseline noise.

The angle of each reflection can then be converted to the distance between the successive planes in the crystal that gave rise to that reflection by the application of the Bragg equation:

$$n\lambda = 2d\text{Sin}\theta \qquad [2.1]$$

where $n\lambda$ is the difference in integral numbers of wavelengths between waves scattered from successive planes of atoms, a distance d apart, when a beam of monochromatic X-rays impinges, at an angle θ to the planes, on the crystal.

Of particular interest in X-ray studies of clay minerals is the d(001) reflection. This is known as the basal spacing, or d spacing, and corresponds to the variable c crystallographic dimension. Thus any change in interlayer hydration or swelling manifests itself as a change in the position of the d (001) reflection.

2.3.12 Scanning Electron Microscopy

The particle sizes of several clay mineral samples were examined using a Cambridge Instruments Stereoscan S90B scanning electron microscope. A linked systems analyser was used for X-ray energy analysis to provide elemental composition data.

Drops of a dilute suspension of the clay samples were deposited on the surface of lightly polished brass sample stubs. After a few minutes, the drops were carefully washed away under a very gentle trickle of deionized water in order to ensure that only a few clay platelets remained on each stub. The stubs were then coated with a layer of gold in order to prevent charge build-up on the sample during analysis.

2.3.12 Solution Nuclear Magnetic Resonance spectroscopy

All solution work was carried out using a Joel FX90Q spectrometer, with an operating frequency of 89.56 MHz for ^{1}H and 22.50 MHz for ^{13}C. All spectra were obtained at 38°C at spinning rates of approximately 20 Hz, and 10 mm NMR tubes were used throughout.

2.3.14 Thermal Gravimetric Analysis

A Stanton Redcroft TG750 thermobalance was used for thermal gravimetric analysis. Approximately 80 mg of sample was used for each run, and a heating rate of 50°C per minute was employed. The temperature was initially raised to 105°C and held for 10 minutes, before being taken to 950°C and held for a further 15 minutes.

2.3.15 Ultraviolet/Visible solution spectrophotometry

Ultraviolet/visible solution spectra were obtained from a Pye Unicam SP8-100 spectrophotometer, using 1 cm quartz cells, over the range 300-700 nm, at a rate of 2 nm per second and at a chart speed of 10 seconds per centimetre.

2.3.16 Volhards method for total chloride determination [175]

The chloride solution to be analysed was first treated with excess of standard 0.1M silver nitrate solution. After filtration through a sintered glass crucible to remove any silver chloride formed, the residual silver nitrate was determined by titration with standard 0.1M thiocyanate solution, using an iron (III) indicator. At first a white precipitate was produced, rendering the liquid of a milky appearance, but as the end-point was approached the precipitate became flocculant and settled easily. The end point was reached when a permanent faint brown colouration appeared, indicating the formation of the thiocyanatoiron (III) complex, $[Fe(SCN^-)]^{2+}$.

The 0.1M silver nitrate solution (17.0 g $AgNO_3$ dissolved in 1 dm^3 distilled water) was standardized with a primary standard 0.1000M sodium chloride solution (2.922 g NaCl dissolved in 500 cm^3 distilled water). The 0.1M ammonium thiocyanate solution (8.5 g NH_4NCS dissolved in 1 dm^3 distilled water) was then standardized with the standard 0.1M silver nitrate solution. The iron (III) indicator solution consisted of a cold, saturated solution of ammonium iron (III) sulphate, $(NH_4)Fe(SO_4)_2$ $12H_2O$, in water, to which a few drops of 6M nitric acid had been added.[175]

2.3.17 X-Ray Photoelectron (XPS) spectroscopy

XPS spectra were determined using a VG Scientific ESCALAB 200-D instrument employing MgK_α (1253.6 eV) as incident radiation. $(C_{18}H_{37})_2N(CH_3)_2Br$ and KBr were employed as standard compounds for study of the Br (3d) spectra, and $(C_{10}H_{21})_2NH$ and $(C_{10}H_{21})NH_2Cl$ were used for the N(1s) spectra. Sample charging problems were overcome by calibrating the spectra internally with reference to the C(1s) photopeak (E_b = 284.6 eV).[176] Deconvolution techniques were employed for analysis of the spectra, with the process being terminated when the simplest fit consistent with a satisfactory reduced χ^2 value was obtained.

Chapter Three

STUDIES OF ORGANOPHILIC CLAYS - THE DISTRIBUTION OF QUATERNARY AMMONIUM COMPOUNDS ON THE SILICATE SURFACES, AND THE ROLE OF NATURAL IMPURITIES

3.1 Preliminary Studies of Wyoming Bentonite

Wyoming bentonite is a natural material, and so some time was taken to characterize it as fully as was practicable. As with all impure materials, the influence of the impurities upon the bulk cannot be ignored unless their nature is well established and understood. Here, various techniques have been employed to establish the nature of the impurities present in the clay, both as received, and after treatment.

The treatment the clay received was an air classification treatment that resulted in the refinement of the material into 'coarse' (70%) and 'fine' (30%) fractions. If this also constituted a genuine chemical separation, it would lead to the development of a purification technique for the clay going into the 'dry' process.

3.1.1 Characterization of Wyoming bentonite GG as received

The Wyoming bentonite GG is a yellowish grey bentonite, with a specific gravity of 2.5 and a pH (5% suspension in distilled water) of 9.3. The material has been milled so that 96% passes a 150 microns mesh as a dry powder (<99% as a wet dispersion) and 63% passes a 53 microns mesh (96% as a wet dispersion).[163]

Comparison of X-ray powder traces (XRD) of Wyoming bentonite GG with standard diffraction patterns [177,178,179] indicated montmorillonite to be the major clay mineral in the sample. An observation of particular interest was a low angle first-order diffraction at an angle of $2\theta = 7.3°$ implying a basal spacing of 14Å, in good agreement with accepted values for such materials.[179] The second-order reflection, characteristically absent in montmorillonites,[14] was not observed.

Other reflections observed could be attributed with confidence to α-quartz, which was the major impurity. Additional impurities suggested by the XRD data included corundum (Al_2O_3), feldspars (Na (or K or $Ca_{0.5}$) $AlSi_3O_8$), calcite ($CaCO_3$), siderite ($FeCO_3$), and possibly Pyrite (FeS_2), and hematite (Fe_2O_3). Concentration of the impurities by centrifugation prior to analysis gave slightly stronger, though not definite, evidence that all the above mentioned minerals are present in small amounts within the bentonite. All are found naturally within the Wyoming/ Colorado area of the United States.

Literature values [178]	Wyoming bentonite GG	Assignment
13.6_x 3.13_8 4.46_7 2.56_2 5.16_1 1.50_1	14.00_x 3.13_4 4.47_6 2.57_2 1.50_4	montmorillonite
3.34_x 4.26_2 1.82_1 1.54_1 2.46_1 2.28_1	3.33_x 4.25_2 1.82_1 1.54_1 2.45_1	α-quartz (SiO_2)
3.03_x 1.87_3 3.85_3 2.09_3	3.03_x	calcite ($CaCO_3$)
2.09_x 2.55_9 1.60_8 3.48_8	2.09_x 2.56_3 1.58_8	α-corrundum (Al_2O_3)
4.05_x 2.49_2 2.84_1 3.14_1	4.04_x 2.48_3	cristobalite (SiO_2)
2.80_x 1.73_4 1.74_3 3.59_3	2.78_x	siderite
	2.28	
	3.18	

Table 3.1 XRD data for Wyoming bentonite GG

The dehydroxylation weight loss of the bentonite was recorded by thermal gravimetric analysis. This is particularly dependent upon the mineral structure and so provides another reliable method of identification. The weight loss obtained, approximately 6%, is in good agreement with literature values for montmorillonite, and in satisfactory agreement with the theoretical loss of 5.0%.[177]

Optical microscopic examination confirmed the presence of impurity phases, the major component of which was a colourless material considered to be quartz. This amounted to approximately 5% of the bentonite, by counting. Other impurity phases identified with the help of pictorial references [180] included small, fine-grained, translucent, red-brown crystals of siderite, pyrite, and/ or some of the feldspar minerals, and large, opaque, dark grey-black crystals not considered to be any of the minerals suggested by the X-ray powder traces.

Such grey-black particles, some approaching 0.5 mm in diameter, are the largest size impurities present in the sample. They also possess a very angular shape, not in keeping with the more rounded shape of the other impurities. Consequently they must also possess significant hardness, and may be most responsible for the abrasive quality of this grade of bentonite. This is further considered in the following section concerned with the mineral as mined.

Two groups of frequency regions usually characterize the infrared spectra of most clay minerals. The first is the functional group region, between 4000-3000 cm^{-1}, attributed to stretching vibrations of adsorbed water and/or lattice OH groups. The second is the fingerprint region, between 1400-800 cm^{-1}, attributed to Al-OH and/or Si-O vibrations. Each is useful in the identification of clay minerals.

Infrared absorption data for Wyoming bentonite is presented in Table 3.2 The spectrum is typical for a montmorillonite with a moderate Fe (III) content (band at 870 cm^{-1}).[177] Quartz is again detectable as an impurity (band at 800 cm^{-1}),[177] but no other minerals may be identified.

A magic angle spinning nuclear magnetic resonance (MASNMR) ^{29}Si spectrum also clearly revealed a considerable amount of quartz to be present in the bentonite. The spectrum consisted of only two peaks, one corresponding to phyllosilicate silicon, and the other, upfield of the first, corresponding to silica polymorphs, in this case the quartz impurity. The standard chemical shift ranges for such condensed silicates, relative to $(CH_3)_4Si$, of -91 to -98 ppm for phyllosilicate silicon, labelled Q^3, and -106 to -115 ppm for silica polymorphs, labelled Q^4, are already established in the literature.[181]

Adsorption bands maxima (4000-300 cm^{-1})		
Literature values [2,177]	Wyoming bentonite GG	Assignments
3625 (st)	3631 (st)	OH stretching
3400 (st, br)	3424 (st, br)	OH stretching (hydration)
2360 (m)	2370 (w)	
1625 (w)	1638 (m)	HOH deformation (hydration)
1077 (st)	1115 (st)	SiO stretching
1042 (st)	1049 (st)	SiO stretching
920 (m)	918 (m)	OH deformation, linked to two Al^{3+}
885 (w)	880 (w)	OH deformation, linked to Al^{3+}, Fe^{3+}
624 (w)	622 (w)	
24 (m)	525 (m)	SiO deformation
468 (st)	466 (st)	AlO stretching
1425 (m)	-	Carbonate
800 (m)	799 (m)	Quartz
780 (w)	780 (w)	Quartz
698 (w)	695 (w)	Quartz
400 (w)	400 (w)	Quartz
373 (w)	373 (w)	Quartz

Table 3.2 Infrared absorption data for Wyoming bentonite GG

A similar study of the quadrupolar nucleus ^{27}Al was perhaps more revealing. Recently it has been shown that from the position of the resonance, it is possible to determine the coordination of the aluminium nuclei giving rise to that resonance, with tetrahedral aluminium resonating in the range 55-80 ppm, and octahedral aluminium in the region of 0 ppm.[182] Two broad peaks were observed in the Wyoming bentonite spectrum, corresponding to aluminium in both octahedral and tetrahedral coordination. A strong peak arising from aluminium in the octahedral layer is to be wholly expected from a sample predominantly consisting of a montmorillonite. However, a second peak indicating the presence of a certain amount of aluminium in the tetrahedral layers shows the montmorillonite to be close to the montmorillonite-beidellite border.

Finally, the cation exchange capacity was measured using the methylene blue dye adsorption method.[174] The value obtained, 74 meq per 100 g, is in good agreement with both the suppliers product data sheet,[163] and other accepted values for montmorillonites.[177]

3.1.2 Wyoming bentonite GG as mined

A 1 kg sample of the bentonite, prior to it being milled, was obtained from Steetley Minerals Ltd., in order to examine the homogeneity of the smectite deposit from which it was mined. The sample was predominantly yellowish grey, and consisted for the most part of fragments of the bentonite bed with an equivalent spherical diameter (e.s.d.) of approximately 5 mm. The largest single rock in the sample measured 40 x 10 x 10 mm. Impurities noted in the previous section could all be identified in this sample in much larger pieces. Quartz and other non-swelling rocks, including the grey-black type, could be found with an e.s.d. of 5 mm. In addition to this, fragments of a bluish-grey material, similar in appearance to the yellowish-grey bentonite, could also be found in quantities amounting to a few percent of the total sample.

All the major components identified microscopically in the milled bentonite are present in larger sized particles in the original mined ore. Thus all have been broken down to a greater or lesser degree by the milling action. However, as the grey-black particles constitute the largest size impurities present in the milled sample, they must be more resistant to such milling than are the other minerals. Therefore it is reasonable to associate the abrasive quality of the milled bentonite primarily to these particles.

On being placed in a muffle furnace at 1050°C for 3 hours a colour change from grey-black to white was observed, indicating that the black colouration was due to the presence of some carbonaceous matter in the particles. Gramme magnetic susceptibility, χ_g, measurements of the particles, made using a Gouy apparatus, indicated that the paramagnetic ion content was also fairly low ($\chi_g = 1.70 \times 10^{-6}$ cgs units g^{-1}).

Wyoming bentonite is mined from beneath an overlay of oil shale,[50] and it is likely that this is present in the clay as received. All the observations made upon the grey-black impurities present are consistent with the explanation. Oil shales may be classified as 'composites' of tightly bound organics and inorganics, comprising quartz, clays, feldspars, bitumens and kerogens.[183] As such, in addition to fitting with all the above experimental criteria, such material would not be individually identifiable by X-ray diffraction spectrophotometry.

However, an X-ray powder trace of the bluish grey clay-like material observed in the sample revealed it to be almost identical to the bulk yellowish grey bentonite. This was further confirmed by the determination of its cation exchange capacity, 74 meq per 100 g. Surveys carried out on the bentonite beds in the Wyoming area reveal many variations in the colour of the clay.[48,49,50] The bentonite at the outcrop is generally light yellow or green, but becomes bluish away from the outcrop. This colour change is due to the oxidation of ferrous ion at the exposed surface of the clay spur.[48]

Interesting features of some Wyoming bentonite horizons are masses of concentric layers of blue bentonite.[33] These so-called 'blue eggs' may be 30 cm or more in diameter, but have the same composition as the surrounding clay. Evidently, such blue bentonite is present in the GG grade bentonite used here, in concentrations amounting to a few percent of the total sample. Other features frequently found in some beds include concretions of siderite,[33] making it very likely that it too will be present in the mined clay, as an impurity.

3.1.3 Air classification

Air classification of Wyoming bentonite as received was carried out at Akzo, Littleborough. Of primary interest was whether this treatment had succeeded in separating the bentonite into fine and coarse fractions, and if so whether a genuine chemical separation, resulting in the removal of the impurities, had accompanied it. It was possible that separation would be achieved primarily on density grounds, considering the specific gravities of the various materials comprising the bentonite, montmorillonite 2.5, quartz 2.6, siderite 3.8, corundum 3.97, pyrite 5.0, and hematite 5.24.[184]

A laser light scattering technique was employed for the determination of particle size, and the data obtained are presented in Table 3.3 The results indicate that, although a small overlap in the range of particle sizes was observed, a good separation on size grounds has been achieved by air classification.

Clay fraction	Particle size range (μm)	Mode particle size (μm)
fines	1.9* - 9.8	2.6 - 3.0
coarse	7.3 - 188	120 - 140

Table 3.3 Particle size data for fine and coarse fractions of air classified Wyoming bentonite

* 18% of fines under the 1.9 μm lower limit of detection.

It should be noted however, that the clay particles being considered here are aggregates of a great many platelets, and that the separation achieved is into fractions of materials milled down to different sizes, and not into fractions consisting of small and large clay mineral crystals. This is not to say though that such fractionation cannot be accomplished. One study of the high-temperature phase transformations of samples of the montmorillonite group of clay minerals has indicated that the dioctahedral montmorillonites do not form a single continuous isomorphic series, and that some bentonites are mixtures of two types of discrete particles which may be separated by particle size fractionation.[56]

These two different aluminous types, Cheto- and Wyoming-, differ primarily in the population of their octahedral layers. In general the Cheto-type montmorillonites have 25-35% of octahedral aluminium replaced by magnesium, and 5% or less of the octahedral positions populated by iron. The Wyoming-type montmorillonites have only 5-10% of octahedral aluminium replaced by magnesium, but 5-15% of the octahedral positions populated by iron. The total octahedral population is generally 2 or slightly less in the Wyoming-type, and slightly greater than 2 in the Cheto-type.

The bentonite from Wyoming is all of the Wyoming-type,[56] however separate studies of several Wyoming bentonites have shown them to contain a sodium montmorillonite fraction and a calcium-magnesium montmorillonite fraction, as a consequence of differences in isomorphic substitution within the crystal lattice.[185]

The question of whether or not separation was achieved on anything other than particle size terms was addressed by utilizing a combination of powder X-ray diffraction spectrophotometry and optical microscopic examination. Analysis of both fine and coarse fractions by XRD generated two very similar traces, indicating that any separation on chemical grounds was at best partial. The spectrum obtained from the coarse fraction does however show sharper, more defined, peaks, which is consistent with the presence of larger crystals from which the reflections are recorded.

The two fractions did however differ slightly in their general colour, the coarse fraction being a darker yellowish grey than the fine fraction. Microscopic examination was used to estimate the amount of each impurity present, in an effort to gauge the extent of chemical separation. The major impurity in both fractions was quartz, approximately 5% in the fines and 4% in the coarse, by counting. The oil shale and the red-brown minerals were, by contrast, found in a higher concentration in the coarse fraction, 3% combined, than in the fines, 1% combined.

It would therefore appear that partial removal of the silica into the fines, with the retention of the denser material in the coarse fraction, has been achieved. However, the total impurity content is similar for both fractions, and so purification of the bentonite through air classification has not also been accomplished.

Reasonable X-ray diffraction and microscopic evidence for a difference in the quantity of iron minerals present in the two fractions then led to the measurement of gramme magnetic susceptibilities. The results showed there to be significant paramagnetic present in both fractions. Indeed, the loadings were rather similar, with the coarse just having a slightly larger loading than the fines (χ_g coarse = 6.5×10^{-6} cgs units g^{-1}, χ_g fines = 6.0×10^{-6} cgs units g^{-1}).

Although this confirmed the presence of appreciable quantities of iron in both fractions, it gave no definite information concerning the chemical form in which it occured. However, by taking the microscopic observations in conjunction with the gramme magnetic susceptibility measurements, some possibilities could be eliminated.

The blackish brown impurities were found in three times greater quantities in the coarse fraction than the fines, yet the paramagnetic ion content was very similar. It is reasonable to assume that most of these impurities are therefore oil shale particles, and so conclude that there is very little contamination by massive iron ore particles in either fraction. Consequently, the high paramagnetic presence in the sample must instead result from either structural substitutions within the aluminosilicate lattice itself, or from the presence of very finely divided iron oxides/oxyhydroxides invariably associated with the more massive quartz particles.

One other result of the high paramagnetic ion content of both fractions would appear to be the ruling out of the use of solid state ^{29}Si MASNMR as an investigative tool. The careful exchange-doping of hectorite with paramagnetic ions such as Cu^{2+}, Ni^{2+}, and Mn^{2+} has led to the determination of the loading level beyond which resolution of Q^n resonances in ^{29}Si MASNMR spectra is lost.[58] In terms of the gramme magnetic susceptibility of the specimen, a well resolved signal is never obtained when $\chi_g > 2.2 \times 10^{-6}$ cgs units g^{-1}. Consequently, the observed value of χ_g for Wyoming bentonite used here was well into the range established to give poor spectral resolution.

However, as it is suggested that the bulk of this paramagnetism is due to iron, the nature of the sample does lend itself well to investigation by ^{57}Fe Mössbauer spectroscopy. Indeed, such a spectrum was collected with relative ease, Figure 3.1, so finally establishing iron as the major paramagnetic species in the bentonite. Interestingly, a sextuplet, commonly observed for iron and indicative of a regular environment for the iron nuclei, and hence large particles, was not obtained. Instead the spectrum collapsed to a doublet, confirming the iron to be present only in very fine particles.

Deconvolution techniques revealed the spectrum to contain two resonances. The parameters for these are presented in Table 3.4 The weak Fe (II) component has parameters in close agreement with other examples of Fe (II) in dioctahedral minerals.[186] The more intense Fe (III) resonance also has parameters typical of Fe (III) in clay mineral environments,[187] but given the large value of Γ (0.70 mm s^{-1}) it is not possible to exclude the additional presence of very finely divided (superparamagnetic) Fe_2O_3 or Fe(O)(OH) which could contribute to the Fe (III) quadrupole split spectrum and to the observed value of χ_g.

Further, the likelihood that a high proportion of the iron present lies outside of the clay structure brings back the possibility of being able to obtain a well resolved ^{29}Si MASNMR spectrum. It will be noted that the nature of the work on the exchange-doping of hectorite [58] ensured that all of the paramagnetic was in close contact (next nearest neighbour) with the bulk ^{29}Si, from where it was able to influence the spin-lattice relaxation of the silicon nuclei and inhibit the attainment of good resolution. Paramagnetic transition metal ions more considerably distanced from the perturbed nuclei will have no effect upon their T_1, so allowing high resolution spectra to be obtained.

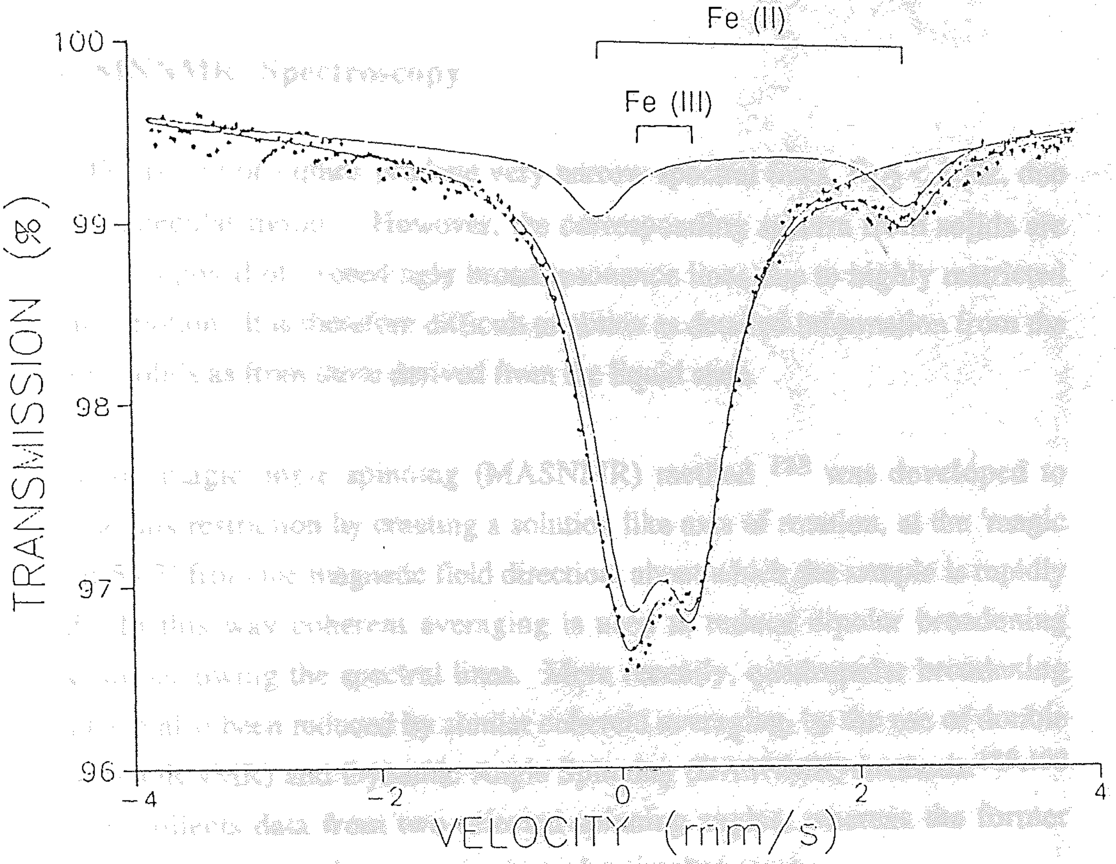


Figure 3.1 ^{57}Fe Mössbauer spectrum of fine fraction of air classified Wyoming bentonite

	∂ (mm s^{-1}) ±0.02 isomer shift	Δ (mm s^{-1}) ±0.02 quadrupole split	Γ (mm s^{-1}) ±0.02 f.w.h.m.
Fe (II) (13%)	1.29	2.57	0.61
Fe (III) (87%)	0.34	0.57	0.70

Table 3.4 ^{57}Fe Mössbauer spectroscopy data for fine fraction of air classified Wyoming bentonite

A ^{29}Si MASNMR spectrum of the fine fraction of air classified bentonite was obtained of excellent quality, see Figure 3.2. The Q^3 and Q^4 resonances are easily resolved, confirming isomorphous substitution of iron into the aluminosilicate sheet to account for only a small percentage of the total paramagnetic content of the bentonite. This leaves the bulk of the paramagnetism to result from the presence of very finely divided Fe_2O_3 or Fe(O)(OH) throughout the sample. Such material may contaminate the surface of the major mineral components, without necessarily exerting influence on the values of T_1, for the bulk ^{29}Si atoms.

3.1.4 SINNMR Spectroscopy

The NMR spectra of liquids produce very narrow spectral lines, $\Gamma_{1/2} < 1$ Hz, due to rapid molecular motion. However, the corresponding spectra from solids are normally composed of exceedingly broad resonance lines due to highly restricted molecular motion. It is therefore difficult to obtain as detailed information from the spectra of solids as from those derived from the liquid state.

The classic magic angle spinning (MASNMR) method [188] was developed to overcome this restriction by creating a solution like axis of rotation, at the 'magic angle' of 54.7° from the magnetic field direction, about which the sample is rapidly rotated. In this way coherent averaging is used to reduce dipolar broadening effects, so narrowing the spectral lines. More recently, quadrupolar broadening effects have also been reduced by similar coherent averaging, by the use of double rotation (DORNMR) and Dynamic Angle Spinning (DASNMR) methods.[189,190] The latter collects data from two selected spinning angles, whereas the former actually rotates a sample about two magic angles simultaneously.

An alternative method of line narrowing, technically simpler than any of the above methods, has also been reported recently.[191] It proposes that when solid particles are suspended in a support medium and irradiated with ultrasound, appreciable narrowing of spectral lines can be obtained. This new technique of sonically induced narrowing (SINNMR) spectroscopy was first thought to produce narrowing by causing solid particles to assume motional characteristics similar to those of rather large molecules, although much uncertainty still exists as regards its true origin. SINNMR was pioneered at Aston by Homer and Patel [192] and work is ongoing to apply SINNMR to a wide variety of compounds.[193]

Several attempts to SIN Wyoming bentonite, laponite, and Muscovite mica, have been made. All have failed, but sample preparations are recorded in some detail herein, in the hope that information on the conditions for SINNMR, and thereafter on the mechanism of operation, may be gained.

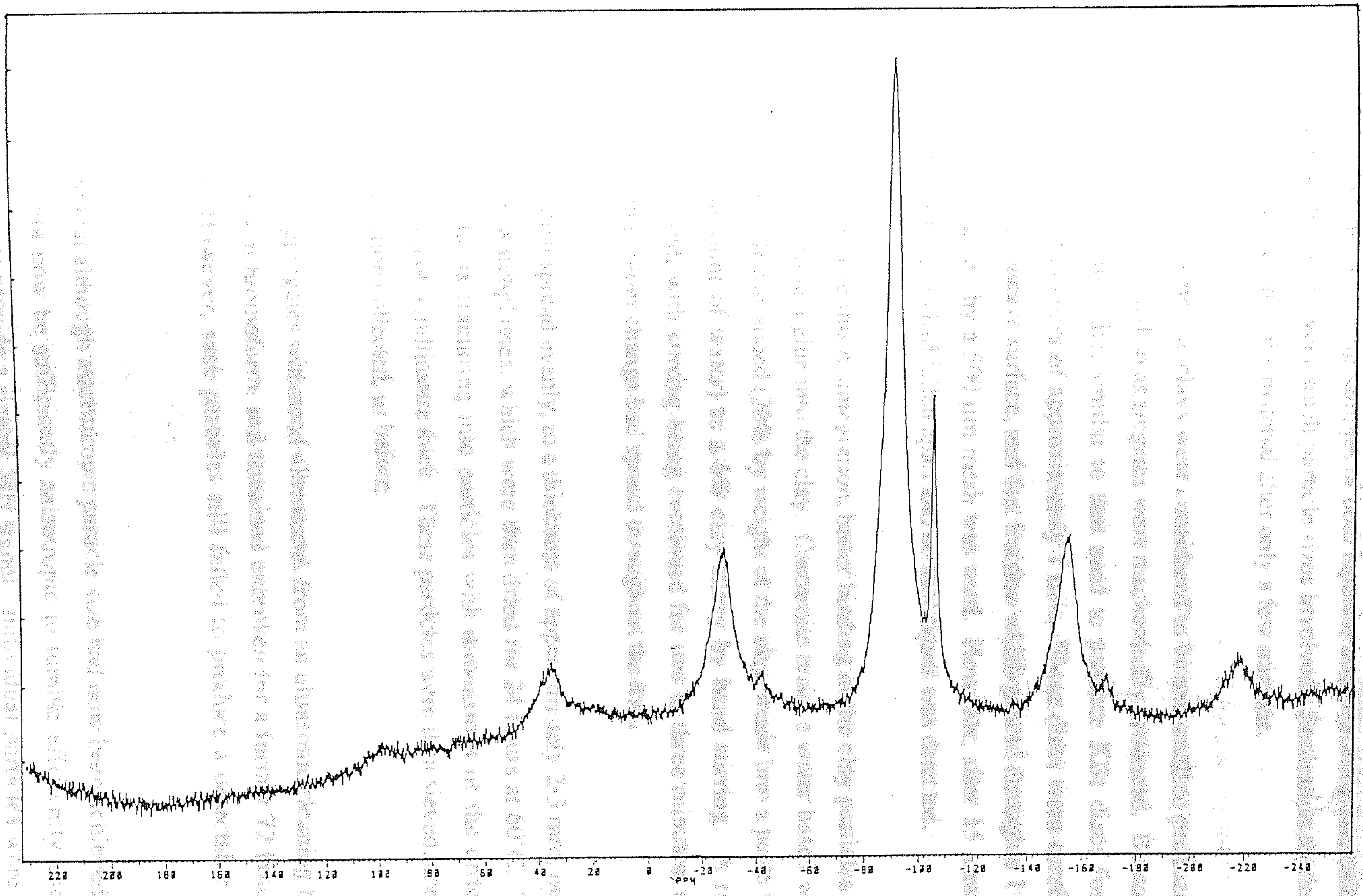


Figure 3.2 ^{29}Si MASNMR spectrum of the fine fraction of air classified Wyoming Bentonite

3.1.4.1 SINNMR sample preparations

In all the attempts carried out, the liquid medium used was either a chloroform/bromoform mixture or pure bromoform, depending upon the density required. Early attempts using samples of both laponite and Wyoming bentonite as received failed due to the very small particle sizes involved. Sonication tended to induce loose aggregation of the material after only a few minutes.

The particle sizes of smectite clays were considered to be too small to produce an appreciable SIN effect, and so aggregates were mechanically produced. Bentonite discs were pressed in a die, similar to that used to produce KBr discs for IR spectroscopy, to a thickness of approximately 1 mm. These discs were carefully fractured against a concave surface, and that fraction which passed through a 1 mm mesh but was retained by a 500 μm mesh was used. However, after 15 minutes sonication the aggregates had fallen apart and no SIN signal was detected.

In an effort to eliminate this disintegration, better binding of the clay particles was sought by incorporating a glue into the clay. Cascamite resin, a water based wood glue, was chosen. It was added (20% by weight of the clay, made into a paste with the minimum amount of water) to a 6% clay slurry by hand stirring. A rapid thickening occurred, with stirring being continued for two to three minutes, until the accompanying colour change had spread throughout the mix.

The slurry was then spread evenly, to a thickness of approximately 2-3 mm, onto a number of large watchglasses, which were then dried for 24 hours at 60°C. This resulted in the sheets fracturing into particles with dimensions of the order of 1 mm^2 by a fraction of a millimetre thick. These particles were then sieved, and the 500-1000 μm fraction collected, as before.

In studies these aggregates withstood ultrasound, from an ultrasonic cleaning bath, for several hours in bromoform, and remained unbroken for a further 72 hours in this medium. However, such particles still failed to produce a detectable SIN signal.

It was decided that although macroscopic particle size had now been achieved, the particles may not now be sufficiently anisotropic to tumble efficiently enough during sonication to provide a sizable SIN signal. Individual particles were then prepared by spotting a clay/cascamite slurry onto a teflon block with a syringe needle. The resulting block of droplets was dried at 60°C as before. When dry, the flat half-spheres, with an average diameter of approximately 500-1000 μm, fell freely from the block and were collected.

The failure of this sample to generate a detectable SIN signal led to the currently held belief that macroscopic crystallinity, as well as anisotropy, was important to the generation of sonically induced tumbling by helping to align the particles in the ultrasonic field. As the smectite clay minerals are renowned for their small particle size, an illite, Muscovite mica, was tried in the SINNMR experiment. This too failed to generate a detectable SIN signal.

All the SINNMR spectra so far obtained have been from highly crystalline materials such as aluminium phosphate, aluminium sulfate, and sodium phosphate.[191] It may well be that alignment of the particles in the ultrasonic field, due to their high crystallinity, is of critical importance as a prerequisite for rotational perturbation by ultrasound, and that any anisotropy of the particles merely aids subsequent rotation. Such alignment may not have been achieved with any of the clay mineral samples so far studied.

Many approaches to the stimulation of such alignment remain to be explored. The use of paramagnetic ions in the samples is one such method, and nontronite, a naturally occurring iron rich smectite would be an interesting mineral to study using SINNMR. Similarly, a variety of 1:1 and 2:1 iron phyllosilicates may be synthesized by the copolymerization reaction of transition metal ions and silicic acid under alkaline conditions.[194] Alternatively, the paramagnetism may be introduced to the clay mineral by a pillaring reaction [171] in order to keep the paramagnetic centres some distance from the NMR nucleus. This approach may offer the additional advantage of introducing greater particle alignment to the sample.

A different approach again would be to assume the magnetic field in the probe area to be too weak to generate the required alignment, and set up an electric field gradient across the probe area. It has recently been shown that a high electric field pulse aligns sodium montmorillonite particles with their basal surfaces parallel to the electric field.[195] However, a better approach may be to return to using the original natural bentonite samples, but attempt to increase the frequency of the ultrasound until satisfactory alignment is achieved.

One final idea is to incorporate a small amount of fine aluminium powder into a clay/cascamite slurry. This may generate fairly powerful inductive forces, through field inhomogeneity from ultrasound and particle movements, and may lead to increased incoherent averaging.

Obviously, considerable work needs to be done to improve the reproducibility of SINNMR experiments and to elucidate the mechanism involved in the production of SINNMR spectra. Whatever proves to the origin of SINNMR spectroscopy, it appears to offer a simpler possible alternative to both conventional MASNMR and the new DAS and DORNMR methods, that may eventually prove to be especially suitable to the study of clay minerals.

3.2 Water Content of Organophilic Clays

It has long been appreciated that when dealing with the chemical analysis of expanding clays such as the montmorillonites, the essential constituent of greatest variability is water.[42] The amount held by a given sample varies with the temperature and humidity of the surrounding atmosphere, so that the same sample may show very appreciable differences in water content when analysed on different days if there is much difference in the relative humidity.

Consequently, in such analyses the amounts of water recorded are not particularly significantly. However, the total water content is always made up of two types, the one being actually water molecules held by the silicate surfaces, and the other being hydroxyl groups within the silicate layers. It is the amount of surface water that is variable. The amount of hydroxyl, or lattice water, is a constant for each particular clay type, dependant solely upon the structural composition of the mineral. Thermal decomposition studies have shown that the water lost above 350°C is usually a close measure of the hydroxyl content, theoretically 5.0% H_2O for montmorillonites.[196]

Although the same is true of a great many organoclays, the ability of clays to absorb surface water is markedly lowered by treatment with compounds that furnish a large organic cation.[172] This is reasonable as such cation exchange would alter, to a marked degree, the nature of the surfaces of the clay particles, and would therefore affect those properties which depend on surface reactions.

3.2.1 An organoclay mass balance

Previous work carried out by the sponsoring company [197] served to highlight the fact that a complete mass balance for the reaction of quaternary ammonium compounds with a dispersed clay slurry, to produce a wet process organoclay, had not yet been satisfactorily obtained. No causes or solutions had been established, although a consistency of imbalance had been achieved. This amounted to being a shortfall of material in the product organoclay relative to the starting materials.

3.2.1.1 Preparation of the organoclays

Prior to use, the quaternary ammonium salt, dioctadecyl dimethyl ammonium chloride was thoroughly washed in acetone to remove any free amine or volatiles that may otherwise subsequently be lost upon heating. The pure product was weighed from a desiccator, and then added to the clay slurry as a hot aqueous solution. Approximately 150 g of slurry, equivalent to 6 g of clay, and 2.5-4.5 g of organics were used in each reaction, yielding 8.5-10.5 g of organoclay. In all cases the clay slurry was first heated to 60°C using a magnetic stirrer/hotplate, and maintained at this temperature for 30 minutes prior to the addition of the ammonium salt. The organoclay suspension was then stirred at 60°C for a further 1 hour to complete the reaction.

In experiments 1 and 2 the clay slurry used was taken from a sample of Akzo plant slurry. The solids content of the slurry was measured in the standard way, by drying a known amount, approximately 6 g for 2 hours or to constant weight at 105°C. The value obtained, 4.51% clay solids, was then used to calculate the weight of clay going into each experiment.

Experiments 3 and 4 used clay slurries made up from known weights of dry, to constant weight at 105°C, Wyoming bentonite and plant slurry respectively, by the addition of an appropriate volume of distilled water. Both were made up to be approximately 4% clay solids, and stirred overnight before the addition of the organics. These experiments sought to eliminate any errors arising from inaccurate determination of the solids content of the slurry, or any inhomogeneity or settling between various slurry samples taken from the same mother slurry.

Experiment 5 used the same plant slurry as experiments 1 and 2, however a different value of solids content, 4.22%, was taken. How this value was determined is explained later in this section.

Once the reaction was complete, all the organoclay/water suspensions were filtered cold through a no. 3 sintered glass crucible. Arquad 218-100 is highly insoluble in cold water, causing the filtrate to contain only the released mineral salts. The organoclays were then transferred to evaporating dishes and dried to constant weight in a desiccator. The filtrates were evaporated down, without boiling, on a hotplate, and the solid residues cooled in a desiccator. Finally, both the solid residues and the dry organoclays were weighed. All relevant data are presented in Table 3.5 and an appendix is given showing examples of all the calculations required in its compilation.

	'Wet' process organoclay experiment				
	One	Two	Three	Four	Five
Weight of Na clay added	6.79[a]	6.53[a]	5.02	3.39	5.09[f]
Weight of quat Cl^- added	3.59	4.59	3.51	1.81	4.74
Theoretical mass of organoclay[b]	10.02	10.77	8.27	5.02	9.57
Theoretical mass of residue[c]	0.36	0.35	0.26	0.18	0.26
Theoretical meq	90.3	120.1	119.4	91.2	159.5
Experimental mass of organoclay	9.61	10.30	8.11	4.90	9.54
Experimental mass of residue	0.46	0.41	0.29	0.18	0.30
Mass of 'lost' organoclay	0.41	0.47	0.16	0.12	0.03
Lost mass as percent of clay	6.0	7.2	3.2	3.5	0.6
Back-calculated percent solids	4.23	4.18	-	-	4.19
Experimental meq[d] (6.2%)	93.3	127.0	-	-	-
Experimental meq (5.0%)	96.8	129.5	-	-	-
Re-calculated theoretical meq[e]	96.1	129.3	123.4	94.5	160.0

Table 3.5 Experimental and theoretical data on 'wet' process organoclays
[a] Grammes of slurry multiplied by the percent solids, 4.51%. [b] Sum of the quat (minus the anion) and the clay (minus the cation) up to the CEC, and the sum of the quat chloride and sodium clay above the CEC, taken as 92 meq. [c] Taken to be NaCl. [d] Using data obtained using TGA. [e] Assuming all mass unaccounted for to be lost from the clay. [f] As a but using 4.22% solids content.

In each of the first four experiments the masses of the starting materials and the final products have been shown not to balance. In each case the discrepancy is in the same direction. The products either weighed too light, pointing to material escaping final detection and weighing procedures, or the starting materials weighed too heavy. In view of the amount of previous work carried out on this subject it must be assumed that poor experimental technique cannot be blamed.

The unaccounted for material can be expressed as being between 3.2-7.2% of the original mineral clay. If this material is surface water, associated with the mineral clay but lost from the product organoclay, two problems may be explained. Firstly, an explanation is found for the failure of this material to be measured in the product weighing procedure, as all the weighings are dry weighings. Secondly, as the lost material would originate entirely from the clay, and not from the ammonium salt, the actual meq of the organoclay would now differ from the original theoretical meq. This is indeed observed in these experiments and must therefore be accounted for in any viable explanation of the mass balance problem.

When the unaccounted for material is expressed not as a percentage of the original mineral clay, but by recalculating the percent solids content of the original plant slurry, a value of 4.22% is obtained. This is necessarily approximately 7% lower than the original experimentally obtained value of 4.51% that was used in experiments 1 and 2, due to the removal of the weight of remaining surface water, and is the percent clay solids figure used in experiment 5.

Two experimental meq values, obtained by thermal gravimetric analysis, are given for each organoclay in Table 3.5. The first is calculated in the standard way,[197] using a value of 6.2% for material other than the ammonium salt being lost in the temperature range 100-1000°C. However, as the theoretical loss in the dehydroxylation range is 5.0%,[177] a second experimental meq is given using this value.

Re-calculating the theoretical meq, after removing the weight of the unaccounted for material from the weight of the clay, does lead to very good agreement with the second of these experimentally obtained values. Thus the phenomenon of more surface water being absorbed by the mineral clay than by the organoclays may be used to account for the shortfall of material experienced on the product side of the equation.

Before such an explanation can be accepted though, two further points have to be addressed. It must be shown firstly that up to 7% of the weight of the clay can be removed from an apparently dry clay, and secondly that this can be done using a clay that is already 'dry' at 105°C.

3.2.1.2 Temperature studies on bentonite clay slurries

Surface bound water is not 'free' water, and so it cannot be expected that it will be liberated at or near the boiling point of water. Neither is it structural or lattice water which may only be irreversibly removed as the silicate framework begins to be destroyed at much higher temperature.

The three principle thermoanalytical techniques are differential thermal analysis (DTA), thermogravimetry (TG), and derivative thermogravimetry (DTG). Figure 3.3 shows the DTA, TG and DTG traces for a typical Wyoming montmorillonite.[177]

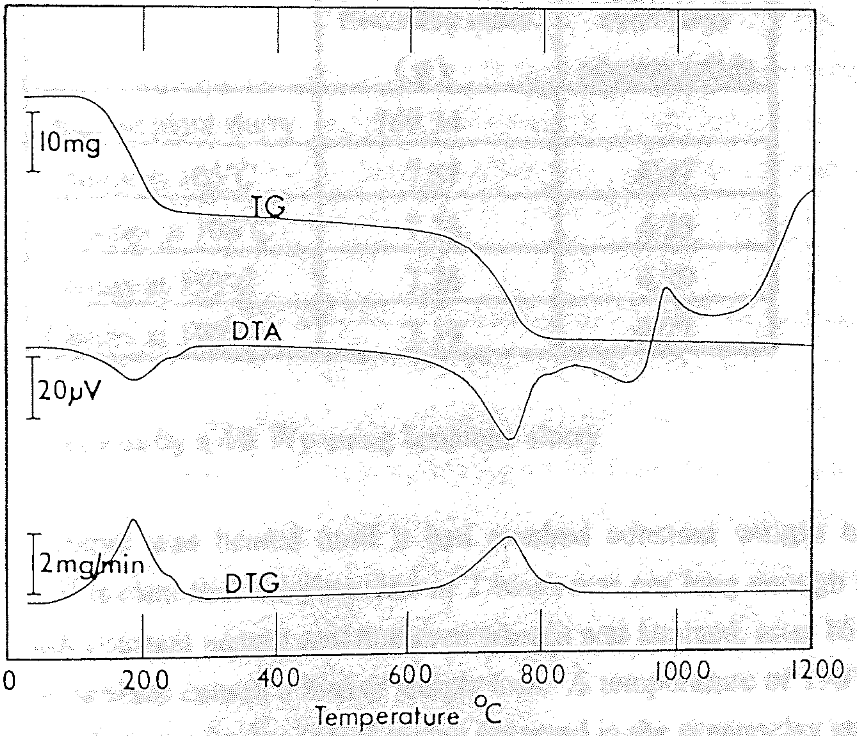


Figure 3.3 DTA, TG and DTG traces for a typical Wyoming montmorillonite [177]

The DTA curve reveals all the energy changes occurring in the sample on heating. For Wyoming bentonite it shows the desorption endotherm of water to peak at 185°C, and the dehydroxylation endotherm to peak at 770°C. The TG and DTG curves reveal only the weight changes occurring on heating. However, they too show that surface water is still being removed from the bentonite surface at temperatures approaching 200°C.

Much earlier work on the physical properties of the minerals of bentonite [42] also concluded that temperatures well in excess of 100°C are required to remove all the surface water. In addition, it was found that when the temperature was increased a few degrees, samples which had previously been brought to constant weight lost additional water.

Here, a study on water loss by Wyoming bentonite slurries was carried out in order to show that an experimental percent solids value of 4.2% could be reached for this particular clay slurry, and that consequently the maximum loss recorded, 7% of the weight of the clay, could be achieved through loss of surface water. In addition, as experiments 3 and 4 had resulted in considerably less of a mass imbalance than had experiments 1 and 2, the drying time required to reach constant weight at 105°C was also examined. The relevant data are present in Table 3.6.

	Recorded mass (g)	calculated percent solids
Original plant slurry	169.34	-
2 hours at 105°C	7.57	4.47
16 hours at 105°C	7.33	4.33
4 hours at 150°C	7.26	4.29
4 hours at 190°C	7.14	4.22

Table 3.6 Water loss by a 4% Wyoming bentonite slurry

The slurry sample was heated until it had reached constant weight at each temperature. It is clear that a drying time of 2 hours was not long enough for the sample to reach constant weight, and that even when it was attained, after 16 hours, a temperature increase caused a further weight loss. A temperature of 190°C was sufficient to produce a water loss equal to that observed in the organoclay reaction, although a small further loss at even higher temperatures may well have been likely. This would merely indicate that some surface water is still present in the product organoclay, either solvating the organic cation or any part of the silicate surface still accessible. This is not unreasonable to assume, as small amounts of interlamellar water in organic-exchanged phyllosilicates are commonly observed.[198]

In conclusion, one can state that all the evidence obtained is self-consistent and that the explanation given, that of a differing amount of surface bound water being present on the mineral and product clays, is valid.

Consequently recommendations can now be made in order to ensure that more accurate mass balances are obtained in the future. Firstly, when carrying out percent solids measurements, a temperature of 105°C is not high enough to remove all the surface bound water that would be displaced by the exchange of a large organic cation, even if the clay is heated to a genuine constant weight. A temperature of approximately 190°C is required, with a heating time of at least 4 hours. Secondly, re-absorption of surface bound water, after drying but before weighing, is going to occur, necessitating the use of a desiccator in the cooling of the sample. Finally, a value of 5.0% loss in the dehydroxylation range should be used in all experimental meq calculations.

3.2.2 Humidity studies of 'dry' process organoclays

As previously stated, the water content of any given clay sample varies with temperature and humidity of the surrounding atmosphere. When the water content is fairly high, it may be determined in terms of the basal spacing recorded in an X-ray powder trace. The basal spacing is a measure of the dimension of the clay structure along the c-axis. This is variable, dependent upon the solvation of the interlayer region.

It has been shown that as relative humidity increases, so does the basal spacing for a range of smectite clays.[13] This results from the step-wise hydration of the interlayer sodium ions, consistent with the sorption of one, two three or four layers of water molecules. In addition to this, at very high relative humidity the amount of free water in the interlayer, resulting from type II swelling, increases, so further increasing the basal spacing. A more recent study of basal spacing as a function of relative humidity has been made using laponite, a higher swelling, synthetic sodium smectite.[199] A basal spacing increase from 13.3Å to 18.6Å is observed as the relative humidity is increased from 15% to 93% RH.

If organoclays too show a variation in their d spacing dependent upon the relative humidity of the surrounding atmosphere, then problems will arise when attempting to use d spacing measurements as an indication of successful or enhanced ion exchange or intercalation.

To study the hydration of 'dry' process organoclays, five controlled-humidity chambers were created using saturated solutions of different desiccating and deliquescent metal salts. Each salt has an inherent water vapour pressure, so that when equilibrium with the surrounding atmosphere in the chamber is established an environment of known and constant relative humidity is attained.

Relative humidity is the ratio of the partial pressure of water vapour in the air to the partial pressure of water vapour in the air when saturated at the same temperature. As the latter decreases with temperature, relative humidity, which is usually expressed as a percentage, is temperature dependent, and so care must be taken when comparing values.

The five deliquescent salts used, and the accompanying relative humidity atmospheres created at 293K, were LiCl (15%RH), $CaCl_2$ (32%), $Mg(NO_3)_2$ (52%), NH_4Cl (79.5%) and Na_2SO_4 (93%).[184,200] The 'dry' process organoclays studied were dihydrogenated tallow dimethylammonium exchanged bentonites, produced from both the fine and coarse air classified fractions of bentonite, as described in Section 2.2.2. All samples were left in the chambers for three weeks, with daily agitation.

After three weeks, an observable physical change in all the samples was apparent. Those at low relative humidities appeared very dusty, whereas those at the two highest relative humidities were sticky and rather lumpy. Clearly an appreciable uptake of water had occured at the higher relative humidities. X-ray diffraction powder traces of all the samples were recorded, in order to ascertain whether or not this was borne out by the basal spacing measurements. XRD data are presented in Table 3.7.

Bentonite fraction	d (001) (Å) after 3 weeks in humidity chambers (after 3 months)				
	15% RH	32% RH	52% RH	79.5% RH	93% RH
fines	12.4	12.4	12.4	12.8 (12.8)	12.8 (13.5)
coarse	12.4	12.4	12.4	12.8 (12.8)	12.8 (13.0)

Table 3.7 XRD data for 'dry' process organoclays at known relative humidities

Although an increase in basal spacing is observed at 79.5% and 93% RH, it is only small, and no variation at all is seen in the range 15-52% RH. This lower humidity range, over which the basal spacing is invariant, also covers the range through which the relative humidity within the laboratory usually fluctuates, as measured by an hygrometer placed on the bench top. Consequently it is not necessary to humidify such organoclays prior to measuring their basal spacings, so long as they are air dry and do not display any of the stickiness shown by the 79.5% and 93% RH samples.

Despite prolonged exposure to a 93% RH atmosphere, the maximum basal spacing recorded was 13.5Å, lower than the 14.Å typical of air dry montmorillonite [179] and recorded in Section 3.1.1 for Wyoming bentonite GG. It is also very considerably lower than the 18.6Å typically recorded for inorganic exchange forms of smectite clays at 93% RH.[199] It would therefore appear that, although uptake of water into an organic gallery is often found,[198] very little interlamellar hydration has occured with these particular organoclays.

However, visible evidence suggested that those at 79.5% and 93% RH had actually taken up some considerable weight of water. Weighing these organoclays before and after they were placed in the humidity chambers succeeded in providing confirmatory scientific evidence of this, both clays showing an increase of approximately 33% by weight at 93% RH.

The assumption must be therefore that absorption of water onto the external crystal surfaces is the primary mode of uptake, and that interlamellar hydration plays only a minor role. This in turn would indicate that the ion exchanged organic is not the major cause of the uptake, but rather that the unexchanged, ion paired, ammonium salt, or more likely the released metal salt, encourages the hydration.

The 'fines' organoclay was selected for further investigation. One sample was washed in a 75% propan-1-ol/water solution until all the salts, organic and inorganic, had been removed. A second was washed only in water, affording a sample that retained any unexchanged organic ammonium salt but was free of the by-product sodium chloride. This was confirmed by washing a portion of the sample a further time, on this occasion in 75% propan-1-ol/water, and retrieving the required amount of organics in the residue from the washings. Both samples were placed in the 98% RH chamber for three weeks, long enough for the original 'fines' organoclay to have developed a quite lumpy and sticky appearance.

Neither organoclay was visibly any more hydrated afterwards than before, both being very fine, dry and powdery to the eye and to the touch. Evidently it is the material residing on the external crystal surfaces that predominantly cause these organoclays to substantially hydrate at high humidities, and that any accompanying interlamellar hydration is not outwardly observable.

Further, it is the released sodium chloride and not the unreacted dihydrogenated tallow dimethyl ammonium chloride that is the surface located material responsible. This is not surprising as sodium chloride is itself a deliquescent metal salt, creating an atmosphere of 30.5% RH at 289K when an excess is in contact with its saturated aqueous solution within a closed space.[184] This indicates too that during, or on completion of, the ion exchange process the released metal salt is expelled from an interlayer region that obviously becomes a very hydrophobic environment.

3.3 Distribution of Quaternary Ammonium Compounds on the Silicate Surfaces of 'Dry' Process Organoclays

Four organoclays were produced using dihydrogenated tallow dimethyl ammonium chloride and Wyoming bentonite, according to the method outlined in Section 2.2.2, with the organic loading being at, or just above, the cation exchange capacity of the clay.

Portions of each dried clay were washed with a solution of 75% propan-1-ol/water until the washings were clear of chloride ion ($AgNO_3$). Washings were carefully conserved and analysed by atomic absorption spectroscopy for released Na^+ and Ca^{2+}. Total chloride analysis of the washings, according to Volhards method, as described in Section 2.3.16,[175] was also undertaken to ensure that all the ammonium salt could be accounted for. The washed clays were subjected to XRD examination; some relevant data are in Table 3.8.

Wyoming bentonite fraction	Arquad 2HT		% exchange sites ion exchanged (% of CEC)	d (001) (Å)
	Meq per 100g added	% added cation ion exchanged		
coarse	84	62	70	12.4
coarse	78	66	68	12.7
fine	86	69	78	12.5
fine	78	75	78	12.5

Table 3.8 Data for 'dry' process quaternary ammonium exchanged Wyoming bentonite

3.3.1 Degree of ion exchange

Analysis of released Na^+ and Ca^{2+} ions revealed that, at best, a 78% level of ion exchange had been achieved with the fines, and rather less, 69%, with the coarse fraction. Fully exchanged long-chain quaternary ammonium montmorillonites usually show basal spacings of approximately 17Å,[201] reflecting the presence of a double layer of ions in the interlameller region.

The samples also show values of d(001) in the range 12.4-12.7Å, indicative of a single layer of ammonium ions in the interlameller space, and consequently of incomplete ion exchange. This results from the dihydrogenated-tallowdimethyl ammonium cation being larger than half the area per exchange site for a typical montmorillonite.[202] Therefore, one such cation, exchanged onto one internal surface, cannot be fitted into the gaps between the others lying on the opposing surface to form a monolayer when the amount adsorbed is equal or close to the exchange capacity of the clay.

It follows that complete ion exchange of dihydrogenated tallow dimethyl ammonium chloride cannot be achieved when the interlayer region is unable to expand to accommodate a double layer complex. The decrease in basal spacing from the original mineral clay value of 14Å simply reflects the lower solvation of the exchanged quaternary ammonium ions.

3.3.1.1 Some explanations of incomplete ion exchange

An explanation of the percentage of ion exchange achieved may be sought in the study of exchange isotherms. They have been used to show that the initial exchange of sodium ions occurs less readily than subsequent exchanges, and that the affinity of the organic cation for the clay increases with molecular size.[105,106] Both these observations are explained in terms of physical adsorption due to van der Waals forces preceding an ion exchange mechanism.

However, such studies have also shown that the affinity of the alkylammonium ions for the clay rises to a maximum at around 70% ion exchange, and then declines at high amounts adsorbed.[106] This decrease in affinity is attributed to the collapse of the interlamellar space, and would almost certainly be exacerbated in the 'dry' process. Similarly, it has been reported that below 70% of the exchange capacity ion exchange is completely reversible, whereas beyond this there is no thermodynamic justification for expressing a selectivity coefficient.[203]

A further explanation is available if one considers the possibility of full exchange at lateral, or edge, sites and external surface lattice sties, with incomplete exchange only occuring at internal surface lattice sites. It is recognised that in general 80% of the exchange capacity of montmorillonites is due to substitution within the lattice, with the other 20% being due to the charges that arise from broken bonds at the edge of the sheets.[18] Montmorillonite is also noted for its extremely thin flakes, 0.004 μm, or 2 unit cells.[203]

Taken in conjunction, and for a flake of average thickness, these figures show half the exchange sites arising from lattice substitution to be external surface sites, making a total of 60% of the exchange sites being either external lattice surface or lateral surface sites. With only a monolayer formation present in the interlayer, only half the internal lattice surface sites would be satisfied. This would cause the total extent of ion exchange to be 80%, just a little higher than the experimentally observed values, see Tables 3.8 and 3.9.

	Number of silicate surfaces per flake	Number of sites as % of CEC	
		Available	Exchanged
Total lateral site contribution		20	20 (20)
Total lattice substitution contribution	4[a] (7)[b]	80	
external lattice surfaces	2 (2)	40 (23)	40 (23)
internal lattice surfaces	2 (5)	40 (57)	20 (28)
Combined contribution			80 (71)

Table 3.9 Data for calculation of contributions to the observed degree of ion exchange for 'dry' process quaternary ammonium exchanged Wyoming bentonite

[a] Assuming the average number of sheets in a flake to be 2[95]

[b] Assuming the average number of sheets in a flake to be 3.5[204]

However, the calculation may be further improved by the incorporation of more accurate data. In a more recent comprehensive study of the size and shape of clay particles in aqueous suspension, a sodium montmorillonite was separated into five size fractions, and the maximum width and the thickness of the flakes in each fraction determined.[204] It was observed that both the width and thickness decrease with decreasing e.s.d. The number of sheets per flake in the coarsest fraction was

8, and in the finest fractions was 1, with the mean over all the fractions being approximately 3.5.

A similar calculation to the one above, substituting 2 for 3.5 as the average number of unit cells in a flake then affords a value of 71% ion exchange, as rather more of the silicate surface is now an internal surface and so able to undergo only partial ion exchange. This slightly lower value is in very close agreement with those experimentally observed, see Tables 3.8 and 3.9.

It is also possible in a similar manner, to begin with the experimentally observed percentage ion exchange values, 69% for the coarse and 78% for the fines, and calculate the mean number of sheets per flake in each fraction. Such a calculation results in an average of 4.5 unit layers for flake in the coarse fraction, and 2.25 unit layers per flake in the fines. Obviously, since external surface ion exchange is assumed to be complete in these calculations, and internal surface ion exchange is not, the fine fraction, which shows the greatest extent of ion exchange, also consists of the smaller flakes.

Whilst it is tempting to accept this result as it is, it should again be remembered that the two fractions, fine and coarse, refer to mined material separated into fine and coarse aggregates, each of a great many flakes. That the aggregates in the fines should consist of smaller flakes than the aggregates in the coarse fraction is a conclusion worthy of consideration.

Support for this conclusion may be sought in the phenomenon of contemporaneous growth, discussed in Section 1.6.1. This is responsible for the interlocking of crystals to form aggregates that are difficult to separate, even when dispersed in water. It is reasonable to assume that in this way larger aggregates are formed through the intricate interlocking of large flakes than are produced through the necessarily more limited interlocking of much smaller ones.

3.3.1.2 Methods of increasing the degree of ion exchange

Swelling the clay, so allowing good access to the interlamellar regions, is considered necessary for complete ion exchange to take place. This may not occur successfully within the high shear mixer of the 'dry' process, causing only monolayer formation of the organics, and incomplete ion exchange.

To study this, another similar organoclay was prepared from the coarse fraction of Wyoming bentonite and dihydrogenated tallow dimethyl ammonium chloride. This time the 'wet' method of preparation was adopted, as described in Section 2.2.1, incorporating a non-swelling, 75% propan-1-ol/water, exchange medium. It was hoped that in this way a similar interlamellar environment would be created to that occuring during the 'dry' process, albeit for a very different reason, and that consequently a similar degree of ion exchange would result.

In addition, this organoclay was prepared with no added sodium carbonate, so that any released calcium ions would be in solution as calcium chloride. This was in response to the possibility that many of the released charge balancing calcium ions may well be in the form of insoluble calcium carbonate, and therefore going undetected through the analysis procedure. Washings were again carefully conserved and analysed by atomic absorption spectroscopy; relevant data are presented in Table 3.10.

Wyoming bentonite fraction	Ion exchange medium (per g clay)	Arquad 2HT		% exchange sites ion exchanged
		Meq per 100g added	% added cation ion exchanged	
Coarse	40 cm^3 75% propan-1-ol/water[a]	84	57	64
Coarse	1 cm^3 H2O[b]	84	72	80
Coarse	1 cm^3 75% propan-1-ol water[b]	84	73	82

Table 3.10 Data for 'wet' process quaternary ammonium exchanged Wyoming bentonite

[a] No added carbonates

[b] Microwave oven for 10 x 1 minute

The 64% ion exchange achieved is in reasonable agreement with the 69% ion exchange of the analogous 'dry' process organoclays, suggesting that poor ion exchange of interlamellar sites is occuring in both cases. The concentration of calcium ions detected by atomic absorption spectroscopy, 2.6% of the released inorganic ions, was also consistent with concentrations found in 'dry' process organoclays, indicating that carbonate formation is not impairing analysis.

The two other organoclays shown in Table 3.10 are results of attempts to take a 'dry' process organoclay and further increase the degree of ion exchange, via the use of microwave heating. This approach was adopted as thorough mixing of the clay and organics proved difficult when added separately. After ten minutes some increase in the degree of ion exchange had been achieved. The magnitude of the increase was similar in both swelling and non-swelling exchange media, suggesting that it truly was the microwave heating that was responsible for the increase, and not the addition of a small volume of solvent.

3.3.2 The distribution of amine salts on the silicate surfaces

The product of the 'dry' process will contain quaternary ammonium exchanged bentonite, mineral impurities, unexchanged quaternary ammonium salt and released inorganic salts. The latter two components may be recovered by washing, but it is still desirable to employ physical methods of analysis to determine the distribution of these materials in the bulk product, so as to avoid having to take the product into solution.

3.3.2.1 Fourier Transform Infrared spectroscopic investigations

In order to aid the differentiation of exchanged and unexchanged materials in the 'dry' process product, a novel approach to the production of exchanged clays was attempted. It was hoped that the addition of a free amine to an acid exchanged bentonite would effect the 'in situ' formation of an exchanged bentonite by combination of the amine with the interlamellar protons. Now, rather than having to distinguish the two different environments of identical amine cations, chloride or basal oxygen counterion, one would simply have to distinguish an amine from its salt.

Acid exchanged Wyoming bentonite, prepared as described in Section 2.2.4, and DL-lysine, $NH_3^+(CH_2)_4CH(NH_2)COO^-$, were reacted together in ethanol, as described in Section 2.2.1. Both reactants and the product organoclay were analysed by infrared spectroscopy.

The most prominent feature of the infrared spectrum of primary amines is the N-H stretching band which occurs as a doublet between 3300-3500 cm^{-1}, and the accompanying deformation between 1590-1650 cm^{-1}. Amine salts may be recognised by a strong ammonium band in the range 2200-3000 cm^{-1}.[205]

The infrared spectrum of DL-lysine showed the expected N-H stretching bands (3360, 3280, 1661 cm^{-1}), and C_{sp3}-H stretching band (2937 cm^{-1}). However, the strongest bands recorded were the stretching bands associated with the carbonyl group. Bands were recorded at 1582 and 1417 cm^{-1}, indicating $RCOO^-$,[206] and implying that the amino-acid existed in the zwitterion form. The accompanying ammonium band (2854 cm^{-1}) was weak, but its presence meant that proving ion exchange by observation of an ammonium band in the products organoclay would be difficult.

The infrared spectrum of the product organoclay retained the primary amine stretching bands of the free amine, but also contained two weak ammonium bands (2875, 2855 cm^{-1}) , indicative of the zwitterion form of the free amine and the amine protonated by the clay surface. Thus exchanged and unexchanged material in the product had been identified, although further evidence was desirable as the ammonium bands are weak and close together.

One observation that helps to confirm ion exchange is the marked reduction in the product organoclay, compared to the acid clay, of the strength of the OH stretch of interlameller water (3424 cm^{-1}) relative to that of the OH stretch of lattice hydroxyl groups (3631 cm^{-1}). This implies a marked reduction in interlamellar hydration for the organoclay, which in turn implies not just external surface but interlamellar uptake of lysine. One must assume that in such circumstances ion exchange would have taken place.

Further confirmation of ion exchange was sought by attempting to remove any unexchanged lysine from the organoclay by means of an aqueous wash. Lysine is very soluble, but constant agitation of the organoclay in a large column of water overnight on a mechanical wrist-action shaker left the filtered product retaining an organic 'feel'. Infrared spectroscopy showed only the ammonium band arising from the ion exchange reaction (2875 cm^{-1}) to be present. The band arising from the zwitterion form of the free amine, observed in the spectra of pure lysine and the product organoclay, was absent.

A similar wash in 1M hydrochloric acid produced a fast filtering clay with a mineral clay appearance. Infrared spectroscopy confirmed no lysine to be present in the dried product, indicating the dominant mechanism of attachment to be that of ion exchange rather than simple sorption. Relevant infrared data are presented in Table 3.11.

Sample	Ammonium adsorption bands maxima (cm^{-1})	
lysine	-	2854
lysine/bentonite	2875	2855
H_2O washed lysine/bentonite	2875	-
1M HCl washed lysine/bentonite	-	-

Table 3.11 Infrared absorption data for lysine exchanged Wyoming bentonite

The above method thus demonstrates a novel way of producing ammonium exchanged clays. However it also has possible applications in the administering of amino-acids to cattle. L-lysine is an essential amino-acid, which cannot be synthesized by the body and must be present in the food for proper growth. Many domestic cattle require supplements, but these must reach the third and fourth stomachs where digestion takes place, rather than dissolve in the first and second stomachs, which are used mainly for storage. By first exchanging the lysine, or other amino-acids, to clay pellets, such supplements will travel through the first and second stomachs, which are approximately pH 7, still bound to the pellet. However, they will be slowly released in the molar acid environment of the third and fourth stomachs.

3.3.2.2 X-ray photoelectron spectroscopic investigations

Fourier transform infrared spectroscopy was able to identity both exchanged and unexchanged organics in an organoclay, so long as the amine was added as the free amine to an acid clay. However, this is a special case, with the amine much more usually being added as the chloride salt. X-ray photoelectron spectroscopy, being a technique sensitive to the inner core electrons, should prove better able to study this type of system, ie. to distinguish between amine salts with different anions, such as chloride ion or a basal oxygen.

Initially, a preliminary investigation, using an organoclay similar to that studied by FTIR in the previous section, was conducted to examine the extent to which the photopeaks in the N(1s) spectrum could be resolved. For this purpose di-n-decylamine, $(C_{10}H_{21})_2NH$, and its salt $(C_{10}H_{21})_2NH_2{}^+Cl^-$, were prepared. The amine was recrystallized twice from a solution of 95% ethanol/water, to yield pure white needle-like crystals, m.p. 44°C. The HCl salt, prepared from an ethanolic solution of the pure amine by the addition of excess 1M HCl, was recrystallized twice from ethanol, yielding pure white platey crystals that decomposed above 195°C. Finally an organoclay was prepared by reacting di-n-decylamine and an acid exchanged Wyoming bentonite in ethanol, as described in Section 2.2.1. The products were all subjected to N(1s) XPS examination, the results of which are presented in Table 3.12.

Sample	N(1s) Binding Energy (eV, ±0.2)	
$(C_{10}H_{21})_2NH$	399.2	
$(C_{10}H_{21})_2NH_2^+Cl^-$		401.1
H-bentonite/$(C_{10}H_{21})_2NH$	399.2	401.9

Table 3.12 XPS N(1s) data for di-n-decylamine bentonite

The two standards, di-n-decylamine and its HCl salt, show binding energies for the nitrogen 1s electron that differ by almost 2 eV. These photopeaks may be easily resolved if both should be present in a single sample. The organoclay prepared by the addition of the amine to an acid bentonite shows just such a combination of photopeaks, indicating the presence of both amine species in the product.

Not surprisingly, the photopeak attributable to the presence of the free amine occurs at a binding energy identical to that recorded for the amine standard. However, the photopeak arising from the presence of exchanged material in the product occurs at a binding energy 0.8±0.4 eV higher than that of the standard. This serves to illustrate the effect the nature of the counterion has upon the binding energy of the cation. It also demonstrates the possibility of being able to add the amine to the clay as its salt, whilst still being able to follow both the exchanged and unexchanged material by physical methods, simply by careful selection of the appropriate anion. This would bring the further possibility of being able to develop the analysis quantitatively. Whilst the unexchanged material remains a free amine, the high vacuum conditions under which the instrument must operate renders the amine highly volatile, and consequently, the technique non-quantitative.

In attempting to follow an amine salt, rather than just the free amine, through the ion exchange process, another possibility now exists. This is to examine the X^- spectra, so endeavouring to differentiate Q^+X^- and M^+X^- on the clay surface, where Q^+ is the ammonium ion, X^- the halide counterion, and M^+ the inorganic ion released in the ion exchange process.

If X = Br, differences in binding energies between Q^+Br^- and M^+Br^- are maximized if Q^+ is a quaternary rather than a primary, secondary, or tertiary ammonium ion ($C_{16}H_{33}Me_3NBr$ 67.3 eV,[176] ($(C_{10}H_{21})_2NH_2Br$ 68.1 eV), and M = K, Na or Li (KBr 68.7, NaBr 68.5, LiBr 69.0 eV [176]). As lithium salts hydrate very readily, resulting in separation of the ions, and an increase in electron density at the bromine nucleus, sodium or potassium bromide will actually show the highest Br(3d) binding energies in the product organoclay.

Accordingly, potassium and sodium exchanged Wyoming bentonites were prepared as described in Section 2.2.4, and dihydrogenated tallow dimethyl ammonium bromide, $(C_{18}H_{37})_2N(CH_3)_2{}^+Br^-$, was synthesized using the reaction of a tertiary amine with an alkyl halide, termed the Menschutkin reaction.[207] The tertiary amine, $(C_{18}H_{37})_2NCH_3$, was dissolved in tertiary-butylmethylether, and an equal molar quantity of methyl bromide in the same solvent was added to it. The reaction mixture was warmed gently for 1 hour, before being left to stand cold overnight. The copious white precipitate was collected and twice recrystallized, yielding white crystals, m.p. 59°C.

The Na^+ and K^+ bentonites were exchanged by the 'dry' process with a 120 meq loading of $(C_{18}H_{37})_2N(CH_3)_2Br$, and the products subjected to Br(3d) XPS examination. Data are present in Table 3.13.

Sample	Br(3d) Binding Energy (eV, ±0.2)	
QBr [a]	67.1	
KBr		68.5
NaBr		68.5
K-bentonite/QBr	67.2	68.3
Na-bentonite/QBr	67.2	68.3

Table 3.13 XPS Br(3d) data for quaternary ammonium exchanged bentonites
[a] QBr = $(C_{18}H_{37})_2N(CH_3)_2Br$

Examination of the Br(3d) spectra of the exchanged clays gave photopeaks whose full width at half maxima were significantly greater than the 2 eV recorded for the Q^+Br^-, K^+Br^-, and Na^+Br^- standards that is typical of Br(3d) photopeaks arising from single environments. Deconvolution techniques were employed, and when the simplest fit consistent with a satisfactory reduced χ^2 value was obtained, two bromine environments were revealed. The binding energies of these are consistent with those of the standard compounds, as affording very good evidence for the presence of sorbed Q^+Br^- in pairs on the silicate surfaces.

3.3.2.3 Solid state nuclear magnetic resonance investigations

The silicate surfaces in question may be those of the clay mineral, or possibly those of the α-quartz impurity. Both may have a thin coating of Fe_2O_3 or Fe(O)(OH), and so sorb significant amounts of organics. In order to examine these surfaces separately, ^{29}Si MASNMR may be employed. It has already been demonstrated, Figure 3.2, that the Q^3 and Q^4 resonances, corresponding to phyllosilicate silicon and silica polymorphs respectively, may be easily resolved for this particular bentonite.

^{29}Si MASNMR spectra of the fine fraction of Wyoming bentonite, together with those for the product direct from the 'dry' process reaction with dihydrogenated tallow dimethylammonium chloride, and the same product following washing with 75% propan-1-ol/water, were determined. Data are presented in Table 3.14.

Sample	Chemical shift (^{29}Si vs TMS)*	
	Q^3	Q^4
fines	-91.47	-105.68
Arquad 2HT 'dry' exchanged fines	-94.91	-108.68
Arquad 2HT 'dry' exchanged/washed fines	-92.34	-106.00

Table 3.14 ^{29}Si MASNMR data for 'dry' process quaternary ammonium exchanged bentonites

* External

(n.b. Q^3 - resonance from 'SiO_4' sharing three vertices

Q^4 - resonance from 'SiO_4' sharing four vertices)

The ^{29}Si shifts, relative to a separate sample of TMS, clearly show that the 'dry' exchange process results in screening of both Q^3 and Q^4 resonances. However, when the product is washed the shifts return towards their natural values. Superficially this behaviour may be associated with the removal of the surface sorbed unexchanged quaternary ammonium salts. Therefore the observation that both resonances are screened and then descreened in this manner indicates that the unexchanged organics are significantly sorbed on both the clay surfaces and the quartz impurity. However, before such a conclusion can rightfully be drawn, the effect of the sorbed quaternary ammonium salts upon the chemical shifts of the two resonances must first be satisfactorily explained.

In solution NMR spectroscopy, intermolecular induced screening changes are well known to be associated with bulk susceptibility (σ_b), van der Waals (σ_w), electric field (σ_E), magnetic anisotropy (σ_a) and specific interaction screening effects (σ_s). Each of the last four screening effects are operative only over relatively short distances. Consequently, because the particles used were in the range 1.9-9.9 µm, see Table 3.3, and a factor of about 1500 times larger than the absorbed species, it is evident that any of these four screening effects could only be operative in the surface layers. If such effects could be detected they must necessarily lead to resonance shift. The observed 'dry' exchanged and 'dry' exchanged/washed lines show no detectable difference in shape, and a change in f.w.h.m. from 400 to 417 Hz. The implications are that the observed shift changes must be due to $\Delta\sigma_b$.

Based on the concepts originally developed by Dickinson,[208] it has been shown that σ_b is controlled by the function ($1\text{-}3\cos^2\theta$), where θ is the angle between the direction of the applied field and the axis of rotation.[209] In the MASNMR experiment $\theta = 54.7°$ so that the controlling function should vanish and there should be no magnetic susceptibility screening effect.

If the magic angle is mis-set there could be residual susceptibility screening effect, but for the present work the magic angle was carefully set, see Section 2.3.7. Consequently it is unlikely that the shift changes presented in Table 3.14 can be explained on this basis. Similarly, changes in instrumental conditions can be ruled out as all were held constant throughout. The same number of FID's were collected in compiling each spectrum, and the phasing was left unadjusted from one sample to another.

However, the notion that chemical shifts in MAS experiments involve no bulk susceptibility corrections hinges on the susceptibility being isotropic.[210] Elegant experiments on films of polyethyleneterephthalate, PET, demonstrated that samples that exhibit macroscopic anisotropy in their bulk magnetic susceptibility may give rise to a bulk magnetic susceptibility screening effect.

A film of highly crystalline PET with aromatic rings parallel to the plane of the film, wound around a capillary of TMS along the rotation axis presented an effectively anisotropic susceptibility environment to the TMS, which was consequently screened by 1.5 ppm. When discs of PET were stacked with their planes normal to the capillary, the TMS experiences an isotropic environment and no susceptibility shift.

In principle, the phenomenon described above might be responsible for the shift differences seen in Table 3.14. However, for this to be the case the question immediately arises as to what constitutes a bulk environment. Little attention appears to have been paid to the effect of the thickness of a material on the susceptibility screening of an enveloped substance.

Work on susceptibility screening involving samples containing disperse phase globules, has shown that the susceptibility screening is independent of the number of globules present.[211] As the samples were essentially emulsions with a range of globular sizes, and no unusual line broadening or asymmetry were observed, it therefore may be reasonable to speculate that any molecular assembly that presents an homogeneous medium for the applied field may be deemed to be bulk.

From a different viewpoint, evidence that the so called anisotropic bulk susceptibility shifts may actually stem from molecular magnetic effects is inherent in the explanation of the PET induced shifts.[210] These shifts are attributed to the anisotropy in susceptibility resulting from aromatic ring current effects. It is not unreasonable to assume that induced bulk susceptibility shifts are dominated by molecular magnetic anisotropy effects. Therefore it may be that the lengthy and mobile, though directionally averaged, steric chains in the quaternary ammonium ions adsorbed on the silicate surfaces may be considered to offer an anisotropic magnetically susceptible environment to the bentonite particles.

It is probable that the quaternary ammonium salts are adsorbed on the silicate surfaces in such a way that, on average, the stearic chains are aligned pseudo-radically from the particles. In this case there must be an analogy with the PET wound film situation. Consequently, even during the eccentric rotation of the clay and quartz particles, they will continually have a magnetically anisotropic environment relative to the direction of the applied field.

The volume magnetic susceptibility for the dihydrogenated tallow dimethyl ammonium chloride salt has been determined, using a gouy apparatus, to be 2.04×10^{-6} cgs units. Although the anisotropy in χ_v is unknown it is almost certain that $\chi\perp - \chi\|$ will be positive, and cause a positive screening of the ^{29}Si nuclei in the silicates, as observed.

Although these results are entirely self-consistent, one final caveat still remains to be examined before the above arguments may be fully accepted. It is just possible that the screening effects observed, although several ppm in magnitude, see Table 3.14, could merely result from preferential packing of the anisotropic clay particles in the probe rotor. Were this to be the correct explanation the recorded shifts would be completely random about one particular value, and subsequent repeat analyses of the samples would fail to produce consistent chemical shifts. Indeed, the observed shift differences would not be seen at all if the mean shifts from several spectra were taken.

To answer this self-criticism, two further spectra were collected for each sample, and the observed variations recorded. Data are presented in Table 3.15. Clearly any variation in the chemical shift resulting from a preferential packing phenomenon is no larger than ±0.1 ppm, and as such is in no way responsible for the large chemical shift differences seen in Table 3.14.

Sample	Variation in ^{29}Si chemical shift	
	Q^3	Q^4
Arquad 2HT 'dry' exchanged fines	0.05	0.00
Arquad 2HT 'dry' exchanged/washed fines	0.12	0.04

Table 3.15 Variation in ^{29}Si MASNMR data for 'dry' process quaternary ammonium exchanged bentonites

It is now proper to conclude that ion exchange of Wyoming bentonite with a long chain alkyl-quaternary ammonium salt, using the 'dry' process, afforded a partially exchanged bentonite with extra quaternary ammonium salt surface sorbed onto both the clay and impurity, quartz, particles. This sorption was aided by a surface coating of Fe_2O_3 or $Fe(O)(OH)$ on both the phyllosilicate and silica polymorphs. The surface sorbed material was somewhat labile to washing, and it produced a measurable shielding of the ^{29}Si, nuclei on both clay and impurity particles.

Finally, the reproducibility of the induced shifts was examined by producing a second batch of the same 'dry' process organoclay and submitting this to the same ^{29}Si MASNMR investigation. Data are presented in Table 3.16.

Sample	Chemical shift (^{29}Si vs TMS)*	
	Q^3	Q^4
Arquad 2HT 'dry' exchanged fines	-94.42	-107.92
Arquad 2HT 'dry' exchanged/washed fines	-93.47	-107.82

Table 3.16 ^{29}Si MASNMR data for a second series of 'dry' process quaternary ammonium exchanged bentonites
* External

The results show that the effect is reproducible, the size of the difference in chemical shift between the two samples being an order of magnitude larger than the variations caused by the preferential packing phenomenon.

However, the actual size of the induced shifts does vary from those recorded in Table 3.14. This though is quite reasonable considering the sample history and the inhomogeneous nature of the 'dry' process. However, the absolute chemical shifts of the two 'dry' process exchanged samples are actually quite similar, and the difference in the size of the induced shift arises largely because of the sizable difference between the absolute chemical shifts of the two washed samples. Thus the difference in the magnitude of the induced shifts is predominantly a consequence of a more incomplete washing procedure for the latter sample.

It is therefore proposed that such sorption of long chain alkyl-quaternary ammonium species might be usefully employed to manipulate chemical shifts of materials studies by MASNMR spectroscopy.[212]

3.4 Conclusions and Further Work

Wyoming bentonite is a natural material containing many impurities, the most abundant of which is α-quartz. Thus the bentonite contains two quite different types of silicate surface that may interact with the cationic surfactant added in the 'dry' process production of organoclays.

Wyoming bentonite also displays a relatively high paramagnetic gramme susceptibility, approximately 6 x 10^{-6} cgs units g^{-1}, that is attributable predominantly to the presence of iron. This value of χ_g is well into the range established to give poor spectral resolution, $\chi_g > 2.2 \times 10^{-6}$ cgs units g^{-1}, of resonances in ^{29}Si MASNMR spectra.[58] However, excellent quality spectra were obtained, demonstrating that most of the iron present in the sample is non-structural. The presence of very finely divided, super paramagnetic, Fe_2O_3 or Fe(O)(OH) contaminating the surface of the major mineral components is the major contribution to the iron (III) quadrupole split spectrum and the to the observed value of χ_g.

The largest size impurity in the bentonite as received are aggregates of oil shale, derived from the overburden. These are chiefly responsible for the abrasive nature of the material, which it was hoped could be considerably reduced by air classification. Such refinement gave some separation by particle size, but impurity phases were significant in both coarse and fine fractions.

Obviously, during the pre-treatment carried out by the suppliers, abrasives had been milled down to a fine enough size to be present in some quantity in the fine fraction, but not down to a size small enough as to be undetectable to the touch. More successful air refinement may result if the bentonite used was more amenable to such a technique.

Abrasives are, by definition, relatively hard materials whereas smectite clays are easily powdered. It may well be that the milling conducted by Steetley Minerals Ltd. is unnecessarily harsh merely for the powdering of montmorillonite. A careful investigation into the powdering of the mined material, possibly sacrificing the high throughput of a gauze mill for the more controlled environment of a ball mill, may afford a procedure that can produce a bentonite ideally suited to air refinement. Such material would contain the clay fraction in a well powdered form, whilst all the impurity phases would be present as large particles. Air classification should then be able to very successfully remove the abrasives, giving a bentonite capable of producing a 'dry' process organoclay that is as pure as the 'wet' process equivalent.

It should also be possible to remove much of the surface coating of Fe_2O_3 or Fe(O)(OH) from the bentonitic minerals prior to the preparation of an organoclay. Many highly effective methods exist for the removal of free Fe_2O_3 from iron oxide rich soils, such as the sodium dithionite-sodium citrate system,[213] but they all have a marked destructive effect on iron bearing silicate minerals, often causing a quite dramatic reduction in exchange capacity. However, it has been shown that this may be easily avoided simply by buffering the system with sodium bicarbonate,[214] which facilitates the complete removal of iron oxide from soils and clays with almost no destructive effect on lattice iron. Thus the extent of alkyl-quaternary ammonium ion pair sorption may be re-examined without the beneficial influence of the oxide coating. In addition, a truer representation of the paramagnetic gramme susceptibility actually attributable to the montmorillonite may be attained.

Although excellent quality ^{29}Si MASNMR spectra were obtained, the acquisition of ^{27}Al MASNMR spectra was more troublesome. Observation of the central transition of tetrahedrally coordinated aluminium was often hindered by the presence of spinning sidebands resulting from octahedral aluminium. These, which arise from modulation of the central transition by sample spinning, are enhanced by an increasing iron content in the sample, which in turn generates an increasing magnetic susceptibility effect.[215] As the magnetic centre is not required to be close (next nearest neighbour) to the NMR nucleus for this effect to be observed, a physical admixture of a diamagnetic sample together with a highly magnetic material will suffice. Consequently any removal of iron from the bentonite by the above method should also facilitate the acquisition of better quality ^{27}Al MASNMR spectra.

Ion exchange of the Wyoming bentonite with a long-chain alkyl-quaternary ammonium salt using the 'dry' process afforded a partially exchanged, 69-78%, bentonite, with extra quaternary salt surface sorbed as demonstrated using X-ray photoelectron spectroscopy. The basal spacings recorded for such organoclays also indicated incomplete exchange, via the formation of a monolayer of ammonium ions in the interlamellar space, rather than the double layer required for complete exchange.

The 'dry' process product is a partially exchanged bentonite with surface sorbed quaternary ammonium ion pairs on both the silicate sheets of the clay mineral and the silicate surface of the quartz impurity. Such sorption is enhanced by the presence of the surface coating of Fe_2O_3 of Fe(O)(OH) on both clay and impurity.

The interlamellar regions of the organoclay are strongly hydrophobic, showing mineral expansion after prolonged exposure to a 93% RH atmosphere, despite the incomplete ion exchange. The by-product of the exchange reaction, sodium chloride, is expelled from the interlayer but causes the material as a whole to hydrate appreciably, even in a 79.5% RH atmosphere.

The surface sorbed material is somewhat labile to washing and induces a measurable shielding of the ^{29}Si nuclei in both clay and quartz impurity particles which is considered to arise from an anisotropic magnetic susceptibility effect. An alternative explanation, that of preferential packing of the anisotropic clay particles in the probe rotor, has been disproved. Successful reproduction of this surface sorption induced shift has led to the proposal that the surface sorption of long-chain alkyl-quaternary ammonium salts may be exploitable as a means of manipulating chemical shifts in MASNMR experiments.[212]

X-ray photoelectron spectroscopy has been used to demonstrate very clearly that a ratio of ion exchanged to ion pair sorbed quaternary ammonium ions exists in the 'dry' process product. It is the only technique that has been used that is capable of studying this ratio without taking the product into solution at any stage, but to date only qualitative results have been obtained in this way. It should prove possible to develop the technique quantitatively.

Some progress has already been made in this direction. By developing the technique using the Br(3d) electron rather than the N(1s) electron, the surfactant could be added as the amine salt rather than as the free amine, thus solving the problem of the high volatility of the sorbed species. Similarly, the use of a sodium exchanged clay eliminated the potential for potassium fixation, ever present when dealing with potassium exchanged smectites.[216]

Both the unexchanged organics and the released metal salts reside outside of the interlayer regions, therefore the depth of profile and penetration angle of the sources X-ray beam should exert little influence over the relative intensities of the two photopeaks. Only the relative sensitivities of the alkyl-quaternary ammonium bromide and the sodium bromide need be questioned. Calibration of standard samples of each material against an internal reference should allow relative sensitivities to be measured. Potassium bromate, $KBrO_3$, may prove to be a suitable reference material, having a binding energy for the Br(3d) electron of

74.6 eV,[176] considerably higher that that of either the alkyl-quaternary bromide, 67.2 eV, or sodium bromide, 68.3 eV.

Accurate measurement of the ion exchanged to surface sorbed ratio would then allow experiments designed to examine the nature of this ratio to be conducted. Within a group of primary, secondary, and tertiary amine salts of identical molecular weight, the ease of ion exchange decreases in the series $R_3NH^+ > R_2NH_2^+ > RNH_3^+$.[106] A similar series may be expected when measuring the exchanged to sorbed ratio, but the behaviour of a mono-, di-, and tri-quaternary series may be less predictable. The influence of pH upon this ratio would also be worthy of study.

However, by assuming monolayer formation in the interlayers of the 'dry' process organoclay, and complete exchange on all external surface lattice sites and all lateral surface sites, the extent of ion exchange recorded allows the mean number of platelets per lay flake to be calculated. On this basis, the observed difference in the degree of ion exchange achieved with the fine and the coarse bentonite fractions implies a difference in the size of the flakes, 2.25 unit layers per flake in the fines, and 4.5 unit layers per flake in the coarse fraction. These figures are in good agreement with the mean number of sheets per flake determined elsewhere using a combination of methods.[204] A difference in the size of the the flakes, rather than merely the size of the aggregates, in the two air classified fractions then suggests contemporaneous growth of the montmorillonite crystals in the Wyoming beds.

Chapter Four

HOST/GUEST CHEMISTRY ON A CLAY SURFACE

4.1 Introduction to Supramolecular Chemistry

The historical development of chemistry led to the concept of the molecule. Such was its usefulness that adequate recognition of graded interactions between the extremes of classical covalent or ionic bonding and weak van der Waals interactions has been slow. All molecules interact with other molecules, but for the most part the intermolecular forces involved are small compared with the covalent or ionic interatomic ones, so there is no problem in actually defining the molecule. However, some interactions between molecules may be sufficiently strong as to warrant description in terms other than simple van der Waals forces.

Supramolecular chemistry is the chemistry beyond the molecule.[217] It is the designed chemistry of the intermolecular bond, just as molecular chemistry is that of the covalent bond. An essential feature is that the component molecules are bound together by non-covalent forces, ion-ion, ion-dipole, dipole-dipole, dipole-induced dipole, dispersion, and electron donor-acceptor interactions.

For many years, it had been recognised that such addition products could be obtained from stable compounds, the formation of which was contrary to the normal rules of valency. Often these products persist in solution, in equilibrium with their component molecules formed by reversible dissociation. Many are highly coloured, a phenomenon inexplicable in terms of all the early theories. However, many of these early addition products are now widely accepted as charge-transfer complexes.[218]

4.1.1 Charge-Transfer (electron donor/ acceptor) complexes

The term is used to describe complexes formed by the weak interaction of electron donors with electron acceptors. It is derived from the successful valence-bond treatment developed by Mulliken [219] to explain the characteristic electronic absorption spectra of these complexes. The theory gives a rational explanation of many of their ground-state properties in terms of a structure which involves mainly dispersion, dipole and similar forces together with a usually small contribution from a covalent dative structure in which one electron has been transferred from the donor to the acceptor component of the complex. The observed electronic absorptions extra to the absorption of the components are accountable as intermolecular charge-transfer transitions.

Charge-transfer complexes usually involve simple integral ratios of the components. The enthalpy of formation is usually of the order of a few kilojoules per mole or less, and the rates of formation and dissociation are so high that the reactions often appear instantaneous by standard techniques. The components of the complex are described as electron donors and electron acceptors, rather than as Lewis bases and acids which are usually applied specifically to molecules capable of donating or accepting pairs of electrons.

Electron donor species may be either increvalent, donating lone-pair electrons, or sacrificial types, donating from bonding orbitals.[220] Sacrificial σ-donors such as hydrocarbons, especially small cyclic ones, are very weak electron donors, whereas sacrificial π-donors such as aromatics, particularly systems containing electron-releasing groups, may be strong donors. Some compounds such as aromatic amines may behave as lone-pair donors towards some acceptors and π-donors towards others. Some species may even be able to behave both as donors and acceptors. This may occur in self-complexes of benzene,[221] and with condensed polycyclic aromatic hydrocarbons such as pyrene and anthracene.[222]

Electron acceptor species may be similarly sub-divided into increvalent, vacant orbital type, or sacrificial, σ- or π-types. The binding of increvalent donors to increvalent acceptors is often so strong that covalent binding results.[218] Sacrificial σ-acceptors include the hydrogen halides, the halogens and the pseudo-halogens, but the most common organic acceptors are the π-acceptors. They include aromatic systems containing electron withdrawing substituents, quinones, acid anhydrides and chlorides, and a variety of planar aromatic cations such as paraquat.[223]

4.1.2 Host/guest (inclusion) compounds

If predominantly electrostatic interactions between the components molecules are decisive for adduct formation, the products are considered as complexes. However many stable addition products exist in which electrostatic interactions play little or no part. These are host/guest, or inclusion, compounds, the driving force for the formation of which is first and foremost the thermodynamically favoured dense molecular packing which results. However, it is important to note that these two classes of addition products, charge-transfer complexes and inclusion compounds, are not mutually exclusive. A great many charge-transfer complexes exist in which one component molecule resides in a cavity within the other. Similarly, it may be viewed that a great many inclusion compounds exist in which electrostatic interactions are the driving force for formation.

A topological subdivision of host systems into those having intramolecular cavities, termed cavitands, and those having extramolecular cavities, ie. formed between different molecules upon crystallization and termed clathrands, is now generally accepted.[224] By the inclusion of a guest molecule in the cavity of the host, or in the cavity formed between host molecules in the lattice, the cavitands and clathrands are converted into cavitates and clathrates respectively.

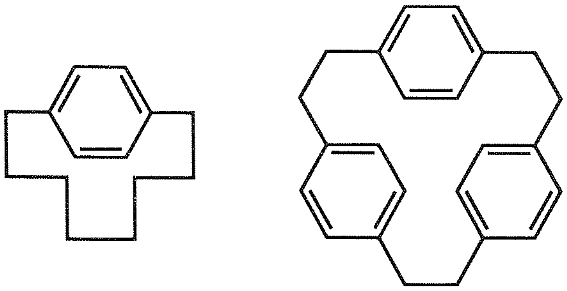
Clathrates, having only extramolecular cavities, can only form in the crystalline state, although the guest may be introduced to the host before or after crystallization. In contrast, cavitands will form cavitates in the solid state and in solution.

Typical cavitands are cyclodextrins, crown compounds, calixarenes, and cyclophanes. All are able to form inclusion compounds with neutral guest molecules. Such host/guest interactions have already found a wide range of applications, for instance the separation of mixtures of substances according to molecular size and shape using reversible crystallization/solution processes, suspension methods, or chromatographic procedures.[225] The selectivity can be sufficient to separate branched from straight-chain hydrocarbons, to fractionate isomers, and to resolve enantiomers.[226] Inclusion compounds are also used to store toxic, radioactive and explosive substances,[227] as specific catalysts,[228] and to promote phase transfer of sparingly soluble hydrophobic or hydrophilic compounds.[229]

In addition, many host molecules with intramolecular cavities, particularly macroheterocyclic onium compounds of the phane type with 'exohydrophilic' and 'endolipophilic' cavities, significantly reflect the basic characteristics of enzymes and have recently been successfully employed as model compounds.[224]

4.1.3 Cyclophanes and macroheterocyclic derivatives

Cyclophanes are benzene derivatives bridged between *p*- and/or *m*-positions with methylene groups. The value of the prefix indicates the number of methylene groups in the structure whilst the number of prefixes refers to the number of benzene rings present, ie. [8]-paracylcophane (I), and [2,2,2]-paracyclophane (II).



I II

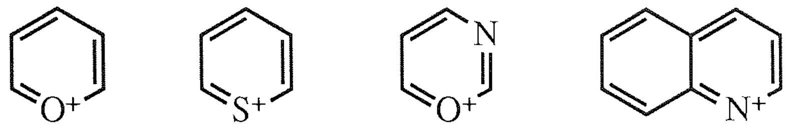
Figure 4.1 Schematic representation of the structures of [8]-paracyclophane (I) and [2,2,2]-paracyclophane (II)

Many-membered cyclophanes are well known to be able to form inclusion compounds with an extensive range of neutral guest molecules.[230] Their charge-transfer chemistry too has been well investigated.[218] A study of the 1:1 complexes of [n]- and [n,m]-paracyclophanes with the strong acceptor tetracyanoethylene revealed that in every case the complex is stronger than the tetracyanoethylene complex of the corresponding non-paracyclophane hydrocarbon *p*-xylene.[231] Similarly, the equilibrium constants of complexes of various 4-substituted-[2,2]-paracyclophanes with tetracyanoethylene indicate that the paracyclophanes containing electron releasing groups form the more stable complexes, as would be expected.[232]

4.1.3.1 Macroheterocyclic onium compounds of the phane type

The charge-transfer interactions between pyridinium and substituted-pyridinium cations and inorganic anions such as the iodide ion have been long recognized. The bis-pyridinium cation paraquat has been shown to form 1:1 charge-transfer complexes with various anionic and neutral donor species. Many of these, such as the complex formed with hexacyanoferrate ion in water, are relatively stable.[223] There is also evidence that a considerable number of other heterocyclic cationic systems such as pyrylium (III), thiopyrylium (IV), 3-azopyrylium (V), and quinolinium (VI) ion, can act as electron acceptors in forming charge-transfer complexes with inorganic anions, and some even with neutral donors.[218]

The importance of organic onium compounds for host/guest interactions in biological processes has also been established for some time, but only recently has the versatility of ammonium, phosphonium, and sulfonium salts as clathrate- and cavitate- forming molecules in abiotic chemistry begun to be recognized. In addition to being suitable as models of enzymes and biological receptors, such hosts may be used to transfer both aliphatic and aromatic guests into aqueous solution. Catalytic activity has also been demonstrated for those having large cavities.

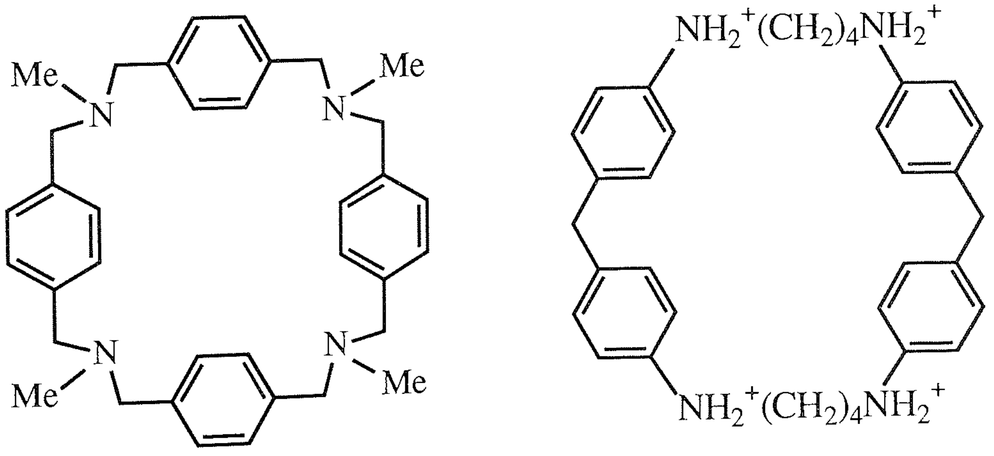


III IV V VI

Figure 4.2 Schematic representation of the structures of the pyrylium (III), thiopyrylium (IV), 3-azopyrylium (V) and quinolinium (VI) ions

Onium cyclophanes can easily be so constructed as to possess a polar exterior and a hydrophobic interior. Thus micelle formation in water is avoided within a relatively large concentration range, whilst guest molecules are still offered a non-polar microenvironment. The onium centres serve the purpose of ensuring the water solubility of the host molecules. At least four positive charges are required because of the size of these hosts and their lipophilic components.[224]

The conformation adopted by the cyclophane may vary considerably from complex to complex, from the dish-shaped conformation exhibited by the azaparacyclophane (VII) in its inclusion compound with 1,4-dioxane,[233] to the 'all-face' conformation shown by the tetraammonium salt (VIII) with durene.[234]



VII VIII

Figure 4.3 Schematic representation of the structures of N,N',N'',N'''-tetramethyl-2,11,20,29-tetra-aza[3,3,3,3]-paracyclophane (VII) and 1,6,20,25-tetra-aza[6,1,6,1]-paracyclophane

The 'all-face' conformation is favoured as a result of intramolecular π-interactions of the diphenyl methane units in the ring.[235] This provides the cavity with a sufficient depth to allow the guest to sit wholly enclosed in the host molecule, as long as there are also a sufficient number of methylene groups in the bridging chains to accommodate the full length of that particular guest. The specific geometries of such crystalline intramolecular inclusion compounds are also observed in solution.[236]

4.1.4 Nanotechnology ('Molecular Meccano')

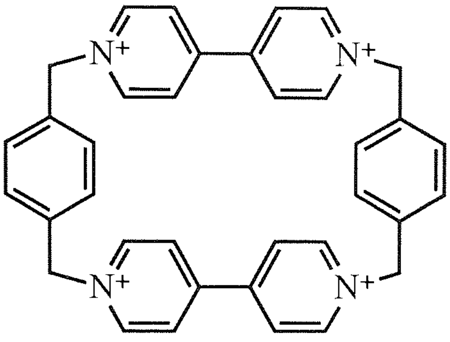
The functions of supermolecules cover recognition, as well as catalysis and transport. In combination with molecular self-organization, they open ways towards supramolecular devices for information processing and signal generation. The development of such devices requires the design of supramolecular components able to perform given functions, and suitable for assembly into an organized array. It is this prospect, of molecular-scale devices capable of performing mechanical or electronic tasks, that has led to the process of self assembly of supramolecular structures to be termed nanotechnology, molecular cybernetics, or more recently, 'molecular Meccano'.[237]

Many of the foundation stones in this area have already been laid. For instance, the feasibility of making a molecular diode by attaching the two ends of a potential diode macromolecule to two different microelectrodes, has already been demonstrated in simple systems involving two separate molecules, such as one thiol and one isonitrile.[238] All that remains to be done is to assemble a difunctional macromolecule that is long enough to span the microelectrodes.

Similarly, the tetracationic cyclophane (IX) has been used to construct interlocked molecular components termed rotaxanes, cyclic components through which are threaded linear dumb-bell components, and catenanes, large heterocyclic rings linked together as in a chain.[239,240] This has shown that rotaxanes and catenanes can provide the ideal models with which to establish the synthetic methodologies that will lead to the realization of efficient self assembly processes at a molecular level.

Already these concepts have been further developed to construct a prototype of a molecular abacus, based on (IX) and a bisdinaphthol ether,[241] and a molecular shuttle or 'train set', based on (IX) and a tetrakisparaphenylene crown ether.[242]

Such building of relatively simple molecules into complex multimolecule structures with precise control of the ordering of the components is an increasingly important scientific goal. Many technologies, such as catalysis, microelectronics, optics, and sensors stand to benefit enormously.[238]



IX. $4PF_6^-$

Figure 4.4 Schematic representation of the structure of cyclobis(paraquat-*p*-phenylene)

At the present time, the role of chemical sensors is continuously increasing, particularly in a wide range of monitoring applications.[243] The increasing severity of standards in environmental control, as well as in pollution, food, and drugs is only one of a number of reasons that may be invoked to explain this recent upsurge in interest.

A sensor, either physical or chemical, has to deliver a signal which is always electrical or optical at the end of a measurement chain, when the process to be detected or measured is occuring. Pillared smectites, and a variety of other pillared layered structures (PLS), have recently been suggested as being suitable for the further development of chemical sensors for gaseous detection.[244] The construction of a membrane with a very low pore size, to control the access of molecules to a physical sensor, or the use of PLS's as adsorbers, prior to the progressive desorption of small molecules into a detector by the use of a heating ramp, are two possible directions which may be followed.

The development of sensors able to work in liquid media is a less fertile area. It is to be hoped that the use of host/guest interactions can provide a route to the development of such materials. Some of the more recently synthesized host systems, such as the cationic cyclophanes (VIII) and (IX), in addition to being good multipurpose receptor molecules, may also act as simple organic cations and undergo ion exchange onto a smectite clay. Indeed, a pillaring of the silicate layers may be achieved, producing a genuine PLS possessing some interesting and useful properties.

4.2 Synthesis of Materials Used

The host system selected for this work is the tetracationic cyclophane cyclobis (paraquat-*p*-phenylene) (IX), one of a new class of phanes continuing two 4,4'-bipyridium moieties connected in a phane-like manner by means of bridges incorporating different aromatic residues.

A series of electron-rich guest species have also been synthesized for incorporation into this host system, based on group VI-substituted *o*-dimethoxybenzenes.

4.2.1 Synthesis of cyclobis(paraquat-*p*-phenylene)

Cyclobis(paraquat-*p*-phenylene) (IX) was first synthesized in two steps from bipyridine and *p*-bromoxylene in aqueous solution in 1983.[245] Here, acetonitrile was used as the solvent, in accordance with more recently reported experimental procedures,[246] as outlined in Figure 4.5.

4,4'-bipyridine (10 mmol, 1.7 g) and *p*-xylenebromide (5 mmol, 1.3 g) were dissolved in dry CH_3CN ($500cm^3$) and the solution was heated under reflux for 6 hours, yielding a brown precipitate of the single bridged bis(pyridinium) dication (XII) in almost quantitative yield.

A further quantity (4 mmol, 1.04 g) of *p*-xylenebromide was added to the reaction mixture and heating was continued for 24 hours. A final addition (1.5 mmol, 0.4 g) of the dibromide was made, and heating continued for another 24 hours. The ochre precipitate which formed was filtered off, turning bright yellow as it dried. The crude product, (IX), was purified by thorough washing with ether and acetone. The tetrachloride and tetra(hexafluorophosphate) forms of the cyclophane have also been produced by careful exchange of the counterion,[246] offering solubility in both aqueous and non-aqueous media. All compounds gave correct elemental analyses.

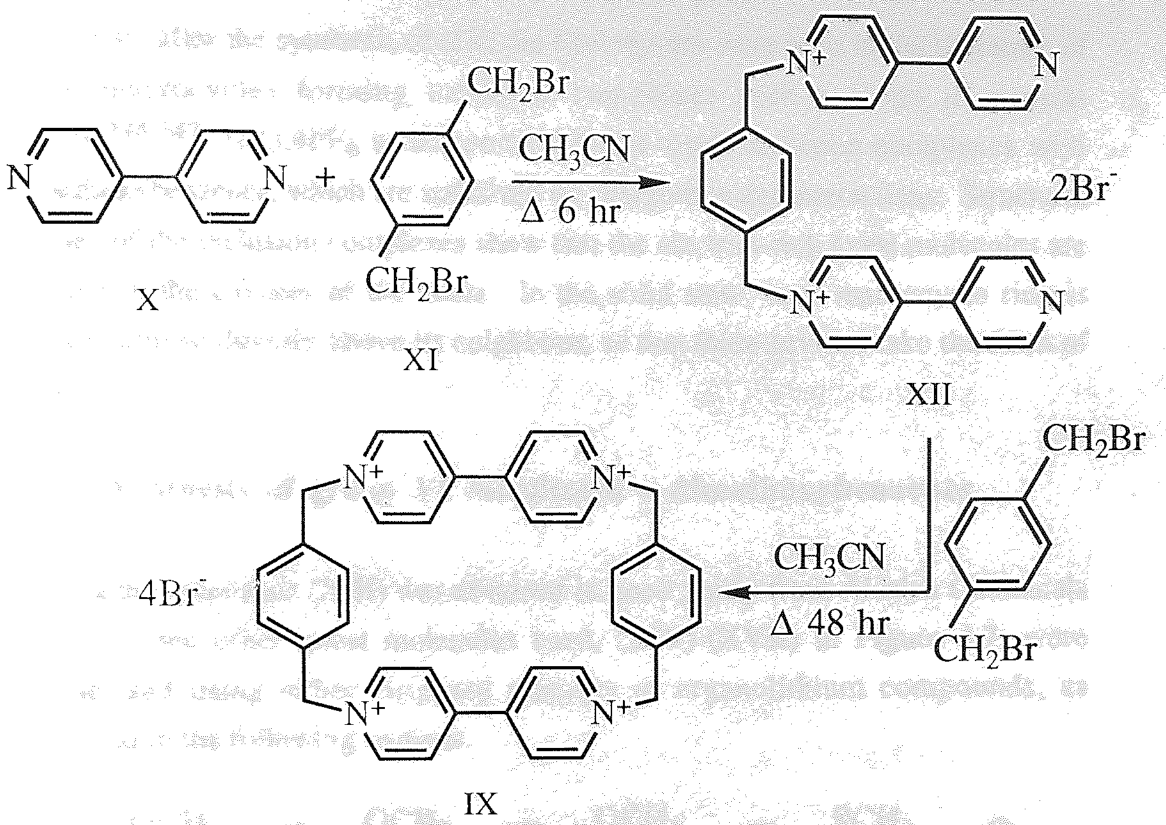


Figure 4.5 Schematic representation of the synthesis of cyclobis(paraquat-*p*-phenylene)

Calculations and X-ray crystallography [246] showed the tetracation to have a box-like structure in which the *p*-phenylene and paraquat units are slightly bent, see Figure 4.6. The overall dimensions of the macrocycle are 10.3Å between the centroids of the two para-phenylene rings and 6.8Å between the centroids of the pyridinium moieties.

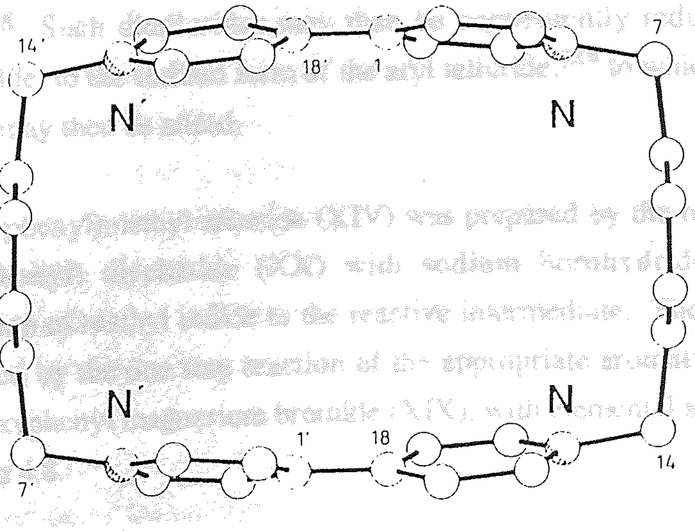
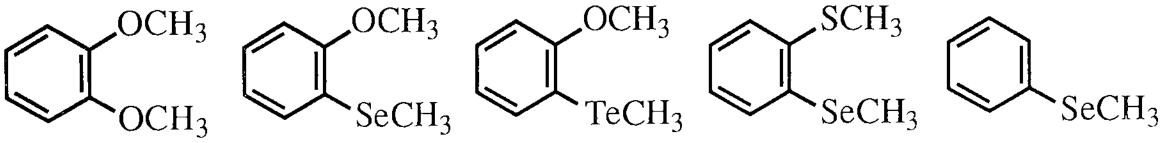


Figure 4.6 Structure of cyclobis(paraquat-*p*-phenylene) in the crystal

Five years after the synthesis of (IX) the first reports were seen in the literature of these macrocycles forming inclusion complexes with a range of neutral guests.[246,247] (IX).4PF_6 in acetonitrile forms weak inclusion complexes with dimethoxybenzenes, which are stabilized by charge-transfer interactions. Structural studies of the inclusion complexes show that the electron-rich guest molecules are located in the cavities of the hosts. In the solid state, each macrocycle ring is stacked almost directly above its neighbour, so that these cavities take the form of channels.

4.2.2 Synthesis of group VI substituted *o*-dimethoxybenzenes

o-Dimethoxybenzene (XIII) was obtained in good purity from Aldrich Chemicals Ltd. All the other guest molecules used, (XIV)-(XVII) in Figure 4.7, were synthesized using either Grignard reagents or organolithium compounds, as described in the following sections.



XIII XIV XV XVI XVII

Figure 4.7 A series of group VI substituted *o*-dimethoxybenzenes

4.2.2.1 Synthesis of (*o*-methoxyphenyl)methyl selenide

It is known that diaryl ditellurides can be formed from the reaction of phenyl magnesium bromide with elemental tellurium, followed by the oxidation of the intermediates.[248] Such ditellurides may then be conveniently reduced, using sodium borohydride, to the sodium form of the aryl telluride,[249] to which a variety of other reagents may then be added.

Thus (*o*-methoxyphenyl)methyl selenide (XIV) was prepared by the reduction of bis(*o*-methoxyphenyl) diselenide (XX) with sodium borohydride, and the subsequent addition of methyl iodide to the reactive intermediate. The diselenide itself was prepared by the one step reaction of the appropriate aromatic Grignard reagent, *o*-methoxyphenyl magnesium bromide (XIX), with elemental selenium, as outlined in Figure 4.8.

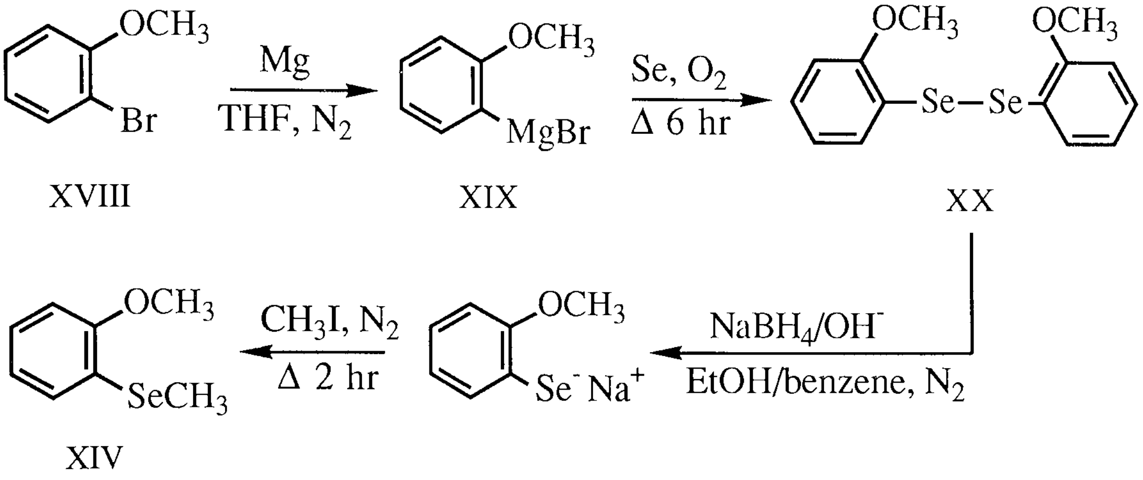


Figure 4.8 Schematic representation of the synthesis of (*o*-methoxyphenyl) methyl selenide

o-Bromoanisole (50 mmol, 9.35 g) and magnesium turnings (50 mmol, 1.22 g) were reacted under nitrogen in dry tetrahydrofuran (75 cm^3), forming the reactive *o*-methoxyphenyl magnesium bromide (XIX) by a Grignard reaction. The reaction was slow, with no ice being necessary. Selenium powder (50 mmol, 3.95 g) was then stirred into the Grignard solution, which was gently warmed.

As a yellow colouration began to appear, indicating the start of the reaction, oxygen was passed into the reaction vessel and heating continued for several hours. After cooling, the reaction mixture was filtered, and the filtrate allowed to stand in contact with the atmosphere overnight. The solid residue was extracted with diethyl ether, and recrystallization of the extract yielded orange crystals of bis (*o*-methoxyphenyl) diselenide (XX).

The bis(*o*-methoxyphenyl) diselenide (15 mmol, 5.5 g) was dissolved in a 70% ethanol/benzene (150 cm^3) solution, which was gently warmed under nitrogen. Sodium borohydride (32 mmol, 1.2 g) in 1M sodium hydroxide (15 cm^3) was added dropwise until the dark red solution became colourless. To this reduced solution, methyl iodide (32 mmol, 4.6 g) was then added, dropwise, and gentle heating and stirring continued for a further 2 hours, before the mixture was finally left to stand open to the atmosphere overnight.

The resultant yellow solution was filtered, and the filtrate dried over magnesium sulphate. Evaporation of the solution produced a sticky residue from which the desired product (XIV), a yellow oil, was extracted with diethyl ether. Any remaining solvent was removed using a vacuum line, yielding a fairly fluid honey coloured liquid.

The material gave the correct elemental analysis. The structure was confirmed by both proton and ^{77}Se solution NMR. A ^{77}Se satellite, arising from spin coupling between ^{77}Se and the methyl protons, was also observed in the proton spectrum, as expected. The ^{77}Se resonance was observed at -157 ppm, relative to dimethyl selenide in dichloromethane, in good agreement with the literature value.[250] In addition, a small solvent dependence of 7 ppm was also noted. This is larger than the ±1 ppm typical of the ^{77}Se chemical shift, but considerably smaller than the 30 ppm variations observed in aryl and alkyl selenols, RSeH.[250] It may though be considered as insignificant compared with the total range of chemical shifts of some 2800 ppm observed for ^{77}Se in organoselenium compounds.[251]

4.2.2.2 Synthesis of (*o*-methoxyphenyl)methyl telluride

(*o*-Methoxyphenyl)methyl telluride (XV) was prepared in a similar way to the selenium analogue, the route to which was described in the previous section, 4.2.2.1. Thus the bis(*o*-methoxyphenyl) ditelluride (XXI) was prepared as a precursor to the desired product, by the addition of tellurium powder to the appropriate Grignard reagent,[248] as previously described.

However, the reduction of the ditelluride was not here carried out by the use of sodium borohydride. Instead the addition of an excess of methyl iodide under reflux conditions was used to cause a smooth decomposition into molecular proportions of iodo-derivatives (XXII, XXIII). Loss of methyl iodide from (*o*-methoxyphenyl)dimethyl telluri-iodide (XXII) on heating, and reduction of the co-product (*o*-methoxyphenyl)methyl telluridi-iodide (XXIII) with potassium metabisulphite, then results in the formation of the desired telluride,[254] as outlined in Figure 4.9.

The bis(*o*-methoxyphenyl) ditelluride (4.3 mmol, 2.0 g) was added to a large excess of methyl iodide (35 cm^3) and heated under reflux for 30 minutes, after which time large amounts of pale yellow crystals had precipitated out of the reddy-brown solution. After standing the solution overnight, the crystals were removed by filtering, and washed in methyl iodide. Gentle heating caused the loss of methyl iodide from the crystals to yield a pure, thick, honey-coloured oil (XV).

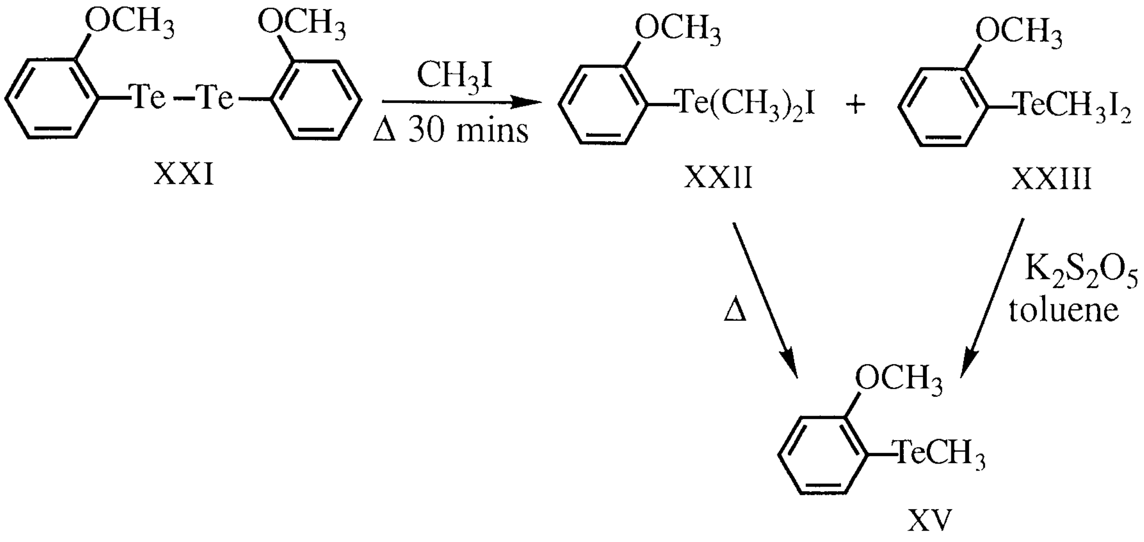


Figure 4.9 Schematic representation of the synthesis of (*o*-methoxyphenyl) methyl telluride

Similarly the extract from the mother liquor, upon vigorous shaking with 1M potassium metabisulphite, yielded the (*o*-methoxyphenyl)methyl telluride (XV). The structure was confirmed by both elemental analysis and ^{1}H NMR.

4.2.2.3 Synthesis of (*o*-methylthiophenyl)methyl selenide

(*o*-Methylthiophenyl)methyl selenide (XVI) was prepared by the ortho-selenation of benzenethiol (XXIV) using n-butyllithium/tetramethylethylenediamine (TMEDA) and elemental selenium,[253] as shown in Figure 4.10.

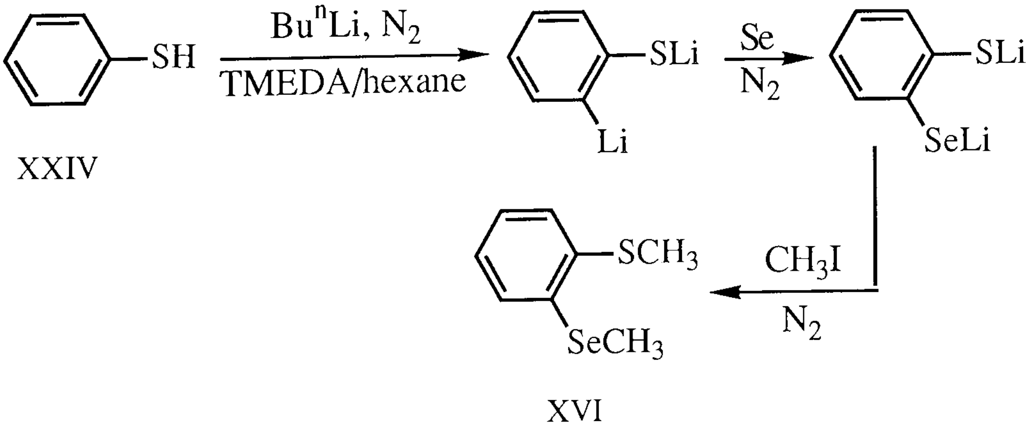


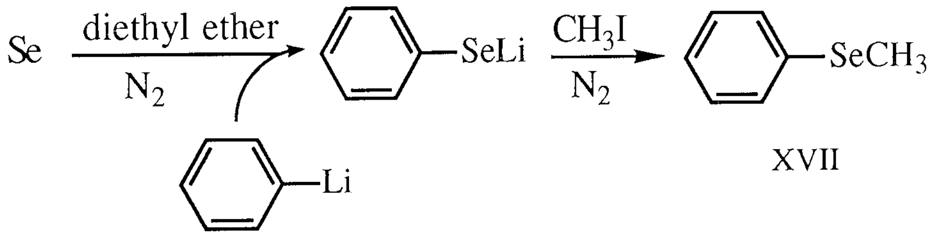
Figure 4.10 Schematic representation of the synthesis of (*o*-methylthiophenyl) methyl selenide

Benzenethiol (10 mmol, 1.0 cm^3) was added to an ice-cooled solution of n-butyl lithium (5.3 cm^3, 10.0M) and TMEDA (3.4 cm^3) in hexane (100 cm^3). After

1 hour at 0°C and 12 hours at room temperature, selenium powder (10 mmol, 0.79 g) was rapidly added to the cream-coloured slurry, causing an orangy-yellow colouration to develop over the next hour. Methyl iodide (20 mmol, 1.3 cm^3) was then added at 0°C and the mixture stirred for one hour. The reaction mixture was finally poured into water and extracted with diethyl ether. Drying over calcium chloride and evaporation of the solvent yielded (*o*-methylthiophenyl)methyl selenide (XVI) as a pungent yellow oil. The correct ^1H NMR and elemental analyses were obtained.

4.2.2.4 Synthesis of phenylmethyl selenide

The selenation of benzene was achieved in a manner similar to that employed for the ortho-selenation of benzenethiol, Section 4.2.2.3. Here the organolithium intermediate, phenyl lithium (XXV), being commercially available, was taken as the starting material. Elemental selenium, followed by methyl iodide, were added in the usual way, see Figure 4.11.



XVII

XXV

Figure 4.11 Schematic representation of the synthesis of phenyl methyl selenide

Metallic selenium (18 mmol, 1.42 g) and sodium-dried diethyl ether (100 cm^3) were stirred under nitrogen at room temperature for 1 hour. Phenyl lithium (18 mmol, 10 cm^3 of 1.8M) was added slowly through a resealable septum, and the solution observed to turn grey/green. After a further 1 hour methyl iodide (18 mmol, 1.1 cm^3) was added, causing a mustard yellow colouration of the solution, and stirring was continued for a further 4 hours. The reaction mixture was extracted with benzene, and evaporation of the solvent yielded phenyl methyl selenide (XVII) as a fluid, bright yellow oil. The structure was confirmed by ^1H NMR and elemental analysis.

4.3 Solution Studies of a Charge-Transfer Complex

The complex investigated is cyclobis(paraquat-*p*-phenylene) tetrabromide (IX) / *o*-dimethoxybenzene (XIII) in aqueous solution. This is a yellow colour, showing a charge-transfer band just inside the visible region of the spectrum.

A variety of methods may be used to determine the position of the equilibrium between charge-transfer complexes and their free component molecules in the liquid phase. The concentration of the various solute species in the solvent is generally assumed to be sufficiently low for the systems to be treated as dilute solutions. The results then provide measures of the free energies of formation of the complexes, and, from their temperature variation, the corresponding enthalpy and entropy changes.

4.3.1 Ultraviolet/Visible solution spectrophotometric investigations

It was for solutions containing an aromatic hydrocarbon and iodine that an electronic absorption band, not present in either component alone, was first reported.[254] It was soon suggested elsewhere [255] that the characteristic absorption of such solutions could arise through an intermolecular charge-transfer transition. The result was the formulation of the valence bond treatment for complex formation between electron donors and electron acceptors.[219]

Today, the position of the equilibrium is most usually determined by optical methods. In so doing, the value of the equilibrium constant, K, is tantamount to a determination of the molar absorption coefficient (formerly the extinction coefficient), ε, of the electronic absorption now attributed to the charge-transfer complex species.

Many methods exist for doing this, although some modification of the original Benesi-Hildebrand procedure [254] is almost always used. Here, a modified Benesi-Hildebrand treatment for weak complexes [256] is employed, incorporating experimental procedures recommended for weak complex formation.[257] The most important criterion in such systems is that the equilibrium constant of the complex is of the same order of magnitude as the equilibrium concentration of the more dilute component. For complexes measured by the Benesi-Hildebrand method, or one of its variations, this condition requires that the donor concentration in the most concentrated solution must be greater than about 0.1/K.

In accordance with this recommendation, and the conditions required by the modified Benesi-Hildebrand treatment for weak complexes,[256] a series of solutions were made up in which the cyclophane concentration was held constant at 5.61 x 10^{-4} M, and the guest concentration varied in the range 1.23-3.50 x 10^{-2} M. The optical density, D, of each solution was measured at 440 nm according to the method described in Section 2.3.15.

Rearrangement of the Benesi-Hildebrand equation [254] gives the form of the equation required here, termed the Foster-Hammick-Wardley equation.[256] It holds that

$$D/b^n = Ka\varepsilon - KD \qquad [4.1]$$

for the conditions stated, where a and b are the initial concentrations of the host and guest respectively. Thus a plot of D/b^n against D should be linear, the gradient being equal to -K, and the intercept with the x axis being $a\varepsilon$. By varying n until a linear relationship is achieved, the stoichiometry of the complex can be ascertained, and both K and ε determined. By adopting this procedure a 1:1 stoichiometry for the complex has been proven. Experimental data are presented in Table 4.1.

Acceptor conc. (M)	Donor conc. (M)	Charge-transfer band		K (M^{-1})
		λ_{max} (nm)	$\varepsilon_{\lambda max}$ ($M^{-1}cm^{-1}$)	
5.61 x 10^{-4}	0.0123-0.0350	440	113	41±2

Table 4.1 UV/Vis data for the complex formed between *o*-dimethoxybenzene and cyclobis(paraquat-*p*-phenylene) tetrabromide in water at 25°C

A value for K, the thermodynamic association constant for the complex, of 41±2 M^{-1} was obtained. This may be compared with a recently published value of 8±0.3 M^{-1} for the same complex in acetonitrile.[246] Such a strong dependence on the nature of the solvent is already well established from previously published data.[218] Indeed, other factors such as deviations from Beer's law and the presence of higher order complexes have also been postulated to account for observed or suspected anomalies in the reported values of K and ε.[258]

4.3.2 ^{1}H NMR spectroscopic investigations

The position of the equilibrium for such complexes may also be determined from NMR data. The observed chemical shift, ∂, for a given nucleus in a molecule in dilute solution is dependent upon its chemical environment. The appearance of a resonance arising from a nucleus which can exist in more than one chemical environment is dependent upon its lifetimes in these different environments.

In the simple case of the nucleus which can exist in just two chemical environments, in either of which alone it appears as a singlet, such as one might expect from an equilibrium between a 1:1 complex and its components, two limiting situations exist. If the lifetimes in the two states are long on an NMR timescale, the two lines are observed. However, if the lifetimes are short, so that the molecular environment of the nucleus undergoes rapid reversible change on an NMR timescale, then only a singlet, time-averaged line is observed.[259]

Further, in such a case the position of the resonance will represent a time-averaged resultant of the behaviour of the nucleus in the different environments, such that the position is dependent on the relative populations of the environments. Consequently, by determining the change in chemical shift, $\Delta\partial$, of a nucleus in one component, by the controlled addition of the second component, the concentration of the complex at equilibrium, and the association constant, K, may be obtained.

Methods of calculation which are analogous to the Benesi-Hildebrand expression [254] may be applied to the treatment of other physical data, such as NMR data, but they are not particularly satisfactory. All require that the concentration of one of the components be substantially in excess of the other, so that the effect of complex formation on the concentration of the major component can be neglected. Such a condition, even when allowed by the solubilities of the components in the chosen solvent, is not well suited to the relative lack of sensitivity of the NMR method.

A method that is particularly applicable to systems containing nearly equivalent concentrations of the donor and acceptor species, that relies upon successive corrections being made for the amounts of interactants present in the complexed form,[260] is used here.

For two species A and D that interact reversibly in solution to form a 1:1 complex C, the time-averaged nature of the observed chemical shift, ∂_{obs}, means that it can be shown [260] that for an observed signal in component D, equation 4.2 holds

$$\frac{[A]_o}{(\partial_{obs}-\partial_D)} = \frac{1}{(\partial_C-\partial_D)}\left([A]_o+[D]_o-[C]\right) + \frac{1}{K(\partial_C-\partial_D)} \qquad [4.2]$$

where $[A]_0$ and $[D]_0$ are the added concentrations of A and D respectively, [C] is the concentration of the complex at equilibrium, and ∂_C and ∂_D are the chemical shifts of the observed nuclei in the complexed form and the non-complexed form respectively. This equation contains two unknowns, [C] and ∂_C, which may be calculated by means of a simple iterative procedure based on successive approximations.

By initially setting [C] equal to zero, a plot of $[A]_0/(\partial_{obs}-\partial_D)$ against $([A]_0+[D]_0-[C])$ yields straight line with a gradient approximately equal to $1/(\partial_C-\partial_D)$, which may then be used to obtain an approximate value of [C] according to equation [4.3].

$$[C] = [A]_0 \, (\partial_{obs}) \; \{ \; 1/(\partial_C-\partial_D) \; \} \qquad [4.3]$$

Replotting using the new approximate value of [C] gives a new, refined value of [C]. These steps are repeated until two successive cycles yield essentially identical convergent values for the slope. The final stability constant, K, may then be calculated, from the limiting slope and intercept values, along with the full induced shift, $\partial_C-\partial_D$, or Δ_0, and the chemical shift of the proton in the complexed form, ∂_C.

In accordance with the conditions required, a series of solutions containing nearly equivalent concentrations of the donor and acceptor species was made up, in which the cyclophane concentration was held constant at 2.2 x 10^{-3}M and the guest concentration varied in the range 1.9-8.5 x 10^{-3}M.

All the experiments were carried out using D_2O as solvent, and employed a ^2D lock. A 180-τ-90 pulse (PW2 60.0 μs, τ 6.4 s, PW1 30.0 μs, PD 30s) was used to suppress the H_2O peak arising from an impurity in the solvent. The chemical shifts of the protons on the guest were recorded relative to the Obset value (44.65 KHz). Data are presented in Table 4.2. It may be noted that the intensity of all the peaks is positive, indicating that they relaxed faster than the suppressed water peak.

$\Delta\partial$, the change in observed chemical shift relative to the chemical shift of free *o*-dimethoxybenzene, is significantly larger for the four identical aryl protons than for the methoxyl protons. However, all the proton resonances of the guest molecule are shifted to some extent by complexation with the cyclophane, and all are shifted upfield from the absorptions of the free guest. If transfer of charge had made a significant contribution to $\Delta\partial$, then a downfield shift of proton resonances in the donor upon complex formation would have been expected. It is suggested, from the increased shift of the aryl resonance, that ring-current effects may be important, a contention supported by many other studies.[218]

Reagent conc. (M)		∂_{obs} (D) (ppm)		$\Delta\delta$ or δ_{obs}-δ_D (ppm)	
$[A]_0$	$[D]_0$	Aryl	Methoxyl	Aryl	Methoxyl
-	1.9×10^{-3}	0.8010	-2.3990		
2.2×10^{-3}	1.9×10^{-3}	0.6907	-2.4358 -2.4563*	-0.110	-0.037 -0.057
2.2×10^{-3}	8.5×10^{-3}	0.7283	-2.4235* -2.4448	-0.073	-0.025 -0.046

Table 4.2 ^1H NMR data for the complex formed between *o*-dimethoxybenzene and cyclobis(paraquat-*p*-phenylene) tetrabromide in D_2O
* indicates the major peak of a doublet

Interestingly, the presence of the host cyclophane has caused the methoxyl singlet to be split into a doublet, the major peak of which is the right hand one when the host/guest stoichiometry is 1:1, but is the left hand one when the stoichiometry is 1:4. There are two possible explanations for this observation.

It may be that the two, previously identical, methoxyl groups on the guest dimethoxybenzene become non-identical upon complexation. If this is correct, then no peak arising from free guest molecules is observed in the spectrum. Alternatively, the two methoxyl groups remain indistinguishable in the complex, and the two peaks arise from free guest molecules in solution and guest molecules in the complex. In this case, the spectrum is still partially time-averaged, as the free guest peak is shifted upfield.

On the addition of excess guest the doublet shifts back slightly towards the ∂ value for free *o*-dimethoxybenzene, and the major peak of the doublet changes from being the right hand one to being the left hand one. This cannot be explained using the idea of non-identical methoxyl groups, as the lack of a free guest peak now implies a time-averaged spectrum, but this would mean the time-averaging of the non-identical methoxyl groups too. The correct interpretation must be that the two peaks of the doublet arise from a partially time-averaged spectrum of free guest molecules, left hand peak, and complexed guest molecules, right hand peak.

The experimentally obtained values of $(\partial_{obs}-\partial_D)$, Table 4.2, were then used to calculate the full induced shift, $(\partial_C-\partial_D)$, and the stability constant, K, of the complex, using the iterative procedure already described.[260] The slope of the first approximate plot was used to calculate the first approximate concentrations of the complex species in solution, [C], which were then used to give plot 2. Plot 2 essentially coincided with plot 3 and successive plots. K and $(\partial_C-\partial_D)$ were calculated from data generated by plot 2, and are presented in Table 4.3.

Reagent concentration (M)		Full induced shift [a] (Hz)	AD complex	
$[A]_0$	$[D]_0$	Δ_0 or $(\partial_C-\partial_D)$	K (M^{-1})	Lifetime (s)
2.2×10^{-3}	$1.9\text{-}8.5 \times 10^{-3}$	160	42±2	$1.9 \pm 1 \times 10^{-3}$

Table 4.3 Stability constant and complex lifetime from ^1H NMR data by an iterative procedure.[260]

A value of 160 Hz for the full induced shift, Δ_0, is large when compared to typical values of 60-80 Hz for interactions between benzenoid acceptors and benzenoid donors, but not unusually so.[218] The direction of the shift, namely upfield from the resonance of the free component, indicates that transfer of charge is not a significant factor in determining the magnitude of Δ_0. This is not to say, of course, that there is no contribution from charge transfer in the complex, merely that it is unimportant when determining Δ_0.

The value of the stability constant obtained here from NMR data, 42±2 M^{-1}, is in remarkably good agreement with the value of 41±2 M^{-1} obtained from the optical measurements reported in Section 4.3.1. This serves not only to corroborate the figure reported therein, but also to confirm the conclusion implied by it. That is to say the strong dependence of the nature of the solvent upon the measured stability constant.

In addition to values of Δ_0 and K, Table 4.3 also gives a value for the approximate lifetime of the complex. This was possible because of the partially resolved nature of the methoxyl peaks in the NMR spectra. As stated earlier, this situation arises when the exchange rate between the complexed and uncomplexed states is approximately equal to the chemical shift difference between the two sites.[259]

This may be expressed numerically such that a two-lined spectrum is observed when the lifetimes in the two states are long compared with $\sqrt{2}(\pi\Delta_0)^{-1}$, and a time-averaged singlet is observed when the lifetimes are short compared with this value. By assuming here the lifetime of the complex to be comparable to $\sqrt{2}(\pi\Delta_0)^{-1}$, the measurement of Δ_0 allows the approximate lifetime of the complex to be calculated as $1.9\pm1 \times 10^{-3}$ seconds.

One would expect such complexes to be short lived on an NMR timescale, causing a time-average singlet to be observed. The relatively slow rate of exchange of this cyclobis(paraquat-*p*-phenylene) complex suggests it to be a stable one, again confirming the relatively large magnitude of the observed stability constant.

4.4 Host/Guest Chemistry on a Clay Surface

The cyclobis(paraquat-*p*-phenylene) tetrabromide/ *o*-dimethoxybenzene complex observed in aqueous solution in the previous section would not be so well suited, when bound to a clay, to solid techniques. Useful NMR data would be difficult to acquire, as proton resonances would be swamped by lattice protons, ^{13}C is not really sensitive enough for accurate chemical shift measurement in such dilute systems, and no other suitable nuclei are present.

^{29}Si MASNMR would provide information on the screening of the silicate backbone, but the formation of a charge-transfer complex on the basal surfaces may not cause a significant shift in electron density to be transmitted through the exchange sites to those silicon nuclei. Therefore it was considered preferable to again attempt to measure the chemical shift of the guest molecule before and after complexation. Consequently, a selenium analogue of *o*-dimethoxybenzene was synthesized, enabling ^{77}Se MASNMR to be employed. The NMR active ^{77}Se isotope is 7% abundant and has a sensitivity three times that of ^{13}C.[261] Importantly however, ^{77}Se chemical shifts extend over some 2800 ppm in organic compounds.[251]

Solution work with the cyclobis(paraquat-*p*-phenylene) tetrabromide/ (*o*-methoxyphenyl)methyl selenide complex, analogous to that described in the previous section, proved to be impossible to carry out. The selenide does not have a high enough aqueous solubility, and other solvents appeared to provide too much competition for the selenide as guest species. However, for complexes in which transfer of charge is not a significant factor in determining the magnitude of Δ_0, such as complexes involving a cyclobis(paraquat-*p*-phenylene) acceptor species, it has been shown [218] that there is a lack of dependence of Δ_0 on the nature of the donor component. Thus it can be expected that, could it be measured, the full induced shift of this complex would also be fairly large.

4.4.1 Cyclobis(paraquat-*p*-phenylene) pillared clays

The cyclophane was ion exchanged onto both Wyoming bentonite and laponite, from both the tetrachloride and tetrabromide forms, using an aqueous medium and a mechanical, wrist-action shaker, following the method outlined in Section 2.2.1. The weight added was based on a CEC of 70 meq per 100 g for Wyoming bentonite [163] and 73.3 meq per 100 g for laponite.[177]

Upon exchange of the tetrabromide form of the cyclophane onto Wyoming bentonite, the product was observed to have a stronger yellow colouration than did the original bentonite. It was considered that this resulted from the retention of a percentage of the bromide ions that gave the cyclophane its yellow colour, i.e. incomplete ion exchange per molecule. It should be remembered that the tetrachloride form of the cyclophane is pure white, and so complete exchange of the tetrabromide form should not impart any colour onto the clay.

By turning to laponite, a pure white synthetic clay, this matter was resolved. Cyclophane exchanged laponites were prepared from both the tetrabromide and tetrachloride forms. Data are presented in Table 4.4 The percent ion exchange achieved was determined by atomic absorption spectroscopy, but as the cation used here is not monovalent this result does not show the percentage of cyclophane molecules exchanged onto the clay, whether by all four ammonium sites or just one. For this reason a total chloride ion determination was also carried out using Volhards method, described in Section 2.3.16. It was realized that the washings could not contain more sodium ions than chloride ions, and that any excess chloride ions, above the sodium ion concentration determined by atomic absorption spectroscopy, would be associated with unreacted cyclophane.

The chloride-derived exchanged clay was a pure white colour, whereas the bromide-derived form was a strong earthy yellow colour. In both cases the halide ion concentration just matched the sodium ion concentration, indicating that indeed all the cyclophane had been ion exchanged onto the clay, but that many of the molecules were incompletely ion exchanged, still having some halide counterions associated with them. Again in both cases, 86% of the cyclophanes positive charges were exchanged, leaving an average of approximately 1/2 of a halide ion still associated with each cyclophane on the clay. It may be that 100% ion exchange is impossible to achieve beyond a certain loading, because of the localized nature, and inflexible intersite distances, of exchange sites on the clay.

Exchange cation			Exchanged laponite			
	Meq added	Percent exchanged	Colour	Percent CEC exchanged	Released ion conc. (x 10^{-3} M)	
					Na^+	X^-
$IX.4Cl^-$	75.5	86	white	89	3.13	3.11
$IX.4Br^-$	57.1	86	yellow	67	9.80	9.88

Table 4.4 Data for 'wet' process cyclophane exchanged laponite

Both these two clays, and the Wyoming bentonite analogue, proved impossible to gel. This suggested that the clays had been pillared, a suspicion that was confirmed by the extraordinarily sharp reflection in the XRD trace at $2\theta = 7.0°$. Such a sharp reflection, when produced from smectite samples, indicates that there is a very high degree of alignment of the clay platelets, which can only come about through the pillaring of the layers.

The position of the reflection, $2\theta = 7.0°$, corresponds to a basal spacing of 14.7Å. By taking the assumed thickness of the individual trimorphic silicate layer to be 9.5Å,[262] the difference due to the expansion of the interlayer, the so-called Δ value,[263] may be obtained. The value for the cyclobis(paraquat-*p*-phenylene) pillared montmorillonite is 5.2Å. The molecular dimensions of the cyclophane are 10.3Å between the centroids of the two para-phenylene rings, and 6.8Å between the centroids of the pyridinium moieties.[246]

The discrepancy between the observed value and the smallest of the two molecular dimensions quoted above is 1.6Å. Such discrepancies are found with a great many clay-organic complexes, and the concept of 'keying' [107] the cations into the ditrigonal holes of the silicate surface has often been used to account for them. However, such contractions are usually taken to be approximately 1Å,[262] although it can readily be demonstrated by the aid of molecular models of the montmorillonite surface that alkylammonium cations can be keyed to give contractions greater than this.[73] It is doubtful whether the cyclophane could be keyed to this extent, but by reducing the bow in the pyridinium moieties the value may be halved to 0.8 Å, making this orientation a possibility.

Alternatively the cyclophane must be orientated so that neither of these molecular dimensions lie along the c axis, normal to the silicate sheet. Instead it must lie flat between the layers, in a 'garden fence' type orientation. The observed value is in agreement with such an orientation.[262]

The first orientation discussed has the advantage of allowing the ammonium centres to get directly next to the basal surfaces, whereas the second orientation requires the smallest expansion of the interlayer. However, as a consequence of this second orientation, access to the cavity within the cyclophane is blocked. Therefore any host/guest interaction observed on the clay substrate is certain to result from complexation with external surface bound cyclophane. This last point allows the correct orientation to be determined by the use of ^{29}Si MASNMR spectroscopy.

4.4.2 ^{29}Si MASNMR spectroscopy investigations

If the second, 'garden fence' type orientation is correct, measuring the chemical shift induced in the silicon nuclei of the clay substrate upon complexation will result in two resonances being observed, one arising from external surface silicon adjacent to cyclophane/guest complexes, and one arising from internal surface silicon adjacent to empty cyclophane hosts. However, if the first orientation, with the para-phenylene moieties lying along the c axis, is correct, all the cyclophane cavities will be available for complexation, and a single resonance will be seen.

The guest molecule chosen was again *o*-dimethoxybenzene, as it was known to form a stable complex with the cyclophane. It was introduced to a pillared laponite, produced from the tetrabromide form of the cyclophane, as an aqueous solution, in a 1:1 stoichiometry with the cyclophane. The suspension was shaken overnight, and the resulting clay was then filtered and dried. It had a definite orange colouration, in contrast to the earthy yellow colour of the same clay before the introduction of the guest.

^{29}Si MASNMR spectra were determined, and data are presented in Table 4.5. That a change in chemical shift is observed at all indicates that the shift in electron density that invariably results from the formation of a charge transfer complex is transmitted through the exchange site, and causes a change in the electronic screening of the silicon nuclei in the silicate backbone. More importantly, the introduction of the guest fails to cause either resonance to be split into a doublet, thereby confirming the correct orientation of the cyclophane within the interlayer to be that which has the para-phenylene moieties lying along the c axis such that the ammonium centres are directly next to the basal surfaces.

Laponite sample	Chemical shift (^{29}Si vs TMS) [a]	
	Q^2 [b]	Q^3
laponite RD [c]	-79.92	-89.48
cyclophane exchanged	-83.23	-92.98
cyclophane exchanged/ *o*-dimethoxybenzene	-85.60	-95.46

Table 4.5 ^{29}Si MASNMR data for cyclophane exchanged laponite

[a] External

[b] Q^2 - resonance from 'SiO_4' sharing two vertices

Q^3 - resonance from 'SiO_4' sharing three vertices

[c] After Mandair [165]

Finally, by comparing these changes in chemical shift with those observed for the 'dry' process organoclays, Table 3.14, it may be seen that the cyclophane and the quaternary ammonium cation give a very similar shielding effect to the silicon nucleus. Both produce an upfield shift of about the same magnitude, relative to the original Na^+ counterion, which represents an increase in nuclear screening. A further increase in screening is obtained by introducing a guest into the cyclophane, as might be expected on the basis of the electron acceptance behaviour of the cyclophane in the charge transfer complex.

4.4.3 Diffuse reflectance ultraviolet/visible and raman spectroscopy investigations

The cyclophane pillared laponite displayed a colour change from earthy yellow to orange upon the introduction of *o*-dimethoxybenzene, as described in the previous section. This colour change was also observed for the complex between the same guest and a similar cyclophane pillared montmorillonite. To be sure that these observations were not due for example to a variation in the moisture content of the clay, but were actually attributable to the presence of the charge transfer complex on the clay, diffuse reflectance UV/Vis. spectra were determined. A clear difference in the spectra after the introduction of the guest, and an accompanying change in the wavelength of maximum adsorbance, was observed, confirming the colour change.

Several group VI substituted *o*-dimethoxybenzenes, synthesized according to the methods described in Section 4.2.2, were then introduced to a cyclophane pillared montmorillonite, and various colour changes observed. None of the synthesized guests were significantly water soluble, and so they were introduced via an ethanolic solution, in a 1:1 stoichiometry with the cyclophane. Again the suspension was shaken overnight, but the solvent was then allowed to evaporate off in a fume cupboard so that no guest was lost by filtering. The observed colour changes, confirmed by diffuse reflectance spectrophotometry, are presented in Table 4.6. In addition, it was noted that the presence of ethanol alone produced no observable or measurable colour change in the cyclophane pillared montmorillonite. Neither did any of the guest species have any effect upon the colour of natural Wyoming bentonite.

Guest species	Observed colour
-	yellow ochre
o-dimethoxybenzene (XIII)	orange ochre
(*o*-methoxyphenyl)methyl selenide (XIV)	dark red/ brown
(*o*-methoxyphenyl)methyl telluride (XV)	yellow ochre
(*o*-methylthiophenyl)methyl selenide (XVI)	orange/ brown
phenylmethyl selenide (XVII)	orange/ brown

Table 4.6 Data for cyclophane pillared montmorillonite incorporating a series of group VI substituted *o*-dimethoxybenzenes

Clearly the most startling colour change occurs with (*o*-methoxyphenyl)methyl selenide (XIV). As only small, though genuine, colour changes are observed with guests XIII and XVII it must be concluded that the presence of both selenium and a methoxy substituent are required for the generation of a strong colour change. It may well be that an interaction between the oxygen p orbitals and the selenium d orbitals is responsible for the strong electron donation to the cyclophane.

The tellurium analogue may be expected to participate in a similar intramolecular interaction, but upon its introduction to the cyclophane pillared clay no colour change is seen. It must be therefore that the guest species is now so large as to not fit into the host cavity. One other way of investigating this possible intramolecular interaction would be to synthesize the para analogue of (*o*-methoxyphenyl)methyl selenide and observe any colour changes generated by it.

The host/guest interactions being observed here are truly reversible. This was easily demonstrated by placing the dark red (*o*-methoxyphenyl)methyl selenide/ cyclophane pillared montmorillonite into a dialysis bag and washing with ethanol for 6 hours. After air drying, the pillared clay had returned to its original yellow ochre colour. Further, the re-introduction of the guest caused a regeneration of the dark red colouration.

It was also demonstrated that the red colouration was not due to the selenide degenerating to the dark red diselenide. Neither the selenide nor the diselenide have any aqueous solubility, yet a crystal of cyclophane 'wetted' with the selenide was observed to completely dissolve in a small volume of water. Thus no diselenide can have been formed, and the guest must really be present in the host cavity, so giving rise to the red colouration.

This also demonstrates that the complex will form in the absence of the clay substrate, although not in solution. Repeating the formation of this supramolecular complex according to the method used for the introduction of the guests to the pillared clays, ie by the evaporation to dryness of an ethanolic solution of the two components, yielded a dark red/maroon powder. Elemental analysis confirmed a 1:1 stoichiometry, and an excellent diffuse reflectance UV/Vis spectrum was obtained showing a charge transfer absorption band at 524 nm, see Figure 4.12.

The value of λ_{max} is the same as that recorded for the complex bound to montmorillonite, indicating that the complexes are identical despite the browner colouration of the clay bound complex. This is due simply to the beige appearance of natural Wyoming bentonite. However, binding the host structure to a clay substrate may offer advantages of transportability, usability and even stability to any complexes formed with it.

4.4.3.1 Tetrathiafulvalene (TTF) studies.

Tetrathiafulvalene (TTF) (XXVI) is a well known, powerful π-electron donor. It is easily converted into a stable radical cation which has been widely used to form charge transfer complexes with π-electron deficient systems such as 7,7,8,8-tetracyanoquinone dimethane (TCNQ) (XXVII).[264]

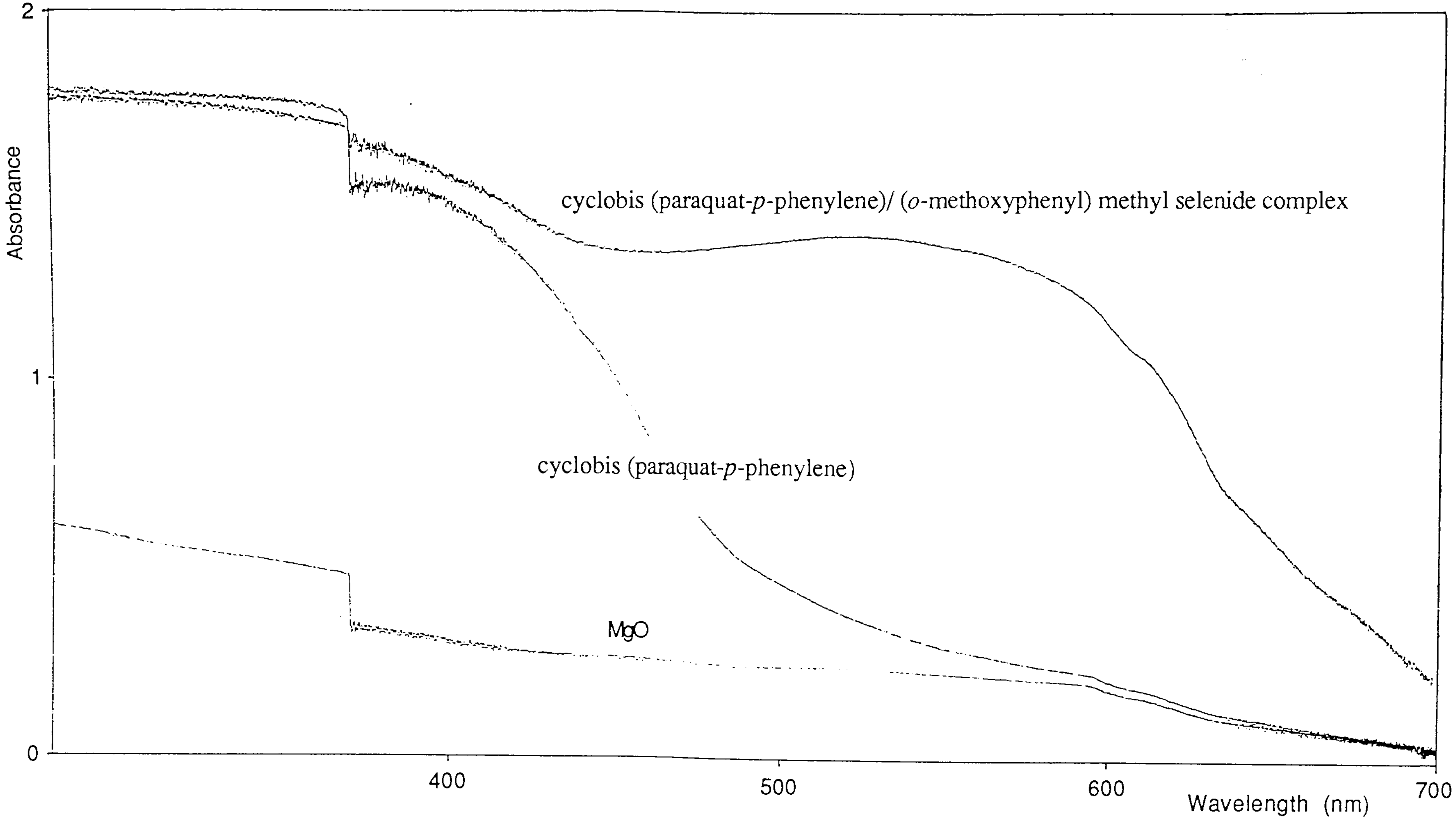
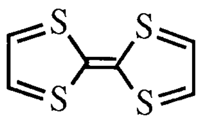
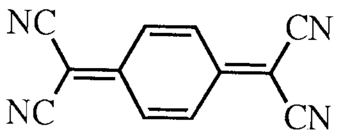


Figure 4.12 Diffuse reflectance UV/Vis spectrum of cyclobis (paraquat-*p*-phenylene)/ (*o*-methoxyphenyl) methyl selenide complex



XXVI



XXVII

Figure 4.13 Schematic representation of the structures of tetrathiafulvalene (TTF) and 7,7,8,8-tetracyanoquinone dimethane (TCNQ)

Recently, it has been shown to form a strong emerald green coloured 1:1 complex with cyclobis(paraquat-*p*-phenylene) in both the solid and solution states,[265] but single crystals of the complex, grown for X-ray crystallography, were highly unstable, instantly desolvating on removal from their mother liquor.

However, by introducing TTF to the cyclophane pillared montmorillonite via an acetonitrile solution, air evaporation of the solvent yielded a dark green clay that was stable to the atmosphere. Again the process was shown to be a reversible one.

The situation is complicated though by the possibility of TTF taking part in charge transfer intercalation in the clay via interaction with structural iron. It has been shown that montmorillonite suspensions readily intercalate TTF as the TTF^+ cation to form highly coloured materials.[266] However, such clays are dark brown in colour, showing a strong UV/Vis absorption band at 435 nm.

A diffuse reflectance UV/Vis spectrum of the cyclophane pillared clay/ TTF complex showed little evidence of an appreciable absorption at 435 nm, and the dark green colouration also strongly suggests the formation of the TTF/ cyclobis (paraquat-*p*-phenylene) complex. Near Infrared/ Raman spectroscopy should confirm the formation of the complex by the observation of the charge transfer absorption band centred on 854 nm.[265]

4.5 Conclusions and Further Work

The tetracationic multipurpose receptor cyclobis(paraquat-*p*-phenylene) may be considered simply as a rather unusual quaternary ammonium compound. As such it may be ion exchanged onto smectite clay minerals in exactly the same way that industrially valuable long chain alkylammonium salts are in commercial processes. Being a multivalent cation though successive unit layers of the clay are effectively held together as each cation is counterbalancing positive charge deficiencies in the unit layer above and below it. The result is a pillared clay with a very regular gallery height of 5.2 Å and a two dimensional zeolite-type structure. A small fraction of the original anion, approximately 0.5 X^- per cyclophane molecule, is retained by the pillared clay. It may be that complete ion exchange is impossible to achieve beyond a certain loading, because of the localized nature, and inflexible intersite distances, of exchange sites on the clay.

The cyclophane is orientated in the interlayer such that the two pyridinium moieties lie flat against the top and bottom of the enclosing basal surfaces, and the bridging para-phenylene rings lie along the c axis, normal to the unit layers. This orientation allows the ammonium centres to get directly next to the basal surfaces, and also allows the cyclophane cavity to remain available for complexation with electron rich guest species.

In aqueous solution the cyclophane forms a yellow 1:1 charge transfer complex with the electron rich *o*-dimethoxybenzene. The complex has a stability constant of 41 M^{-1} as determined by spectrophotometric methods (42 M^{-1} determined by NMR spectroscopy methods) and an unusually long lifetime, demonstrating its stability.

The same charge transfer complex will form with cyclophane pillared smectite clays, and the associated colour change is bestowed upon the product material. The reaction is completely reversible, with removal of the guest by dialysis causing the colour to be lost and the original pillared smectite to be regenerated. ^{29}Si MASNMR reveals the change in electron density that accompanies the formation of such complexes to be felt in the silicate backbone of the clay substrate.

Several group VI substituted *o*-dimethoxybenzenes have been synthesized and they too have been introduced to cyclophane pillared smectites. Various colours have been observed, the most startling being a dark red brought about by the inclusion of (*o*-methoxyphenyl)methyl selenide. It may be that an interaction between the oxygen p orbitals and the selenium d orbitals is responsible for such electron donating ability. This may be further investigated by synthesizing the accompanying meta and para analogues.

Clearly, binding the host structure to a clay substrate in this manner does not hinder its stability to participate in useful host/guest interactions, and it may be that doing so offers advantages of transportability, usability, and even stability to any complexes formed with it. The cyclophane/ tetrathiafulvalene (TTF) complex is an emerald green colour, stable in solution but highly unstable as the crystal.[265] However, TTF will interact reversibly with a cyclophane pillared smectite to yield a dark green clay that is stable to the atmosphere.

There is no doubt that charge transfer interactions provide an additional mechanism to van der Waals interactions by which an organic molecule may be reversibly but strongly bound to a clay. Powerful associated colour changes in many cases provide clear evidence of when this is happening. It may well be that such interactions could also provide another mechanism by which environmental pollutants may be removed from aqueous discharges, and the use of host/guest interactions should allow materials with specialized sorptive properties to be designed.

Bentonite has had limited use as a coagulant in the purification of both water and wastewater.[148] Quaternary ammonium exchanged bentonites have also been shown to effectively adsorb priority pollutants such as phenol and its chlorinated congeners.[146,147] It has been shown in this work, see Appendix 2, that a 50: 50 pillared organoclay shows enhanced sorptive properties compared to either the pillared clay or organoclay end members. It has also been reported recently that a similar material, designated an inorgano-organo-clay, binds priority pollutants as strongly as granulated activated carbon.[150]

Modification of commercially valuable benzalkonium chlorides by the introduction of several electron donating groups to the benzene ring may be one way to enhance the sorption of pentachlorophenol by utilizing charge transfer interactions in unison with van der Waals interactions. Another approach would be to harness host/guest chemistry by employing an electron rich host system to bind the electron deficient guest.

This is the converse of what has been demonstrated in this chapter, where an electron deficient host has been bound to a clay substrate, and an electron rich guest has been held by it. The switch to an electron rich host means that a crown-type compound may now be a more suitable receptor molecule than a cyclophane, although the generation of a positive charge with which to bind it to the clay would not help the electron donating ability of molecules of either class.

Such a problem seems ideally suited to the layered double hydroxides (LDH's), the so-called anionic clays. They are, in terms of charge, mirror-images of the vastly more common cationic clay minerals, and consequently will undergo anion exchange, intercalation, and pillaring reactions in just the same way. These materials have already found use as effective heterogeneous base catalysts, anion exchangers and adsorbents.[267] Crown-type compounds may thus be ion exchanged onto anionic clays using the metal salts of acid or alcohol groups on the crown in just the same way as cationic cyclophanes may be exchanged onto the smectites.

The variety of podands (open-chain crowns), coronands (cyclic), and cryptands (spherical) is enormous, so that a cavity suitable for all the probable pollutants should be attainable. Mixed oxygen, nitrogen, sulphur and phosphorous crowns exist, heteroaromatic nuclei may be incorporated into the crown ether ring, and donor sites may be incorporated into functional groups.[268] Consequently many crown-type compounds are actually suitable for ion exchange onto cationic clays, and such materials could also prove to be very useful.

Much work is currently being done to improve the conductivity of laponite, especially for use by the paper industry in electrographic printing.[199] This work has suggested that the major contributions to the measured conductivity is by an ionic mechanism, with potassium ions in the interlayer proving to be the most effective. A further increase in conductivity is achieved through the pillaring of the layers by the ion exchange of a percentage of the exchange sites with a number of group V and VI metal complexes. Crown-type compounds can offer similar pillaring capabilities.

It is well known that K^+ ions are instrumental in the synthesis of [18]crown-6, via the template effect,[269] and that other, variously sized crown ethers will act as cation receptors to other alkali metal ions, with the degree of tolerance being dependant upon the closeness of the fit.[268] Intercalation of [18]crown-6 will produce a pillared laponite, but may also aid the mobility of the K^+ ions in the interlayer by establishing a 'safe house' type environment whereby the interlayer cations can move in a series of steps. A partial ion exchanged laponite, using a suitably charged coronand, may also be worth studying.

Another obvious application of these charge transfer-inspired highly coloured clays is in the field of chemical sensor technology. Pillared smectites and a variety of other PLS's have recently been suggested as being suitable for the further development of chemical sensors for gaseous detection,[244] but only as crude protection devices upstream of the detector. This work demonstrates the further suitability of pillared clays to deliver an optical signal at the end of the measurement chain, when the process to be detected is occuring.

The pursuit of 'molecular Meccano' the molecular level self-assembly of relatively simple molecules into complex multimolecule structures, has already led to the development of interlocked molecular components, termed rotaxanes and catenanes, incorporating cyclobis(paraquat-*p*-phenylene).[239,240] The powerful electron donor TTF has also been incorporated into cyclobis(paraquat-*p*-phenylene) although the product is unstable out of solution.[265] A possible next step in this direction would be for formation of a catenane incorporating cyclobis(paraquat-*p*-phenylene) and a cyclophane containing TTF units. Such a donor cage, consisting of two TTF and two hydroquinone units, has recently been synthesized.[270]

Finally it should be mentioned that the ^{77}Se MASNMR work that was planned was never carried out, although it would undoubtedly still be interesting to do so, because of the heavy demand placed on spectrometer time. In addition, the possible mobility of the guest species in the cavity would make an attempt to find a pseudo-*solution-like ^{77}Se resonance from a static sample a worthy one.*

Chapter Five

THE RELATIONSHIP BETWEEN PARTICLE SIZE, CATION EXCHANGE CAPACITY AND CHEMICAL COMPOSITION

5.1 An Introduction to the Implications of the Nature of the Cation Substitution Sites in Phyllosilicates

The cation exchange capacity (CEC) of smectite clay minerals is generally understood to be equivalent with the layer charge. This is determined by isomorphous substitutions within the crystallites, hence CEC is considered a material constant for a particular clay. However, the measured CEC is only equivalent with the layer charge if all charge balancing cations are accessible for exchange. This is not true for illites, but is equally not so for partially collapsed smectites exhibiting a high layer charge and potassium fixation.

Despite this, the constant charge concept for clay minerals, whether equivalence with layer charge exists or not, is generally accepted. However, isomorphous substitution is not the only cause of negative layer charge, as described in Section 1.6.4.3. Edge surfaces of clay particles carry unsatisfied charges due to the presence of broken bonds. The electrical double layer on these surfaces is a function of the pH of the equilibrium solution, hence the exchangeable charge balancing ions associated with the edge surfaces may be anions or cations, depending on pH.

Consequently, if the contribution of the edge surfaces cannot be neglected with respect to the contributions of the face surfaces, the total CEC will also vary with pH. Then, the CEC is no longer a material constant. Edge sites contribute approximately 20% of the overall CEC for most smectites,[2] and yet for montmorillonite it is generally considered that the CEC does not change substantially with particle size, salt concentration or pH.[73]

Further, if CEC is truly independent of particle size then either the extent of isomorphous substitution, and hence chemical composition, or the 80: 20 substitution: broken bonds ratio must vary with particle size, as the number of edge sites per unit area will certainly increase with decreasing particle size.

5.1.1 Kaolinite

The chemical composition of kaolinite is necessarily invariant with particle size because its structure contains very little isomorphous substitution, and consequently the permanent charge per unit cell, if not zero, is also very small. However, primarily due to the presence of exposed hydroxyl groups, it does have a variable, pH dependent, negative charge, giving it a small CEC in the range 3-15 meq per 100 g.[2] This is considerably smaller than the 90 meq per 100 g that is typical of montmorillonite, and so the small but increasing contribution of edge sites to the total exchange capacity, that should be seen as particle size decreases, should be seen more easily for kaolinite than for montmorillonite.

However, because kaolinite is a non-expanding clay mineral, all of its exchange reactions take place at the crystal surface, be it via exposed hydroxyls at a basal surface, or via broken bonds at a crystal edge. Consequently, any reduction in particle size causes an increase in effective surface area, and an appropriate increase in exchange capacity. Conflicting evidence may be found in older literature as to whether the CEC of kaolinite varies linearly with the surface area of the sample [271] or not. [272] What is not in question is that a clear increase in CEC is observed as the particle size decreases.

5.1.2 Montmorillonite

Even such a broad agreement as this is not easy to find in the literature concerning montmorillonite. Early work indicated that there is an increase in exchange capacity with decreasing particle size for kaolinite, illite and montmorillonite.[273] Support was lent by calculations based on the then recent observations of particle thickness that confirmed that exchange capacity is directly related to the broken Si-O, Al-O, or Al-OH linkages.[95] From such work it was concluded that the exchange phenomena in both kaolinite and montmorillonite arise similarly from unsatisfied linkages around the edges of the particles, and that substitution may not be a factor in determining exchange capacity.

However it was soon also proposed [94,274] that "while the other minerals (kaolinite and illite) show an increasing capacity with decreasing size, the base exchange of montmorillonite does not vary with particle size".[274] This observation was accepted for many years afterwards.[275]

If edge sites do make a significant contribution to exchange capacity, increasingly so as the particle size decreases, then an invariant CEC would imply that isomorphous substitution necessarily decreases with decreasing particle size. However, this was not observed, and it was generally accepted that there was "no consistent increase or decrease in interlayer charge or type or amount of isomorphous substitution with variation of particle size",[276] leaving one to conclude that edge sites do not make a significant contribution to the overall CEC, and that therefore the negative charge of montmorillonite arises predominantly from isomorphous substitution.

Irrespective of this conclusion, at around the same time it was reported that the exchange capacity of montmorillonite is 80% satisfied by substitution, but that a significant 20% arises from broken bonds around the crystal edges.[277] This 80: 20 ratio has gained widespread acceptance over the decades that have followed,[2] and it is universally recognised today.[278] By assuming a constant chemical composition though, it may be easily shown that over a reasonable particle size range this ratio varies very considerably.

Table 5.1 has been compiled by assigning an 80: 20 ratio arbitrarily to a 0.2 μm particle size fraction. The different functionality of the number of sites in the interlayer to those at the crystal edge means that any variation in particle size causes a much greater percentage variation in the number of substitution sites than in the number of edge sites. Thus, for example, a decrease in particle size from 1.0 to 0.1 μm^2 causes a decrease in the substitution: edge site ratio from 20: 1 to 2: 1, and an increase in CEC from 84 to 120 arbitrary units, see Table 5.1. Clearly if all of the above holds then any quoted ratio is only the mean value of a large range of values, unless the particle size range of the clay mineral in question is very small.

Particle dimensions (μm)	Relative number of exchange sites per particle		Substitution site: Edge site ratio	Relative total CEC (arbitrary units)
	Interlayer f (area)	Crystal edge f (length)		
1.0 x 1.0	2000	100	80: 4	84
0.2 x 0.2	80	20	80: 20	100
0.1 x 0.1	20	10	80: 40	120

Table 5.1 Variation of Isomorphous substitution site: Edge site ratio with particle size

The above figures are based on the assumption that chemical composition is independent of particle size. In theory, a large enough increase in chemical composition as particle size decreases would hold the substitution: edge site ratio constant, but would also increase the total CEC enormously. This clearly does not occur, but the chemical composition may not be as invariant as was first believed.

Separation by centrifugation of samples of Wyoming bentonite has been reported in fine fractions and coarse fractions, that are predominantly Na- and Ca-montmorillonite respectively.[279] It was suggested that the greater preference for Ca^{2+} ions of montmorillonite in coarser fractions arose from a difference in chemical composition compared with that of the montmorillonite in the finer fractions. Confirmation that exchangeable Na^+ and Mg^{2+} ions are more abundant in the finer than the coarser fractions came in a similar study a few years later.[280]

At much the same time a similarly size fractionated montmorillonite was shown to comprise a coarse fraction that developed high temperature phases characteristic of the Cheto-type, and a fine fraction with high temperature phases characteristic of the Wyoming-type.[56] The former, Cheto-type, contain many octahedral Mg^{2+} ions and possess large values of interlayer charge, whereas the latter, Wyoming-type, contain fewer octahedral Mg^{2+} ions and smaller interlayer charge values, see Section 3.1.3. A change in chemical composition with particle size was also proposed in a separate study soon afterwards, with a variation in hydration characteristics of a series of fractions of Na-montmorillonite being attributed to an increase in the structural charge density of the montmorillonite with increasing particle size.[281]

This is not to say that such workers suggest the overall CEC to increase with increasing particle size, as the magnitude of the contribution from edge sites unquestionably increases in the opposite direction, and may well be the dominant factor. Indeed, many of these studies do not include any measure of the total exchange capacity, and today it is accepted only that differences in effective particle size are important in the determination of cation exchange capacity.[282]

It is intended that the application of modern instrumentation to the study of the relationship between particle size, chemical composition, and cation exchange capacity will enable some of the contradictions mentioned above to be resolved, and a more complete understanding of the nature of the cation exchange sites in phyllosilicates to be gained.

5.2 The Measurement of Particle Size, Cation Exchange Capacity and Chemical Composition

A variety of experiments and instrumental techniques will yield information on any one of these variables. Wherever possible however, the emphasis in this work has been on utilizing modern instrumentation to supplement data already in the published literature, from which the conclusions discussed in the previous section are born.

5.2.1 The measurement of particle sizes in clays

At around the same time that X-ray analysis of clay minerals was in its infancy, during the 1930's, most of the already considerable mass of data on the size of clay particles were derived from sedimentation methods. One study of the larger clay fractions with an optical microscope found that the particles averaged 20% larger than when computed from settling rates, but that such a conversion factor was similar for all clays.[283] Various other indirect methods, such as elutriation, centrifugation, the hydrometer method and a number of optical methods, were reviewed by Norton and Speil in 1938,[284] but as yet no direct comparison between the true and computed diameters could be made for the finer clay fractions.

A more recent evaluation of fine experimental techniques, electro-optical birefringence, ultracentrifugation, viscometry, optical transmission and electron microscopy, concluded that for the measurement of particle size the technique of electron microscopy is best.[204] Consequently, the particle size fractions used in this work were measured directly by electron microscopy, as described in Section 2.3.12.

5.2.2 The measurement of cation exchange capacity in clays

In order to determine the CEC the total amount of cations in exchange positions on the clay surface must be measured. In most methods the various cations which are present on the natural clay are replaced by a single cation, and the total amount of this cation species is then determined after washing and isolating the clay.

The ammonium acetate method is perhaps the best known. The clay is treated with an excess of ammonium acetate solution, and then either the ammonium content of the washed clay is determined by means of the Kjeldahl method, or the adsorbed ammonium is extracted with 10% NaCl solution and determined colourimetrically by direct nesslerization.[285] Alternatively, the clays are converted to the barium form, and the amount adsorbed is subsequently eluted with ammonium chloride solution, precipitated and weighed as barium sulphate.[286]

Another possible method, when displacing the natural exchange ions with an ammonium salt, is to determine the displaced cations in the ammonium salt solution. In addition to measuring the CEC, this method also yields information on the nature of the natural exchange ions. With the development of inductively-coupled plasma emission spectrometry, ICPES, capable of measuring the concentration of various metal ions in solution simultaneously, such a method is not now as time consuming as it once was, and can yield reliable results.[287] However it will also determine cations of soluble salts present in the clay, and thus will produce a value for the sum of displaced cations that is larger that the CEC if such soluble salts are present.

Other time-saving modifications of the ammonium acetate method have also been proposed recently. One such proposal involves the use of a mechanical extractor to control a vacuum induced leaching of the clay samples.[288] It is reported that a single 8 hour leaching of clays with 35 cm^3 of salt solution was found to be comparable to multiple saturations or displacements using a centrifuge.

An alternative series of methods exist though, based on the strong preference of the clay for the adsorption of organic cations. Such methods usually derive the amount of adsorbed organic cation from the change in concentration of the organic cation in the equilibrium solution, either roughly by watching the colour of the equilibrium solution with stock solution diluted to known amounts,[289] or more accurately by UV/Vis spectrophotometry.[290]

However, despite this proliferation of methods, despite the growing commercial value of the smectite clay minerals, and the importance of cation exchange capacity to their value, industry still had no fast, accurate method for the measurement of CEC. This was finally achieved by titrating an aqueous clay slurry directly with methylene blue dye to an end-point, recognised by spot-testing the titrated slurry on filter paper for a sign of free dye.[174] This appears as a light blue tint radiating away from the darker blue spot of dyed clay solids, and indicates the true end-point when it is still observed 2 minutes after the last addition of dye. The method is fully described in Section 2.3.8, and has been largely adopted by both the drilling industry [43] and the foundry and ceramics industries.[291]

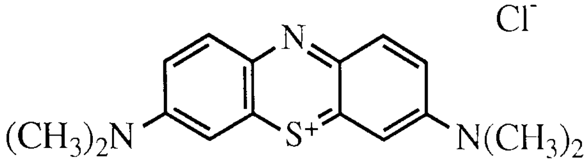


Figure 5.1 Schematic representation of the structure of methylene blue dye

However, the method was designed to measure CEC in order to accurately determine the montmorillonite content of a mud, and was not really intended for very accurate measurement of variations in CEC itself. Consequently, modifications were made to the method for use in this work.

It was noted that the end-point is approached very suddenly, even after familiarity with the method has been gained, necessitating that many drops of titrated sample must be spotted onto filter paper in order to be certain that the end-point is not missed. Each removal of a drop of clay slurry before the end-point introduces a cumulative error into the final result, as each drop contains clay particles only partially exchanged with the organic cation. The value obtained for the CEC will in every case be lower than the true value. This error obviously increases with the number of spots that are required, but is also larger the earlier into the titration the spot testing is started. The need to reduce the number of spots necessary to accurately reach the end-point was apparent. Similarly, it was felt that the accuracy with which the end point was determined could be improved. The literature method [174] claims accuracy only to within 0.3 - 0.4 cm^3 of titrant.

The first problem arises because of the very strong colour of methylene blue dye solutions coupled with the almost total dispersion of montmorillonite in water, causing the sample solution to turn a very dark blue at a very early stage in the titration. The strong colouration of the dye is required in the spot test part of the determination so the use of a less strongly coloured organic cation is not possible. Other solvents, which cause the clay to flocculate, also strongly solvate the dye, producing strongly coloured solutions.

However, in the aqueous clay suspension very nearly all the dye is associated with the clay particles, so that centrifugation for 30 seconds in a test tube centrifuge at 4000 rpm causes the clay to collect at the bottom of the tube, leaving a pale blue supernate. Moreover, as the 1 cm^3 additions of the dye increase in number as the titration proceeds, flocculation of the clay particles is encouraged and the supernate pales still further. As the end-point approaches though, the adsorption by the clay is slower and a darkening of the supernate is observed. It is only at this point that the spot testing need begin.

The end-point itself may also be observed more clearly by first removing the dyed clay solids from each spot sample. This is done quite easily by spotting onto two sheets of filter paper, one underneath the other, rather then just onto one. The end-point is then reached when a blue colouration is observed, two minutes after the last addition of dye solution, on the bottom filter paper.

5.2.3 The measurement of chemical composition in clays

A vast number of chemical analyses of clay materials have been published. Even amongst analyses of materials whose clay mineral composition is well established and which are monomineralic, quite a considerable range of composition is found.[2] Most clay minerals probably have considerable variation in composition from one unit cell to the next.[18] Thus any chemical analysis of a clay mineral is only an average, and there is little chance of determining the range and standard deviation until analyses can be made at the unit cell level.

However, the average concentration of one element or another in the structural formula may vary consistently with particle size. The two ions most likely to cause a variation in structural charge density, by substitution for Al^{3+} in the octahedral layers, are Mg^{2+} and Fe^{2+}. Variations in the concentrations of these three species in different size fractions of Wyoming bentonite, either by implication or direct observation, should prove to be measurable, and solid-state instrumentation is perhaps better suited to such a study than is traditional chemical analysis.

The work carried out in Chapter 3 has highlighted a number of facts that will be of additional use here. Wyoming bentonite is considered to be monomineralic, and is one the of purest natural sources of Na-Montmorillonite in the world. Any impurity is predominantly quartz, easily recognized by both XRD and ^{29}Si MASNMR, and overlying shale. Although it is mostly non-structural, the major paramagnetic ion present in the material is iron. Thus gramme susceptibility measurements will give a good indication of variations in total iron content, and Mössbauer spectroscopy may well reveal any variations in structural iron content.

Both ^{27}Al and ^{29}Si MASNMR spectroscopy should also be of great value in monitoring any compositional changes. ^{27}Al MASNMR can readily determine the coordination of aluminium in aluminosilicates,[182] so that substitution of Al^{3+} into the tetrahedral silicate sheet, indicative of increased isomorphous substitution generally may be followed. However, there are problems associated with obtaining quantitative ratios of tetrahedral: octahedral aluminium from ^{27}Al MASNMR spectra.[292] These difficulties are not merely attributable to the inconvenient position of spinning sidebands resulting from octahedral aluminium when observing the central transition of tetrahedral aluminium, or vice versa, but are probably associated with different quadrupolar interactions in the two structural environments.[293] Consequently, no use will be made of the absolute value of this ratio, but any variation in its magnitude may be considered as real.

Substitution of Al^{3+} into the tetrahedral silicate sheet, such that Al^{3+} enters the second coordination sphere of a silicon-oxygen framework, may also be observed in the ^{29}Si MASNMR spectrum.[294] A small low-field shift relative to the main ^{29}Si signal, Q^3 (0Al) to Q^3 (1Al), results in a shoulder to low field of that resonance.[295]

Information on the paramagnetic presence within the sample is also readily forthcoming from such spectra. Spinning sidebands arise from modulation of the central transition by sample spinning, and are enhanced by an increasing iron content in the sample due to magnetic susceptibility effects.[215] Randomly distributed paramagnetic ions in a naturally occuring mineral also have a significant broadening effect on its solid-state MASNMR spectrum. This is due to both scalar electron-nuclear coupling, and modulation of the magnetic field experienced by the subject nucleus.[296] As the paramagnetic presence increases so the quality of the spectrum is reduced, until eventually no signal is obtained. In ^{29}Si MASNMR of clay minerals a gramme susceptibility value greater than 2.2×10^{-6} cgs units g^{-1},[58] or an iron content greater than approximately 5% (expressed as Fe_2O_3),[294] causes excessive broadening and precludes collection of usable spectra.

5.3 Measured Variations with Particle Size

Particle size fractionation of a Wyoming bentonite slurry was achieved using an IEC chemical centrifuge, model 43100055, at Akzo, Littleborough. Five fractions were obtained, varying slightly in colour from the pale, opaque ochre of the coarsest fraction to the richer, translucent honey colour of the finest fraction. Particle size was measured by SEM, and data are presented in Table 5.2.

Bentonite .fraction	Average platelet dimensions (μm)			Substitution site: Edge site ratio (arbitrary units)	Relative importance of edge sites
	Length (l)	Area (l^2)	Total Edge (4 x l)		
1 (coarse)	1.75	3.06	7.00	1: 2.28	1.00
2	1.25	1.56	5.00	1: 3.20	1.40
3	1.10	1.21	4.40	1: 3.64	1.60
4	1.00	1.00	4.00	1: 4.00	1.75
5 (fine)	0.85	0.72	3.40	1: 4.70	2.06

Table 5.2 SEM data for particle size fractions of Wyoming bentonite

It should be noted that the platelet dimension given for each fraction is an average of the range of platelet sizes present in that fraction. A range of particle sizes exists within each fraction, and some overlap between fractions was observed, such that complete particle size fractionation cannot be claimed. Nonetheless, a very definite reduction in average platelet size with each successive fraction was observed, making these fractions suitable for a study of this type. It may be that such a statement would also be valid for many of the clay fractions studied in earlier works on variations with particle size, the conclusions from which have been quoted earlier in this chapter, had any direct measurements of particle size been made.

Average platelet area (l^2) and average platelet total-edge-length (4l) have also been calculated from the observed average particle length for each bentonite fraction. These calculations are based on an approximately square morphology, see Figure 5.2. It has already been shown that particle size has a huge effect on the scale to which edge site charge manifests itself. For each tenfold decrease in edge length, a tenfold increase in importance of the edge sites should be observed, see Table 5.1. As a result, platelet edge sites are of greater stoichiometric importance for smaller particles than for larger ones.

A tenfold decrease in total edge length is not observed in these particular bentonite fractions. The edge length of the finest fraction is only a factor of 2.06 times smaller than that of the coarsest fraction. Nevertheless, theory predicts that as a result of this, edge sites should still be necessarily 2.06 times more important to the total CEC of the finest fraction than to that of the coarsest fraction. Agreement with this theoretical requirement will be examined in Section 5.3.1.

Figure 5.2 Scanning electron micrograph of a montmorillonite platelet

Wyoming bentonite is taken to consist of about 85% montmorillonite and 15% non-clay minerals such as quartz etc.,[279] so that any variation in CEC may result from an increase in the purity of successive bentonite fractions. Consequently, the impurity content of each fraction was estimated from its XRD trace by measuring the area of the major α-quartz peak at $2\theta = 31.1°$, relative to the area of the major montmorillonite peak at $2\theta = 7.3°$. The impurity contents recorded, presented in Table 5.3, were then used to adjust the measured value of CEC to give a value representative of a pure sample.

Bentonite fraction	Percent non-clay material
' as received '	15
1.75 μm	7.2
1.25 μm	2.8
1.10 μm	2.6
1.00 μm	0.2
0.85 μm	< 0.1

Table 5.3 Impurity content of particle size fractions of Wyoming bentonite

The values obtained in this way are only approximations. However, it is important to realise that any error in the estimated value will always result in an over-estimate of the non-clay content of each fraction, and consequently in an over-compensation for impurities in the adjusted CEC, because of the highly crystalline structure of α-quartz when compared to montmorillonite. Thus any variation still remaining in impurity-adjusted CEC with particle size, if in the direction of increasing CEC in the purer fractions, must definitely result from something other than an increase in the purity of successive fractions.

5.3.1 Variation in cation exchange capacity

Before any of the particle size fractions were studied, the CEC of a sample of the bentonite 'as received' was measured, by the methylene blue method described in Section 5.2.2, and checked against the product data sheet provided. The CEC was measured as a function of pH, by the controlled addition of solutions of HCl or NaOH. Data are presented graphically in Figure 5.3.

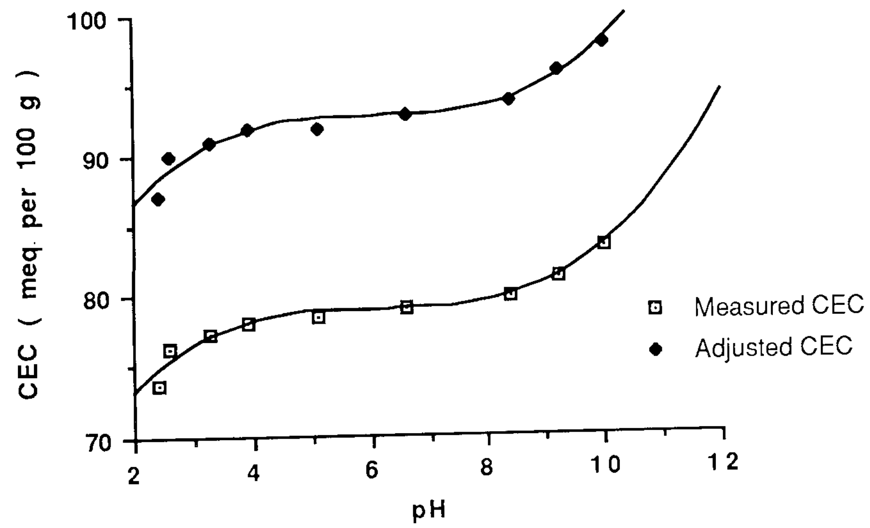


Figure 5.3 Graph of cation exchange capacity against pH for Wyoming bentonite 'as received'

The variation in the CEC arises from the pH-dependent variation of the edge structure of the clay platelets. The charge on the surface is often reported to change from positive to negative within the pH range 4-5,[297] although recently substantial evidence has been collected which suggests that the edges of montmorillonite particles are not positively charged at any pH.[298]

At pH 2 it can be assumed that the platelet edges are either negatively charged, or contribute very little to the total CEC. The value obtained at this pH, 73.8 meq per 100 g, is thus due almost exclusively to isomorphous substitution, is termed the permanent charge, and agrees well with the product data sheet for Wyoming bentonite GG.[163] The adjusted value, representative of pure Wyoming montmorillonite, is also in agreement with the CEC of the pure bentonite slurry used in the commercial manufacture of 'wet' process organoclays at Akzo.[299]

Figure 5.3 also allows the relative importance of the edge sites to be obtained, as any pH induced increase in CEC above the permanent charge will result from their contribution above. For the Wyoming bentonite 'as received' edge sites contribute approximately 9.5 meq per 100 g, or approximately 11% of the total exchange capacity. This is significantly lower than the 20% edge site contribution usually quoted, but may stem from the relatively high degree of substitution in montmorillonite compared to other smectites.

Importantly though, it is this value which, so long as chemical composition remains invariant, should increase by a factor of 2.06 from the coarsest to the finest fraction, about an average value of 11%. One could reasonably expect the isomorphous substitution site: edge site ratio to vary from approximately 93:7 in the coarse fraction to 86:14 in the finest. The implication, if this is not observed, would be that the extent of isomorphous substitution is also varying with particle size so as to alter the measured ratio.

5.3.1.1 Cation exchange capacity vs particle size at pH 2

The CEC of each of the particle size fractions was measured at pH 2 so that possible edge site contributors could be eliminated. The measured values were then adjusted to allow for the non-clay material present in each fraction using the impurity contents given in Table 5.3. Both the measured and adjusted values are presented graphically in Figure 5.4

It is apparent that the measured exchange capacity increases with decreasing particle size. The line through the adjusted values also has a marked gradient, indicating that increasing purity of sample is not the major cause of this measured increase. It should also be remembered that direct studies of the structure of clay particles in aqueous suspension have concluded that they are mostly present as individual platelets,[60] separated by over 100Å.[61] This is particularly true of Na-montmorillonite, and so the possibility of easier access to interlamellar regions within the smaller particles may be eliminated as a cause of the observed increase in CEC. Instead, and as edge sites play virtually no part at such a low pH, it must be tentatively concluded that the permanent charge resulting from isomorphous substitution within the lattice increases with decreasing particle size.

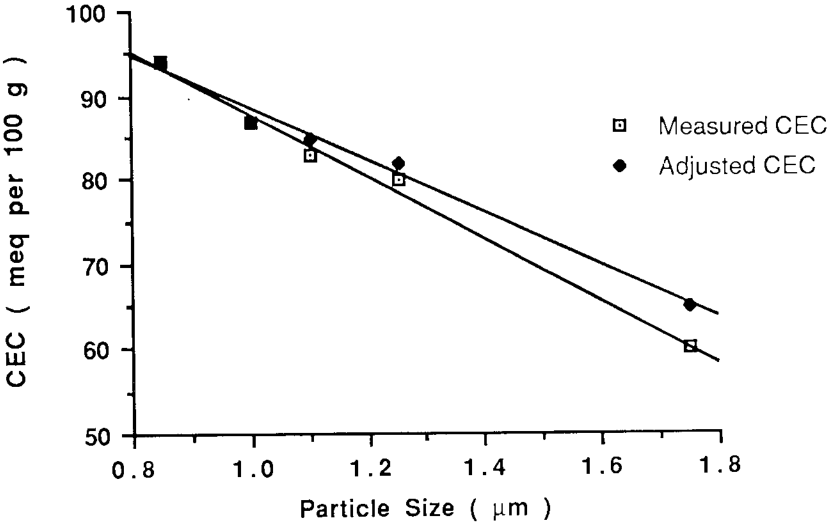


Figure 5.4 Graph of cation-exchange capacity against particle size at pH 2

5.3.1.2 Cation exchange capacity vs pH

The relative importance of the edge sites to the overall CEC of different particle size fractions may be obtained by plotting the cation exchange capacity as a function of pH. This is done for the coarsest (1.75 μm) fraction and the finest (0.85 μm) fraction, using impurity adjusted figures, in Figure 5.5.

Clearly the CEC of the finest fraction greatly exceeds that of the coarsest, throughout the entire pH range. This suggests increasing isomorphous substitution with decreasing particle size, but the extent of the increase due to edge sites as the pH is raised must also be examined for each fraction. These are drawn from Figure 5.5 and presented in Table 5.4.

It has already been shown, see Table 5.2, that the rules of mathematics insist that for the particular particle sizes involved, the contribution of the edge sites to the total CEC must increase by a factor of 2.06 from the coarsest to the finest fraction, so long as all other variables remain constant. It can be seen from Table 5.4 that the edge site contribution does indeed approximately double between these fractions, but that in percentage terms the increase is considerably less than twofold.

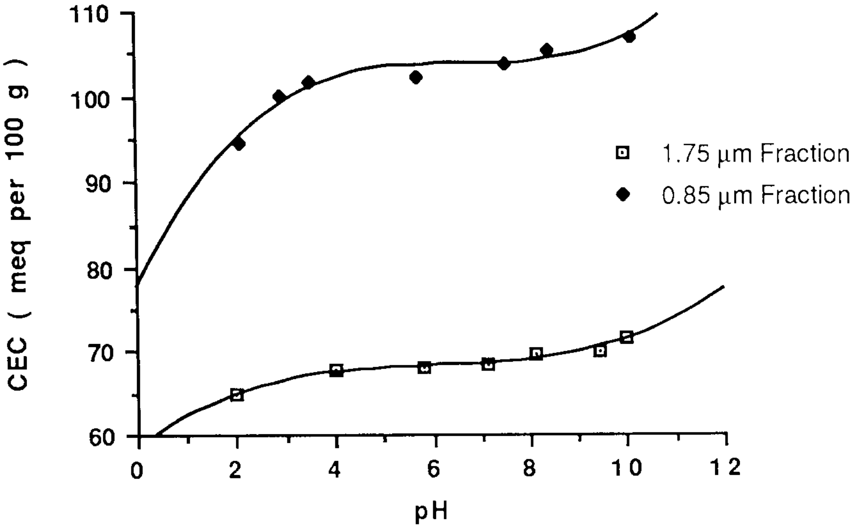


Figure 5.5 Graph of cation exchange capacity against pH for the 0.85 μm and 1.75 μm fractions of Wyoming bentonite

Particle size (μm)	Increase in CEC (pH 2-10)	
	Actual (meq per 100 g)	Percentage
1.75	7	9.7 %
0.85	13	12.1 %

Table 5.4 Increase in cation exchange capacity from pH 2-10 for the 0.85 μm and 1.75 μm fractions of Wyoming bentonite

Thus edge sites are contributing just as much as geometrical considerations predict, but the effect on the substitution site: edge site ratio is less noticeable because it is being partially offset by a similar increase in the contribution from isomorphous substitution sites. This has the additional effect of increasing the measured CEC faster than would be the case if increasing edge site contributions were the sole cause. Finally, it should be noted that although the percentage increase is less than predicted, the two values do average very well to the 11% value obtained in Figure 5.3 for Wyoming bentonite 'as received'.

5.3.1.3 Cation exchange capacity vs particle size at pH 10

The experimental behaviour of methylene blue at pH 10 was found to be no different from that at pH 2. Methylene blue remains blue in colour in an alkaline environment, and it was found not to be necessary to continually adjust the pH during the course of the titration. It may thus be assumed that the exchanging species is the same at pH 2 and 10.

Figure 5.6 shows a plot of the cation exchange capacity, after adjustments for impurities, against particle size at pH 10, and the corresponding plot at pH 2. This clearly shows the increasing contribution of both isomorphous substitution sites and crystal edge sites as particle size decreases (gradient of the lower line, and increased gradient of the upper line, respectively).

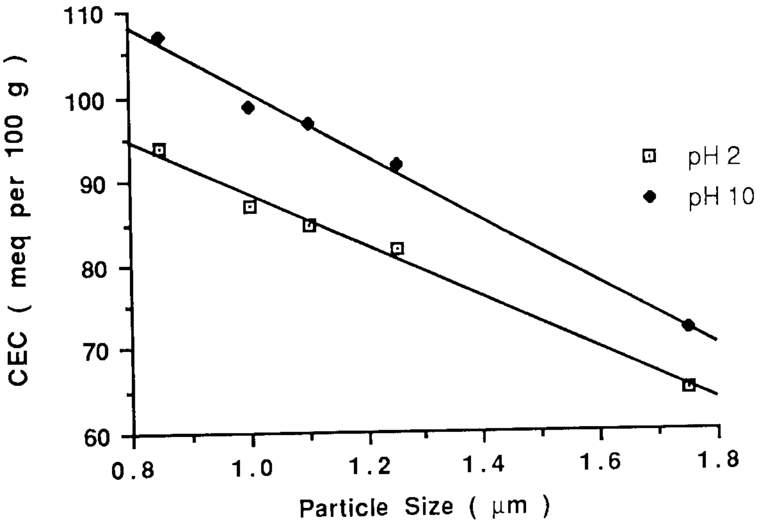


Figure 5.6 Graph of cation exchange capacity against particle size at pH 2 and pH 10

From these figures the substitution site: edge site ratio may be calculated for each particle size fraction. Results are presented in Table 5.5. It may be concluded that this ratio remains essentially constant across the particle size range studied.

Of the four variables discussed in Section 5.1, namely total CEC, concentration of substitution sites, concentration of edge sites, and substitution: edge site ratio, one, the relative concentration of edge sites, must vary with particle size. Each of the others has been reported to remain unchanged as a function of particle size at one time or another. However, it is impossible for them all to remain invariant together, whilst the edge site contribution necessarily varies.

Particle size (µm)	Substitution site: Edge site ratio	
	Actual (meq per 100 g)	Percentage
1.75	65: 7	90: 10
1.25	82: 10	89: 11
1.10	85: 12	88: 12
1.00	87: 12	88: 12
0.85	94: 13	88: 12

Table 5.5 Substitution site: edge site ratio as a function of particle size for Wyoming bentonite

This work has concluded, perhaps surprisingly, that the substitution site: edge site ratio remains essentially constant. Consequently, a percentage increase in isomorphous substitution almost comparable to the percentage increase in the concentration of edge sites is observed. Both increases act in the same direction to cause a sharp increase in total cation exchange capacity with decreasing particle size. In the following section instrumental techniques will be employed to look for this implied variation in chemical composition with particle size.

5.3.2 Variations in chemical composition

It is possible, using the techniques mentioned in Section 5.2.3, to follow any variations in Fe^{2+} content directly, without resorting to destructive procedures. Any variations in tetrahedral substitution may also be seen directly, and would indicate a large variation in the degree of octahedral substitution generally.

5.3.2.1 Variations in Fe^{2+} content

Simple gramme magnetic susceptibility measurements will give a reliable indication of variations in total iron content for Wyoming bentonite. Measurement of χ_g of each of the particle size fractions was carried out. Data are presented in Figure 5.7.

Evidently fairly good correlation exists between particle size and iron content, although one must be cautious in drawing conclusions. The samples are impure, and thin layers of Fe_2O_3 or Fe(O)(OH) are known to coat both the clay and non-clay minerals. Similar measurements on air classified samples of Wyoming bentonite, see Section 3.1.3, revealed the coarse fraction to have a higher χ_g value than the fines. This was shown to result from a concentration of the iron mineral impurities into the coarse fraction by virtue of their greater specific gravity.

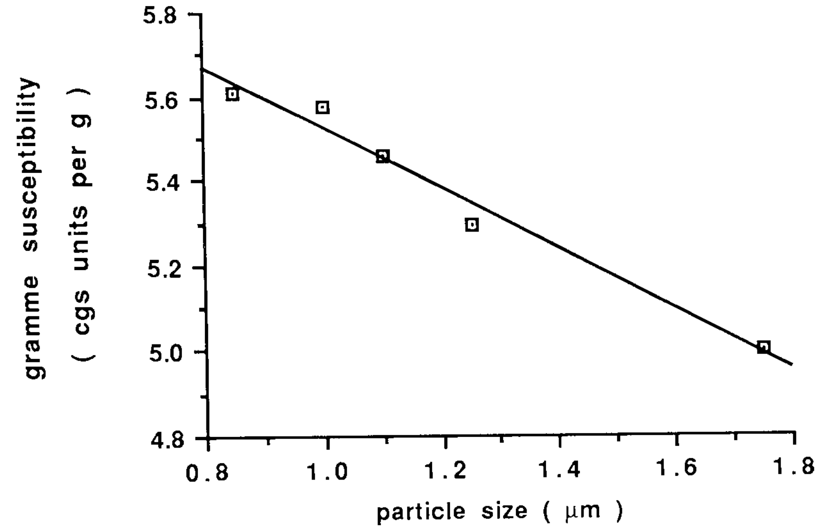


Figure 5.7 Graph of gramme magnetic susceptibility against particle size

However, it can be assumed that virtually all such sources of bulk iron have been removed from the particle size fractions studied here, as no reflections arising from iron minerals were found in the XRD traces of even the largest fraction. Consequently, the measured increase in iron content can be assumed to arise predominantly from an increase in structural iron. In addition, on the basis of a predominantly impurity generated iron presence in the fractions, one would expect to see an increase in χ_g in the opposite direction to that actually observed.

An increase in structural iron content with decreasing particle size would, if correct, be consistent with the proposed increase in permanent charge with decreasing particle size. This may be seen as an increasing ratio of Fe(II): Fe(III) with decreasing particle size. Thus ^{57}Fe Mössbauer spectroscopy may be able to provide information in support of this proposal. Unfortunately, adequate access to the technique has not been available to the author. However other techniques, sensitive to paramagnetic ions in lattice positions, have been employed.

The magnitude of spinning sidebands in solid-state MASNMR spectra is increased by an increasing iron content in the sample, as described in Section 5.2.3, although the magnetic centre is not required to be close (next nearest neighbour) to the NMR nucleus for this effect to be observed. However, such a requirement is necessary for an accompanying broadening of the central resonance to be observed.

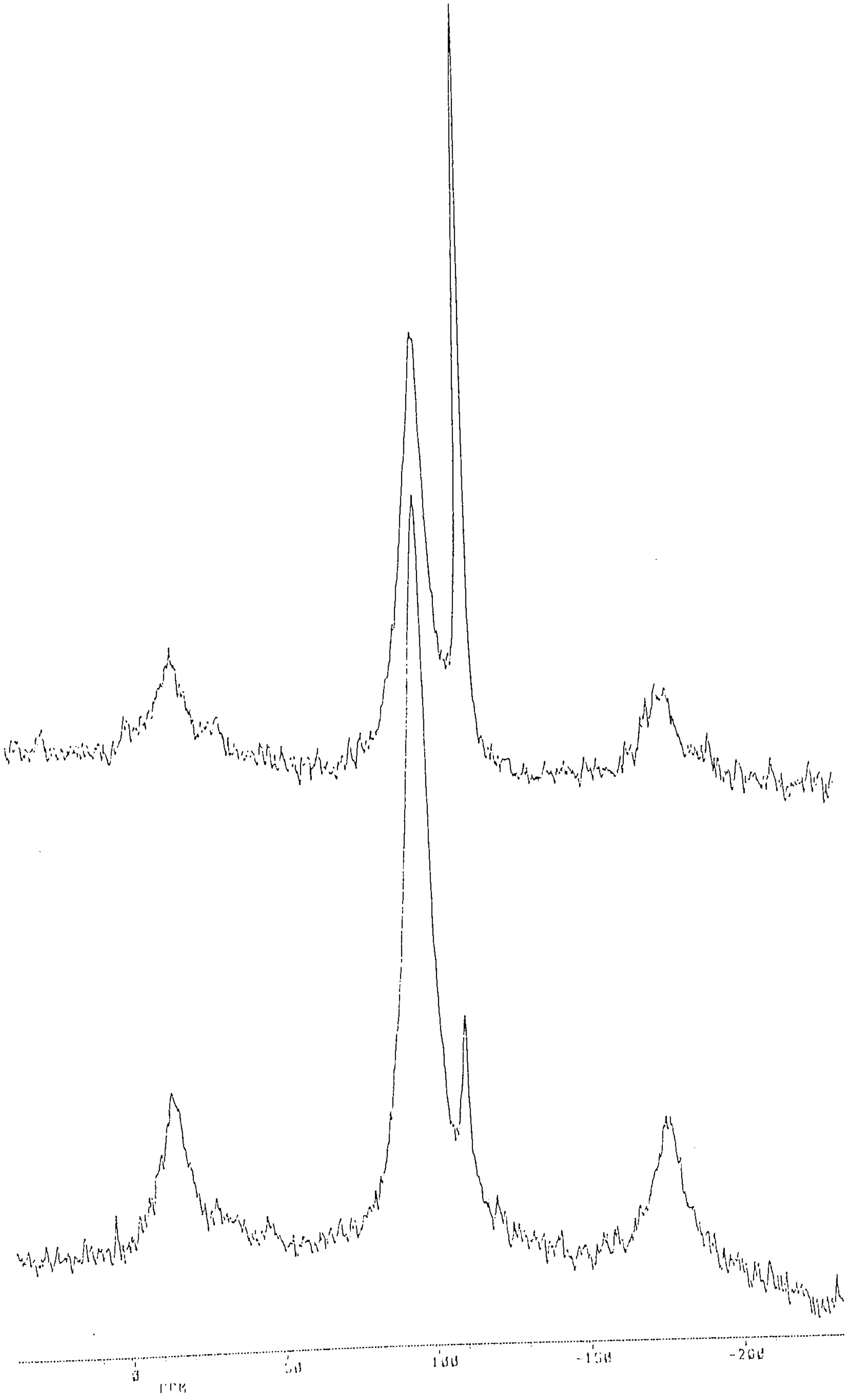


Figure 5.8 ^{29}Si MASNMR spectra of the 1.75 μm (top) and 0.85 μm (bottom) fractions of Wyoming bentonite

Noticeably larger spinning sidebands are observable in both the ^{27}Al and ^{29}Si MASNMR spectra of the finest fraction than in those of the coarsest, see Figure 5.8. This may or may not arise from an increase in structural iron content, but the broadening of the ^{27}Al MASNMR spectrum of the smallest particle size fraction provides unambiguous evidence. It should be noted that all other variables, particularly the number of FIDs acquired, were held constant when these spectra were collected.

5.3.2.2 Variations in Al^{3+} content

The substituting ion present in the greatest number in montmorillonite is Mg^{2+}, so one can hope to infer any variation in its concentration from variations in total octahedral layer substitution. As this increases, and the octahedral sheets expand in the a and b directions, there is a tendency for this expansion to be matched by substitution of Al^{3+} into the tetrahedral sheet. Thus an increase in tetrahedral aluminium may be looked for.

However, no significant difference in the tetrahedral: octahedral aluminium ratio between the finest and coarsest particle size fractions is observed by ^{27}Al MASNMR. Similarly no Q^3 (1Al) shoulder is observed downfield of the main Q^3 resonance in the corresponding ^{29}Si spectrum of either fraction.

In concluding that no spectroscopic evidence can be found for any variation in the tetrahedral: octahedral aluminium ratio with particle size, one can therefore assume that Mg^{2+} content does not mirror Fe^{2+} content and increase substantially with decreasing particle size, as any such variation would surely be observable as an increase in tetrahedral Al^{3+}. Similarly, it may be assumed that for this particular bentonite Mg^{2+} content does not increase with increasing particle size, such that particle size fractionation affords separation into Cheto- and Wyoming- type montmorillonites.

5.3.3 Implications and feasibility of variations in cation exchange capacity and chemical composition

Even in the unlikely event that all the paramagnetism recorded in the gramme magnetic susceptibility measurements is due entirely to Fe^{2+} in lattice positions, the total octahedral Fe^{2+} content is within the maximum allowable limit required for the formation of a stable 2:1 layer structure.[18] However, such a high iron content in the octahedral sheet, approximately 12%, is unusual, with many clay minerals showing a very considerably lower value.

Indeed, it is well known that the most significant features of pyrophillite, the prototype mineral of the montmorillonite group, are a very low amount of isomorphous substitution generally, a correspondingly low CEC, and a large crystal size. These properties are not unrelated. An important feature of a large crystal is that every element must fit perfectly upon every other element, and this requires the composition to be uniform throughout. Replacement of Al^{3+} by the divalent cations Mg^{2+} and Fe^{2+} causes the octahedral sheet to expand relative to the tetrahedral ones. It is probably the large crystal size that limits isomorphous replacement in pyrophillite as compared with montmorillonites.

This idea has already been expressed slightly differently in the clay literature, in that the size of the platelets of a clay mineral species may be limited by the creation of tensions in the lattice.[65] It has already been proposed that the small particle size of montmorillonite is determined by the substitutions in the lattice, which so distort the individual layers as to limit their stacking. Thus extensive isomorphous substitutions in montmorillonite as compared with pyrophillite are possible, since the lattice is essentially only a few layers thick and the crystals are small.[300]

It is fair to assume that the same reasoning may apply to different size fractions of montmorillonite itself. Thus the larger montmorillonite platelets may only be so because they contain relatively little isomorphous substitution, whereas the smaller ones may be limited in size because of the greater extent of replacement in their lattices. In this case, Fe^{2+} is of particular importance as it has the largest ionic radius of all the possible substituting species, see Table 5.6.

Substituting species	Ionic radius (Å)
Si^{4+}	0.41
Al^{3+}	0.50
Mg^{2+}	0.65
Fe^{2+}	0.76

Table 5.6 Pauling ionic radii of selected ions commonly found in montmorillonites

The fact that no increase in the tetrahedral: octahedral aluminium ratio could be found with decreasing particle size further supports this argument. It suggests that the expansion of the octahedral layer, commensurate with the Fe^{2+} content in its lattice, is not accompanied by a comparable expansion of the tetrahedral layers. Thus lattice tensions are further exacerbated in the smaller platelets. Thus the observed increase in Fe^{2+} content with decreasing particle size is both structurally possible, and good evidence of lattice tension being the major cause of lattice limitation in montmorillonites.

By looking at the mechanism of genesis one final observation may be made. Montmorillonite is most usually formed as a result of a transformation, and Wyoming bentonite is no exception. Consequently it is correct to say that it is the level of substitution into the, for example, illite lattice that governs the breakdown of the lattice and the size of the resulting montmorillonite particles, rather than the other way around.

5.4 Conclusions and Further Work

It is readily accepted that there is a definite increase in CEC with decreasing particle size for kaolinite. This must arise from an increasing contribution from edge sites towards the total exchange capacity, because there is virtually no isomorphous substitution in this mineral. Consequently the permanent charge is approximately zero and the chemical composition is invariant with particle size.

The situation is far more complicated for montmorillonite, and as a result of this no one view on the nature of the variations with particle size is accepted. Four variables have been studied in this work, namely total CEC, concentration of substitution sites, concentration of edge sites, and the substitution site: edge site ratio. One, the concentration of edge sites per unit area, must vary with particle size. Each of the others has been reported to remain unchanged as a function of particle size at one time or another. However, it is impossible for them all to remain invariant together, whilst the edge site concentration necessarily varies.

Elementary geometry requires that for each tenfold decrease in edge length, a tenfold increase in the importance of the edge sites shall be observed, so long as chemical composition remains invariant. For the particular average particle sizes of the five fractions of Wyoming bentonite used here, an approximate twofold increase in edge site contribution was predicted between the coarsest and finest fractions.

After adjustments to the measured values of exchange capacity for the impure nature of the samples, it was observed that the edge site contribution does indeed approximately double between these fractions in actual, milliequivalent terms. However, in percentage terms the increase is considerably smaller. In other words, edge sites are contributing just as much as geometrical considerations predict, but the effect on the substitution site: edge ratio is very much less noticeable because it is being partially offset by a similar increase in the contribution from isomorphous substitution sites.

Further, this ratio was observed to be essentially constant, at 88: 12, across the entire particle size range studied. A similar study of the parent Wyoming bentonite also resulted in a similar ratio being obtained. Interestingly, this value is significantly different from the much quoted 80: 20 ratio considered to be usual for smectite clays. This is probably due to the relatively high extent of isomorphous substitution observed in Wyoming bentonite as compared with other smectites.

The implication of a constant ratio is a varying chemical composition. Good correlation was observed between particle size and the gramme magnetic susceptibility of the sample, which has been shown previously, see Chapter 3, to be due primarily to iron. By employing ^{27}Al and ^{29}Si MASNMR, this was shown to be predominantly structural, mainly octahedral Fe^{2+}. An increase in structural iron content with decreasing particle size is consistent with the observed increase in permanent charge with decreasing particle size.

In addition, no spectroscopic evidence could be found for any variation in the tetrahedral: octahedral aluminium ratio with particle size. Thus not only does the increase in permanent charge arise solely from the octahedral layer, but the expansion of that layer, commensurate with its increased Fe^{2+} content, is not accompanied by a comparable expansion of the tetrahedral layers. Consequently, tensions formed in the lattice by isomorphous substitution, are further exacerbated such that the larger montmorillonite platelets may only be so because they contain relatively little isomorphous substitution, whereas the smaller ones may be limited in size because of the greater extent of replacement in their lattices. This suggests lattice tension to be the major cause of lattice limitation in montmorillonites.

In essence, it is probable that smaller platelets are so sized because their octahedral and tetrahedral layers are ill-matched, causing lattice distortions and tensions which may be withstood only to a certain lattice dimension. These severe lattice tensions result from increased octahedral substitution relative to tetrahedral substitution, causing smaller platelets to possess a much larger CEC, made up from greater contributions per unit area from both edge sites and isomorphous substitution sites, than their larger counterparts.

The results presented herein are self consistent and succeed in fulfilling the aim of this piece of work, in defining the nature of the variation, if any, with particle size of the contribution causes of cation exchange capacity. Consequently, other than attempting to acquire similar information by utilizing other techniques or by making more use of ^{57}Fe Mössbauer spectroscopy, useful further work is limited.

It is really restricted to the study of fundamentally different types of clay minerals. A similar study of kaolinite is perhaps unnecessary, but other smectite could prove to be interesting. During the course of this work particle size fractionation of laponite, a synthetic hectorite, was attempted. Despite the use of MSE high speed centrifuge, capable of speeds of up to 17000 rpm, scanning electron microscopy revealed that significant particle size fractionation had not been achieved.

It was hoped that, if particle size fractions had been produced, chemical composition of a controlled, laboratory synthesized clay mineral could have been investigated. It may be that such materials exhibit a far more uniform chemical composition than do natural clay minerals. To this end, the anionic clay minerals may prove more manageable than laponite, as their synthesis is well understood and may be controlled almost to produce platelets of a certain particle size to order.

In a similar vein, analysis of a natural montmorillonite formed by a process of neoformation rather than transformation may provide a very interesting comparison. Such a mineral is formed from solution, whereas during transformation the inherent 2D sheet framework is maintained throughout, so a similar variation in chemical composition would be particularly noteworthy.

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Appendix One

CALCULATIONS USED IN SECTION 3.2.1
AN ORGANOCLAY MASS BALANCE

(i) Calculation of percent clay solids

	Recorded mass (g) (samples A and B)	
Empty weighing dish	92.59	46.53
Weighing dish plus plant slurry	98.81	52.52
Weighing dish plus plant slurry (2 hrs 105°C)	92.86	46.78
Mass of slurry	6.22	5.99
Mass of clay solids	0.27	0.28
Percent clay solids	4.34%	4.67%
Average solids content	4.51%	

(ii) Theoretical meq calculation

$$\text{Quat (g)} = \frac{\text{meq x RMM (quat) x Clay (kg)}}{\text{Activity (quat)}} \qquad [1]$$

eg. Experiment 1

(3.59 x 100) / (585.5 x 0.00679) = 90.3 meq

(iii) Theoretical mass of organoclay and residual mineral salts calculation

Below the CEC all surfactant added is assumed to have undergone ion exchange. All surfactant added above the CEC is assumed to be sorbed onto the clay ion pairs.

eg. Experiment 2

Quat Cl^- added	4.59 g
(i) Up to the CEC	4.59 x (92/120.1) = 3.52 g
	3.52 x (550/585.5) = 3.31 g quat, 0.21 g Cl^-
	0.21 + { 0.21 x (23/35.5) } = 0.35 g NaCl
(ii) Above the CEC	4.59 - 3.52 = 1.07 g
Quat plus quat Cl^- in organoclay	3.31 + 1.07 = 4.38 g
Mass of clay in organoclay	6.53 - { 0.21 x (23/35.5) } = 6.39 g
Total mass of organoclay	4.38 + 6.39 = 10.77 g

(iv) Back calculation of percent solids

eg. Experiment 1

Mass of clay slurry	150.51 g
Clay solids content (4.51 % solids)	6.79 g
Mass unaccounted for in organoclay	0.41 g
Back calculated clay solids	6.79 - 0.41 = 6.38 g
Back calculated percent solids	(6.38/150.51) x 100 = 4.23%

(v) Experimental meq calculation

$$\text{Experimental meq} = \{(I_d - 6.2^*) / (100 - I_d)\} \times 10^5 / \text{RMM (quat+anion)} \qquad [2]$$

where $I_d = \{(I_w - \%\ \text{moisture}) / (100 - \%\ \text{moisture})\} \times 100$

I_w = Total loss on ignition

* = alternatively a value of 5.0% is used

eg. Experiment 1

I_w	38.2%
% moisture	0.3%
I_d	38.01
Experimental meq	93.3

(vi) Re-calculation of theoretical meq of organoclay

Use equation [1] and back calculated clay solids

eg. Experiment 1

(3.59 x 100) / (585.5 x 0.00638) = 96.1 meq

Appendix Two

ENHANCED PENTACHLOROPHENOL SORPTION BY PILLARED ORGANOCLAYS

The following piece of work was carried out during a period of time spent at the collaborating company's research laboratories at Littleborough, Lancashire. Whilst it really only constitutes an initial study, the results are encouraging enough to warrant its inclusion. Further development of the approach adopted may well lead to improved materials for the removal of priority pollutants.

Enhanced Pentachlorophenol Sorption by Pillared Organoclays

Activated carbons are among the most effective adsorbents known for the removal of organic toxicants from aqueous effluents and contaminated groundwater. However, in the past few years there has been an increasing interest in designing materials with improved, perhaps specialized, sorptive properties.

Organoclays such as quaternary ammonium exchanged bentonites have become increasingly utilized in attempts to enhance the immobilization of organic toxicants such as benzene and toluene from industrial wastewaters.[148,151] Phenol and chlorophenols have also been successfully adsorbed onto organophilic bentonites in similar experiments.[146]

A recent systematic study of the uptake of pentachlorophenol, PCP, from water, using organoclays prepared from a range of organic amine salts, has demonstrated that in general the more hydrophobic the cation on the smectite, the greater the uptake of PCP.[147] For such highly organophilic clays the sorption is via non-polar interactions between the alkyl groups on the organic cation and PCP. In a mechanistic sense this interaction appears to be similar to a partitioning process between water and the organic phase of the clay-organic complex.

By pillaring the organoclay it may be anticipated that the volume of the organic phase will be increased, so leading to enhanced sorption of PCP. A series of partially pillared/ partially exchanged bentonites were produced by a modification of the 'wet' method in order to examine this idea.

Preparation of pillared organoclays

2.5 dm^3 of a clean 2% bentonite slurry was heated to 66°C on a hotplate, stirring continuously. To this, a known amount of pillaring agent was added, causing an immediate sharp increase in viscosity.

The pillaring agent used was aluminium chlorohydrate, ACH, with an empirical formula of $Al_2(OH)_5Cl$. It exists predominantly as the complex ion $[Al^{IV}Al^{VI}{}_{12}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, with the aluminium in tetrahedral coordination. The complex is spherical, with a diameter of approximately 10Å when in position as an interlamellar prop. Ion exchange with ACH gives very regularly pillared clays. Increased thermal stability of these pillars can be attained by calcining the product at 350-540°C. The complex ions are converted to Al_2O_3 pillars, which are also approximately 10Å high, so confering thermal stability to over 1000°C upon the clays. Calcining is prefered for catalytic applications for this reason, and ACH is a much used commercial pillaring agent.

Sufficient cationic surfactant dihydrogenated tallow dimethyl ammonium chloride, was then added so as the total cation loading, ACH plus ammonium salt, was exactly equal to the CEC of the clay. The pH of the suspension was then adjusted to 4.8 using solutions of NaOH and HCl, and stirring continued at 66°C for a further one hour. Finally the product clay was filtered, extended, dried and milled as described in Section 2.2.2. A series of pillared organoclays were produced in this manner, with ACH : Ammonium salt ratios of 10: 90, 15: 85, 50: 50 and 100: 0.

Dispersion testing was carried out on the product clays to assess the extent of the pillaring. 0.5 g of pillared organoclay was weighed into a boiling tube, 25 cm^3 of xylene was added, and the suspension vigorously mixed for five minutes. 0.3 cm^3 of methanol was then added and the mixing re-commenced for a further five minutes. The settling out of the suspension over time was observed; data are presented in Table A.

Very generally, the higher the percentage ACH in the product the less well it dispersed, hence the more completely pillared it is. This is obviously consistent with what one would expect.

Pillared organoclay	Appearance	Dispersion volume upon standing (cm^3)		
		30 seconds	5 minutes	1 hour
10: 90	cream/soft	25	10	5
15: 85	cream/soft	25	10	5
50: 50	cream/soft	25	5	5
100: 0	dark brown/hard	0	-	-

Table A Dispersion test data for pillared organoclays

Pentachlorophenol sorption studies

Sorption studies were carried out on the pillared organoclays using the batch equilibration method.[147] The PCP stock solution was prepared by dissolving 0.20 g PCP in 10 cm^3 methanol, and adding 1 cm^3 of this solution to 1000 cm^3 of distilled water. The PCP concentration in the aqueous phase was determined after filtration, by UV adsorption at 318.3 nm to be 4.6×10^{-5} mol dm^{-3}.

50 mg of each clay was then weighed into a screw-top jar, 100 cm^3 of the stock solution was added, and the jar placed overnight in a roller oven at 20°C. At the end of the equilibration period the solid and liquid phases were separated by filtration, and the final PCP concentration determined. Data are presented in Figure A.

Interestingly it may be noted that the 100% ACH pillared clay showed a significant uptake of PCP, comparable with that of a typical organoclay. This is not unreasonable as the oxyhydroxy complexes of aluminium and iron are both known to have a strong affinity for hydroxy moieties generally.

More significantly, enhanced sorptive properties are obtained when the alkylammonium salt is used in tandem with the pillaring agent. A synergism is observed, the pillaring of the unit layers have enabled the cationic surfactant to act more effectively in drawing the PCP molecules into the organic phase of the clay-organic complex. Conversely, if Figure A is viewed from left to right, the synergism may be viewed as resulting from the increase in affinity of the microporous interlayer adsorption sites that the surfactant brings to the conventionally pillared clay.

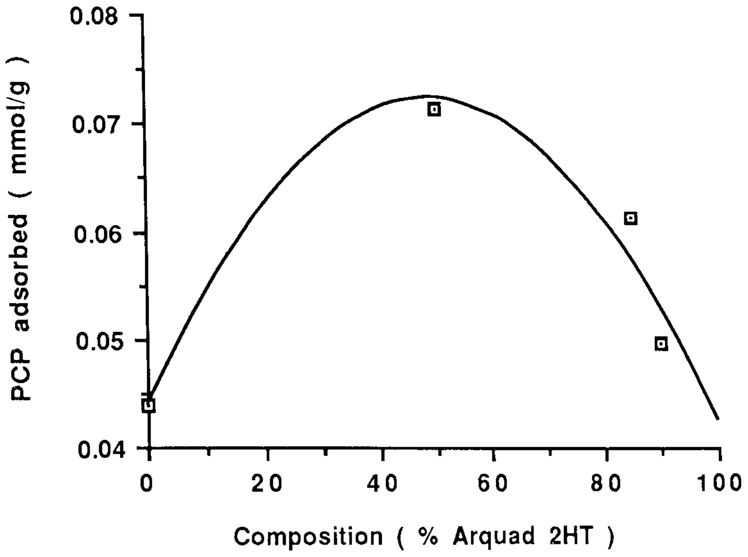

Figure A Graph of PCP adsorbed (mmol/g) against composition of pillared organoclay

Since this work was carried out, similar results have been reported in the literature for aluminium pillared clay-based adsorbents incorporating a nonionic surfactant.[301] It is noted that, from the point of view of increasing the sorptive properties of pillared clays with surfactants, rather than improving conventional organoclay adsorbents by pillaring, the surfactant has a dual effect. Firstly, there is the improved affinity of the interlayer adsorption sites, but secondly new adsorption sites are created on the external lattice surfaces by the surfactant molecules, so allowing greater uptake of pollutant.

If ^{19}F MASNMR is available, it may well prove useful in future work to adopt fluorophenols rather than chlorophenols as model toxicants. This may provide useful information on the location and mobility of the bound toxicant, and may highlight the existence of more than one type of adsorption site.