Aspects of substoichiometry: The rare earths

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Summary

Substoichiometry has been studied in relation to the analytical chemistry of the rare earth metals. Substoichiometric analysis by solvent extraction is difficult with these metals due to the lack of strong, readily extractable chelates. There are, however, clear advantages in having new methods of trace analysis among current developments in the chemistry of this group. In seeking a solution to this problem, it has been possible to investigate more fully some of the underlying principles of substoichiometry as applied to isotope dilution analysis, and to a lesser extent activation analysis.

No specific reagents are available for rare earth substoichiometry, but complexones such as EDTA can be used after preliminary separation of interferences. Use of this reagent involves substoichiometric reaction in aqueous solution, and the separation step requires the removal of unreacted metal into the second phase. The reagent system rare earth, EDTA, thenoyltrifluoroacetone was studied. A theory was developed and verified from which optimum conditions could be calculated under which substoichiometric separation of the EDTA complex was possible. Model analyses were conducted using standard known solutions of terbium and ytterbium.

Salicylic acid was studied as an extractant for rare earth metals, to decide whether such ion association systems offer useful alternatives in substoichiometry. The higher concentrations required introduce complications to the theory cited above. Despite this, and the lower degree of accuracy attainable in the experimental results, this type of extractant can be considered in an extension of the theory and its behaviour predicted in the same way.

Ion exchange resins have been examined as an alternative to solvent extraction for removing free metal from the substoichiometric complex. The results confirmed that substoichiometry is possible under these conditions. A detailed study of the complex equilibria emphasised the importance of kinetics, and the need for more strict control of solution parameters.

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Abbreviations Used for Aminocarboxylic Acids

NTA	Nitrilotriacetic acid
EDTA	Ethylenediaminetetraacetic acid
HEDTA	2-hydroxyethylethylenediaminetriacetic acid
EGTA	Ethyleneglycol bis (2 aminoethylether) tetraacetic acid
DTPA	Diethylenetriaminepentaacetic acid

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CHAPTER 1

Introduction

1.1 The Project

The material presented in this thesis was obtained during three years of research in the Department of Chemistry, The University of Aston in Birmingham, from September, 1965, to September, 1968. The experiments were conducted in the radiochemistry laboratories and the research was supervised by Dr. G. B. Briscoe. It forms part of the work of a group of students, eventually four in number, whose common interest was trace metal analysis by substoichiometry.

By 1965 there was already an appreciable number of publications concerning substoichiometry in the literature, many published by the original authors and their associates. Most of these deal with the development of methods of trace metal analysis by neutron activation or radioactive isotope dilution analysis, whilst the earlier ones outline the ideas upon which substoichiometry is based. These have been reviewed by the authors and are presented in a new book.[1] The original idea for this project was to link together substoichiometry and rare earth metal analysis, primarily because rare earths represented one of the few groups of metals which had not yet been analysed by the technique. It was quickly realised, however, that the value of the work lay not only in this direction but also as a study of substoichiometric reactions and separations in a more general sense.

For analytical purposes the experiments were almost exclusively conducted with isotope dilution in mind. The rare earth metals are analysed by activation analysis relatively easily. They have a high cross-section for thermal neutron capture and with the aid of carriers can be isolated and estimated by ion exchange and precipitation without great difficulty. Thus the major advantages offered by substoichiometry, such as avoiding the need for radiochemical yield determination, are lost. These will be dealt with in detail below. Furthermore, the most rapid advances in such analyses today are purely instrumental. It is felt that the parallel developments in actual radiochemical techniques will be of most use in such methods as isotope dilution analysis, which will also be described in more detail below, 1.2. It suffices here to say that isotope dilution methods can be used where irradiation sources are not available or whenever the high activities in activation analysis cannot be tolerated. By no means unimportant also is the fact that isotope dilution analysis can be considerably less expensive.

For the second part it must be realised that the rare earth metals are not easy to analyse using substoichiometry. By this it is meant that there is no reagent ideally suited for use with the method. The need for such a reagent will be fully realised later on, e.g. 1.3. Thus it is necessary to search more deeply into the capabilities and limitations of substoichiometry for a successful method, and by doing so it is possible to gain a much deeper insight into the chemistry involved. Experiments are described which hopefully illustrate ideas on substoichiometry which were developed during this time, with the object of making a useful addition to knowledge of the technique and to rare earth metal analysis. The many valuable hours spent in gaining proficiency in the design of experiments or the experience gained in overcoming practical difficulties involved in the work can, of course, never be adequately reported.

1.2 Radiochemical Methods in Trace Metal Analysis

Radiochemical techniques, although still somewhat specialised, are becoming increasingly appreciated in analytical methods. The most popular applications are those already mentioned, namely activation and isotope dilution analysis. Activation analysis does not enter directly into this present work but since it is useful in rare earth analysis, the method will be briefly discussed so that comparisons can be made when necessary.

Activation analysis depends upon a measurement of radioactivity produced when the sample is irradiated in a flux of thermal neutrons. It is not an absolute method since neutron flux cannot easily be accurately calibrated. Usually a standard and unknown sample are irradiated together and the activities produced in each are compared. The theory need not be discussed in detail here since it is not applied. Equations for calculation of activity produced on irradiation are given in Chapter 2..

The measured activity is proportional to the capture cross-section of each isotope present and its abundance, and to the time of irradiation and decay characteristics of the product. There are also a number of practical factors affecting the analysis such as shielding of the sample by the matrix containing it, or the container, etc. Most rare earths are suitable for activation analysis such that the sensitivity achieved compares favourably with the best spectroscopic methods provided high flux sources are available.

Dysprosium can successfully be analysed with a very low flux source such as Ra/Be with a flux of about 10^5 n/cm^2/sec because of the high cross-section and abundance of dysprosium 164, and the short lives of higher isotopes. Thus many rare earths could be analysed at 10^{-9}g level whilst cerium and neodymium would perhaps succeed at 10^{-7}g and dysprosium at 10^{-12}g.

Isotope dilution analysis will be dealt with in more detail. For isotope dilution analysis much less severe restrictions apply and the technique can be used in any well-designed analytical laboratory which has facilities for storing a few millicuries of active stock solutions. The earliest applications of isotope dilution analysis were in organic chemistry, to resolve mixtures for components which were impossible to separate quantitatively in high purity. Inorganic applications were fewer until recently, and indeed substoichiometry has played a major role in improving the method for this purpose.

Isotope dilution analysis is not the only application of tracers in analytical chemistry, but it is probably the most important. The technique is not confined to radioactive tracers but can also be used in mass spectroscopy. In this thesis, all tracer work refers to experiments using radioactive materials.

Basically the method is as follows. If a radioactive material, X*, is added to a non-active form of the same component, X, then the unit activity, or specific activity (S) will be changed. If this change in specific activity can be measured, then either X or X* can be determined. Separations involved need not be quantitative so long as sufficient material is available for the determination of S.

The result can be calculated as follows:

Suppose the unknown sample contains W_u of component X and the standard active solution contains W of component X and has a measured activity of A counts per second.

The measured specific activity of the standard is

$$S = \frac{A}{W} \text{ counts } s^{-1} \text{ ml}^{-1} \qquad (1)$$

If we mix together standard and sample

$$\text{Total weight} = (W + W_u) \qquad (2)$$

$$\text{Measured activity} = A \text{ counts } s^{-1}$$

$$\text{Measured specific activity } S_1 = \frac{A}{(W + W_u)} \text{ counts } s^{-1} \text{ ml}^{-1} \qquad (3)$$

By comparing these specific activities, measured under identical conditions,

$$\frac{S}{S_1} = \frac{A}{W}\left(\frac{W + W_u}{A}\right) = \frac{W + W_u}{W} \qquad (4)$$

$$\text{or} \quad 1 + \frac{W_u}{W} = \frac{S}{S_1} \qquad (5)$$

$$W_u = W\left(\frac{S}{S_1} - 1\right) \qquad (6)$$

In practice one would determine S by weighing and counting W. Then mix together $W + W_u$, and separate enough of the mixture to again weigh and count in order to determine S_1. W_u is calculable from equation (6) above. W and W_u need not, of course, be weighed but can be determined in any conventional way depending upon concentration and the nature of the component. It is essential to isolate a portion of the mixture as pure X in order to determine S_1, but it is not important how much of $(W + W_u)$ is sacrificed in order to attain this purity. Isotope dilution analysis, in most cases, lacks the sensitivity of activation analysis but the advantages are quite clear.

1.3 Substoichiometry

With these points established, it is now possible to discuss the basis of substoichiometry. If, in the previous section, the quantity of metal isolated from both the sample $(W + W_u)$ and the standard W is exactly the same, being less than the total contained in either, the calculation and thus the actual method can be considerably simplified. The measured aliquots of sample and standard will be exactly alike in all but the activity. Therefore, there is no need for the analyst to determine the yield of his separation step. It is sufficient to compare the measured activities to determine W_u.

$$\text{Thus} \quad W_u = W\left(\frac{\text{A standard}}{\text{A sample}} - 1\right) \qquad (7)$$

This is the concept first proposed by Ruzicka and Stary in 1961 and used by them in many subsequent analyses.[1] It can be summarised. Substoichiometry is a process by which equal amounts of material are separated from a number of different solutions regardless of the original concentration or volume, by an amount of reagent less than that required to react with all the metal in any one of them. The name is misleading and is often taken to mean non-stoicheiometric reactions. This is not so. The reaction is stoicheiometric but takes place between non-equivalent quantities of reagent. The prime requisite of substoichiometry is that the reagent must be completely consumed.

Ruzicka and Stary proposed that such reactions should be possible in almost any conventional separation system, such as solvent extraction or precipitation, etc. Solvent extraction with chelating agents forms by far the neatest way in which the technique can be applied and has received both the most attention and the most rigorous theoretical treatment.

Solvent extraction theory can be used to emphasise the main points of substoichiometry. These ideas have had to be further developed in respect of the rare earths and are partly repeated later in 3.2. Only the essential points are drawn out here.

Firstly, conditions need to be calculated under which the metal M^{n+} will be complexed by the reagent to give an extractable chelate MA_n. These can be obtained from a knowledge of the equilibrium conditions of the reaction

$$M + nHA_o \longrightarrow MA_n + nH$$

expressed by the extraction constant

$$K = \frac{[MA_n]_o[H]^n}{[M][HA]_o^n} \qquad (8)$$

where HA represents the chelating agent which is a weak acid and subscript o indicates organic phase. Electrical charges are omitted for simplicity in writing.

In practical terms the formation of MA_n must use up, say, 99.9% of the total concentration, C_{HA}, of the reagent

$$[MA_n]_o.V_o \geqslant \frac{0.999.C_{HA}.V_o}{n} \qquad (9)$$

where V_o is the volume of the organic phase.
Thus the equilibrium concentration M is given by

$$[M].V = C_M.V - \frac{C_{HA}.V_o}{n} \qquad (10)$$

where V is the volume of the aqueous phase and C_M the total concentration of M.

Similarly

$$[HA]_o\ V_o \leqslant 0.001\ C_{HA}.V_o \qquad (11)$$

Substituting in the equation for K_e and taking logs

$$pH \geqslant \frac{1}{n} \log \frac{C_{HA}}{n} - \frac{1}{n} \log \quad C_M - \frac{C_{HA}.V_o}{nV} \quad - \frac{1}{n} \log K \qquad (12)$$

This expression is applicable provided that HA is not dissociated, and there are no masking agents present.

A fuller account of how these requirements fit into the general scheme of solvent extraction equilibria is presented later in Chapters 3.2 and 4.7. Further detail is unnecessary in order to introduce the ideas to rare earth chemistry. Instead it is important to observe the requirements of our chosen method, i.e. isotope dilution analysis. The dissociation and partition of the reagent and the extraction constant will set limits upon the minimum pH at which substoichiometry can be achieved. It will be realised that substoichiometry by direct solvent extraction requires a very strong chelating agent, preferably specific in action, which forms highly extractable complexes. Such reagents are diphenylthiocarbazone (dithizone) or diethyldithiocarbamate having values of K in the order of 10^{20} or greater. Much of the work on substoichiometry to date has used these extractants.

Provided such a reagent is available, substoichiometry can offer marked increases in selectivity if more than one metal is present. Consider the equilibrium of the extraction of two metals M^{n+} and M^{m+} with HA.

From equation (8)

$$\frac{[MA_n]_o}{[M'A_m]_o} = \frac{K\ [HA]_o^{(n-m)}[M]}{K'\ [H]^{(n-m)}[M']} \qquad (13)$$

In the case where M and M' have the same total concentration and n = m, separation can be achieved, i.e. $[MA_n]_o/[M'A_m]_o \gg 100$, when $K/K' \gg 200$, provided only half of M is extracted. For the same separation, allowing for all of M extracted, K/K' would have to be $\gg 10^4$.

1.4 Analysis of Rare Earth Metals

The rare earth elements are the largest single group in the periodic classification. There are fourteen metals in the group which is placed in IIIA from number 57-71. Two lighter metals, scandium and yttrium, are often placed together with the rare earths because of their common occurrence and similarity of reaction. Thus the complete group is as follows:

	Atomic No.	Approx. Classification
Lanthanum	57	
Cerium	58	
Praseodymium	59	
Neodymium	60	Light rare earths
Promethium	61	
Samarium	62	
Europium	63	Middle earths
Gadolinium	64	
Terbium	65	
Dysprosium	66	
Holmium	67	Heavy rare earths
Erbium	68	
Thulium	69	
Ytterbium	70	
Lutetium	71	

Promethium is radioactive and has no naturally occuring isotope. The other metals are not exceptionally rare and the name is traditional rather than truly descriptive. Cerium compares in abundance in igneous rocks to zinc, whilst lanthanum or neodymium are as abundant as molybdenum or lead. Even the rarest rare earth, thulium, is more abundant than silver and only slightly less than cadmium. The rarity of each one is ascribed rather to the fact that until recently it was extremely difficult and in some cases impossible to separate individual rare earths from the mixtures in which they occur.

The co-ordination chemistry of the rare earths has been recently reviewed.[2] Stable complexes are formed only when strongly chelating ligands are used, particularly electronegative ones containing oxygen as donor. Thus bonds are strongly electrostatic and compare to those of calcium, strontium and barium. Electrostatic attraction for any anion increases as cation radius decreases, and this gradation of stabilities is apparent in the rare earth series. There are three distinct trends in formation constant data, although to date there are really too few data for accurate correlation. Most chelates have been studied in aqueous solution only and in addition there are good examples of ion association complexes such as LaX^{2+} where X = F, Cl, Br, I or isolable adducts such as $LaCl_3.xNH_3$ where x = 1 to 8.

The rare earth metals form a large number of 'insoluble' compounds with both organic and inorganic reagents. Classical methods of analysis include precipitation and titration with complexones such as E.D.T.A.

Instrumental analysis apart from the radiochemistry previously mentioned is principally spectroscopic. Absorption spectra of these ions are extremely complicated but determinations are made and excellent reproductions of spectra are available.[3]

Emission spectra are prepared with both copper and carbon electrodes. The main difficulty arises from inter element interference which causes enhancement or suppression of lines. Table 1.1 gives limits of detection of various rare earths in mixtures.

Another valuable tool for rare earth analysis is X-ray fluorescence spectroscopy. Table 1.2 shows how the results of this method compare with the carbon electrode emission of Table 1.1.

Table 1.1

Limits of Detection (p.p.m.) of Rare Earth Metals in
Rare Earth Matrices by Emission Spectroscopy (from Carbon)

	Matrix				
Impurity	La_2O_3	Sm_2O_3	Gd_2O_3	Er_2O_3	Lu_2O_3
Ce	> 1000	> 1000	> 1000	> 1000	20
Nd	> 1000	> 1000	> 1000	> 1000	100
Gd	20	> 1000	-	> 1000	1
Tb	100	> 1000	> 1000	> 1000	1
Tm	50	20	10	1	1

Table 1.2

Limits of Detection (p.p.m.) of Rare Earth Metals in
Rare Earth Matrices by X-ray Fluorescence

	Matrix				
Impurity	La_2O_3	Sm_2O_3	Gd_2O_3	Er_2O_3	Lu_2O_3
Ce	300	200	200	200	200
Nd	100	100	100	100	200
Gd	100	100	-	100	100
Tb	100	100	100	100	100
Tm	100	100	50	50	100

These data are available in several texts and were confirmed by information received from Johnson Mathey Limited in 1965.

One factor is clear from the outset. Substoichiometry, being essentially a chemical separation technique, will only achieve such sensitivity for the analysis of mixtures in the most exceptional circumstances, if at all. There is, however, an increasing number of excellent ion exchange separation techniques available for rare earth separation, some requiring only simple eluents such as perchloric acid. Substoichiometry presents a most useful rapid analytical technique for the analysis of a component separated in this way, or indeed in any other preliminary separation. It should also be applicable to the determination of gross rare earths in solution at concentrations which might be too dilute for spectrophotometry, say, about 1-10 μg/ml.

1.5 Solvent Extraction of the Rare Earths

To conclude this introduction it is necessary to give the reader a picture of solvent extraction methods in rare earth chemistry. This is without doubt the most versatile application of substoichiometry and deserves full consideration.

Solvent extraction techniques have been mainly of interest on an industrial scale either for the separation of mixtures of rare earths or separation of rare earths as impurities in uranium, thorium and other nuclear fuels. The diversity of reagents used can be seen with reference to the NASA monograph on the radiochemistry of the rare earths[4] by Stevenson and Nervic, which groups together the following reagents as typical rare earth extractants:
(a) Tri-n-butyl orthophosphate (TBP), (b) salicylic acid,
(c) thenoyltrifluoracetone (TTA), (d) di(2-ethyl hexyl)phosphate D2EHP, (e) mono and di-n-butyl orthophosphate, (f) 8-hydroxyquinoline and (g) cupferron.

From this list one can conclude that extractable chelates are formed, (c), (f), (g), as would be expected. Secondly, that the metals extract into the organic liquids which might be termed chelating solvents for the purpose of this introduction such as TBP or D2EHP, and that more complicated associations also lead to extraction, e.g. salicylic acid. Herein lies adequate scope for attempting substoichiometry with less straightforward systems than for instance dithizone or diethyldithiocarbamate, which have received much attention so far, although even these have shown on further investigation abnormal behaviour under substoichiometric conditions.[5] The rare earths are not extracted by these sulphur containing reagents.

Not many of these reagents are sufficiently well reported to be able to predict immediately their possible usefulness for substoichiometry, and only a few extraction constants are quoted in general texts on solvent extraction. Little consideration need be given to the direct use of TBP and similar reagents, which are weak chelating reagents and require high concentrations of nitric acid. Similarly, cupferron and oxine can be dismissed because of non-quantitative extraction even with a large excess of reagent. Acetylacetone and derivatives are better, but are again weak reagents. For example, the extraction constants of rare earth thenoyltrifluoroacetonates are of the order 10^{-7} - 10^{-10} which can be compared with 10^{26} for mercury dithizonate.

The strongest and best characterised of all the rare earth complexes are those used as eluents in ion exchange, that is EDTA and other long chain carboxylic acids. This project leans heavily upon these for the application of substoichiometry to rare earth metals. Thus the substoichiometry presented here is essentially an indirect process in so far as the two phase systems used always present a fraction of the original aqueous solution for measurement and the actual substoichiometric step does not involve transfer of metal to the second phase. Some attention has been given to this idea already in connection with ion exchange and is reported in Chapter 6, which deals with this topic. No work has been attempted which could in any way be described as designing a new or more powerful extractant, although there is clearly some scope in this direction.

The results of the work are presented in the five subsequent chapters which deal with substoichiometry using EDTA and thenoyltrifluoroacetone, the reaction of rare earths with salicylic acid, and further comment on the use of ion exchange resins in substoichiometry.

CHAPTER 2

Preparation and Standardisation of Solutions, and Description of Instruments

2.1 Preparation of Solutions

The techniques employed in the experimental work follow common practices of most analytical laboratories and will not need extensive description.

Solutions were prepared in water which was twice distilled in an all glass Scorah still. Whenever possible analytical reagent (AR) grade reagents were used. Unfortunately, for many of the important reagents, including the metals themselves, AR grade is not available, and a general purpose or laboratory reagent grade (LR) had to be used instead. For many experiments, this was not a serious disadvantage. The least desirable effect was the possible introduction of trace metallic impurities.

(a) The Rare Earth Metals

Some rare earth metal oxides were donated by Johnson Mathey Limited, but the majority of samples were purchased from British Drug Houses Limited (BDH). These are generally contaminated with about 0.1% of adjacent metals in the series. No attempt was made to purify them further. This would have been very costly and would have added nothing to the conclusions drawn from much of the experimental work, when solutions were of such low concentration that the major metallic component was present at approximately 10^{-5} or 10^{-6} M.

The oxides are soluble with varying degrees of difficulty in concentrated HNO_3 or, in very resistant cases, e.g. Tb_4O_7, in concentrated $HNO_3 + H_2O_2$. Solutions were prepared wherever possible at concentrations of $> 10^{-2}$ M so that standardisation could be made with EDTA using xylenol orange indicator. The AR EDTA standardised against AR zinc or lead salts was found to be itself good enough as a primary standard. Moreover, the rare earth oxides were also found to be true enough to specification to require no further standardisation in many cases.

(b) Other Reagents

Some organic solvents, e.g. xylene, toluene and iso-amyl alcohol were obtained as AR grade. Hexone was only available as LR grade and was used as purchased. Occasional use of LR grade iso-amyl alcohol showed no difference to when AR grade was used. Other organic reagents are also available as 'pure' reagents from a number of suppliers, but not as AR grade. Among these were thenoyltrifluoroacetone (Koch-Light Laboratories Limited), which was available in good crystalline form and used directly.

Salicylic acid is available as AR grade but sodium salicylate, though both dry and crystalline, is only LR grade. Dilute salicylate solutions were standardised by developing the colour of the complex in excess iron III, and measuring the optical density at 520 nm. Fe III itself is completely transparent at this wavelength and there is no reagent effect. Salicylic acid was used to prepare the calibration. There was never any noticeable effect in the salicylate reactions of possible heavy metal contaminants, such as lead which might be as high as 10 ppm in the sodium salt. LR grade hexamine used also contains up to 2 ppm of lead which cannot be conveniently removed, although it is extractable with dithizone and was determined approximately by extractive titration with this reagent. In solution it presented a negligible interference in the experiments for which it was used.

Ion exchange resins were purchased from BDH. All of those used are available in a clean, dry form and free from fine particles. They were oven dried to remove all water before being measured for use.

2.2 Preparation of Radioactive Tracers

Samples of five long lived active rare earths were purchased from The Radiochemical Centre, Amersham. They were:

	Half Life
^{141}Ce	32.5 d
^{144}Ce	284 d
^{153}Gd	242 d
^{160}Tb	73 d
^{170}Tm	127 d

Others were prepared by irradiation in the thermal neutron flux of the Liverpool and Manchester Universities Research Reactor at Risley.

The amount of radioactivity produced as a result of neutron irradiation (disintegrations per second) is given by the following equation

$$D = \frac{\phi . m . N . f . \sigma \, (1 - e^{-\lambda t})}{A}$$

where D = disintegration rate at time t

ϕ = neutron flux in $n.cm^{-2}.s^{-1}$

m = mass of element

λ = decay constant of nuclide produced

f = fractional abundance of element

σ = reaction cross-section $cm^2.atom^{-1}$

N = Avagadro's number g.g $atom^{-1}$

A = atomic weight of element g.g $atom^{-1}$

The neutron flux at Risley is about 10^{12} neutrons per cm^2 per second. Using this facility it was possible to produce the following isotopes in a one day irradiation for the required experiments.

Element irradiated (oxide)	Nuclide produced. Available for use at Aston.	Half Life
La_2O_3	^{140}La	40.2 h
Pr_6O_{11}	^{142}Pr	19.2 h
Nd_2O_3	^{147}Nd	11.1 d
Tb_4O_7	^{160}Tb	73 d
Yb_2O_3	^{169}Yb	31 d
	^{175}Yb	4.2 d

Approximately 50-100 mg of the oxides were irradiated in sealed silica ampoules in a standard 'A' irradiation can.

Irradiated samples were dissolved in the same manner as inactive oxides, and stock solutions were made in dilute acid to avoid hydrolysis and loss by adsorption. These isotopes presented no handling difficulties except in the case of the ^{140}lanthanum which has an exceptionally high gamma ray energy and requires more effective shielding precautions.

Half life measurements were not usually made. Identification of active nuclides was confirmed by comparison of the gamma spectrum with available standard data.[6] Experiments requiring tracers, with very few exceptions, were conducted using the appropriate isotope from the table above to label the metal. This fact is assumed in reporting the experimental part of each section, and further details of the labelling will only be repeated in exceptional cases.

2.3 The Counting Equipment

Two sets of equipment were used during the course of the research. The first was valve equipment by Research Electronics Limited. Much of the work of Chapter 3 used this equipment, which had a dead time of about 100 μ s. Dead time can be determined quickly and simply, so that corrections can be made, provided the count rate is not excessively high. The method is as follows:

Suppose the dead time of counter = T s.count^{-1}

Count rate measured = N_o counts.s^{-1}

$$\text{True count rate} = \frac{N_o}{1 - N_oT} \text{ counts.s}^{-1} \qquad (1)$$

If the specific activity = A $\text{counts.s}^{-1}.\text{g}^{-1}$ for dead time = 0, and the measured specific activity = S $\text{counts.s}^{-1}.\text{g}^{-1}$

$$S = (1 - N_oT)\,A \qquad (2)$$

$$S = A - ATN_o \qquad (3)$$

Thus a graph of S versus N_o is linear and of slope AT, and intercept A.

$$\text{Dead Time } T = \frac{\text{Slope}}{\text{Intercept}} = \frac{AT}{A} \qquad (4)$$

The second set of equipment was fully transistorised apparatus by Nuclear Enterprises Limited. The dead time of this equipment cannot be determined as described above. It is very short, about 1 μ s, and consequently is negligible even at very high count rates. Table 2.1 gives details of the various assemblies.

Table 2.1

Details of Instrumentation

Detector	Shielded NaI(Tl) crystal. (a) Nuclear Enterprises. 2" x 2" cryst. $1\frac{1}{8}$" x $1\frac{1}{2}$" well. Volume 20 ml. (b) Research Electronics. 1.75" x 2" cryst. $\frac{5}{8}$" x $1\frac{1}{2}$" well. Volume 5 ml.
Amplifier common to all assemblies	N.E. 5260
Single channel analyser common in spectrometers	N.E. 5159
Scaler	N.E. 5079
Recording spectrometer with strip chart	N.E. 6530
Recording spectrometer Multi-channel	Laben Mod. 100 Laben Mod. 400
Single channel spectrometer with automatic sample changing	N.E. 8651 gammamatic
Liquid scintillation spectrometer, three channel	N.E. 8305
Single channel γ-ray spectrometer	R.E. 9000 series

2.4 Choice of Counting Conditions

With the exception of experiments requiring ^{14}carbon, (see Chapter 6), all counting was achieved by means of a well type NaI(Tl) crystal associated with a single channel gamma spectrometer. An important part of all counting is constant geometry. This was facilitated by using solution counting in screw top vials. Comparison was always made between equal volumes of sample and hence detection efficiency was constant.

^{14}Carbon was counted by liquid scintillation. Aqueous solutions were used, and it was necessary to determine conditions under which the solution could be mixed with scintillator to give a homogeneous sample for counting. N.E. 220 scintillator was used, which tolerates about 10% of aqueous solution, depending on the nature and concentration of the solute. Blank tests were prepared for background counts, and both these and calibration standards were treated in exactly the same manner as the samples. No serious quenching problems were encountered in the experiments cited.

Counting of the chosen rare earths by way of their gamma emission is simple. Most of them have complicated gamma spectra and display peaks corresponding to a wide range of energies. The main peaks are tabulated in 2.2.

With so many gamma rays it is possible to choose many conditions for discrimination within the spectrum without impairing the experimental results in any way. Often the reverse is true, and the analyst is restricted in his technique by difficulties of counting, for example, low energy X-rays as his only radiation. The extra licence allowed in the present case was welcomed and every advantage was taken of it.

Table 2.2

Peaks Corresponding to Main Gamma Rays from Chosen Nuclides

	Energy MeV
^{140}La	0.33, 0.49, 0.82, 0.89, 1.60, 2.54
^{141}Ce	0.145
^{144}Ce	0.034, 0.042, 0.054, 0.081, 0.10, 0.134
^{142}Pr	1.57
^{147}Nd	0.092, 0.53
^{153}Gd	0.070, 0.097, 0.103
^{160}Tb	0.045, 0.087, 0.216, 0.299
^{170}Tm	0.084
^{169}Yb	Many 0.008-0.31
^{175}Yb	0.025, 0.053, 0.114, 0.283, 0.396

The sensitivity of any analysis is that of the instrument on which it is made. In this case, radioactive counting, the limit of sensitivity is set by the difference between background and sample. High sensitivity was always sought and so discriminator bias was set low, at about 20-50 KeV, to count all the radiation except the characteristic K X-rays of the decay products. These are often subject to self shielding and absorption problems. However, in the case of low count rates, discriminator bias could be adjusted to give a suitably low background. These settings are rapidly found using the cathode ray tube display of the Laben 100, or 400. Bias voltages, being characteristic of individual instruments, will not normally be quoted when all the gamma radiation is counted as described above. When selected peaks are counted, the energies will be indicated.

In all experiments the counting was comparative. That is, the object was always to determine a distribution or percentage extraction, etc. Whenever absolute concentrations were required, they could be obtained by reference to a standard labelled solution counted at the same time, under identical conditions.

When data had to be transferred from one experiment to another, or one instrument to another, a normalising standard was always counted. This type of experiment was not often used as there are always dangers in such work arising from losses due to hydrolysis or adsorption. Both occur in experiments employing trace rare earths and preclude the use of near neutral solutions for long periods of time.

2.5 Other Instruments in Regular Use Throughout the Work

pH meter E.I.L. model 23A

Spectrophotometer Unicam model S.P. 600.

2.6 Experimental

2(i) Determination of Dead Time of R.E. 9000 Series Counter

Solutions: ^{160}Terbium solution.

Method. The terbium solution was diluted x 2 several times, so as to prepare a series of labelled samples whose concentration in relation to the first sample was known.

A 5 ml aliquot of each was counted under identical conditions and the activity recorded. The specific activity was calculated using that metal present in the 5 ml of most concentrated solution as the unit weight. The dead time was calculated as described in 2.3 from a plot of observed activity versus specific activity.

Results Table 2.3

Determination of Dead Time

	Set 1		Set 2	
Dilution	Observed activity counts.s^{-1}	Specific activity	Observed activity counts.s^{-1}	Specific activity
1	2486	2486	4049	4049
2	1420	2840	2475	4950
4	782	3128	1429	5716
8	395	3160	772	6170
16	214	3427	415	6640
32			222	7100

Dead Time Set 1 97 μs

Dead Time Set 2 101 μs

A table of corrections was prepared based for ease of calculation on a dead time of 100 μs. The result is shown conveniently on a parallel scale or graph such as Fig. 2.1.

2(ii) The Determination of Salicylate Colorimetrically with Ferric Iron, by S.P. 600 Spectrophotometer. Preparation of a Calibration Graph of Optical Density Versus Salicylate Concentration.

Solutions: 10^{-2} M Ferric chloride

1% Ferric chloride

10^{-3} M Sodium salicylate

1:10 Acetic acid.

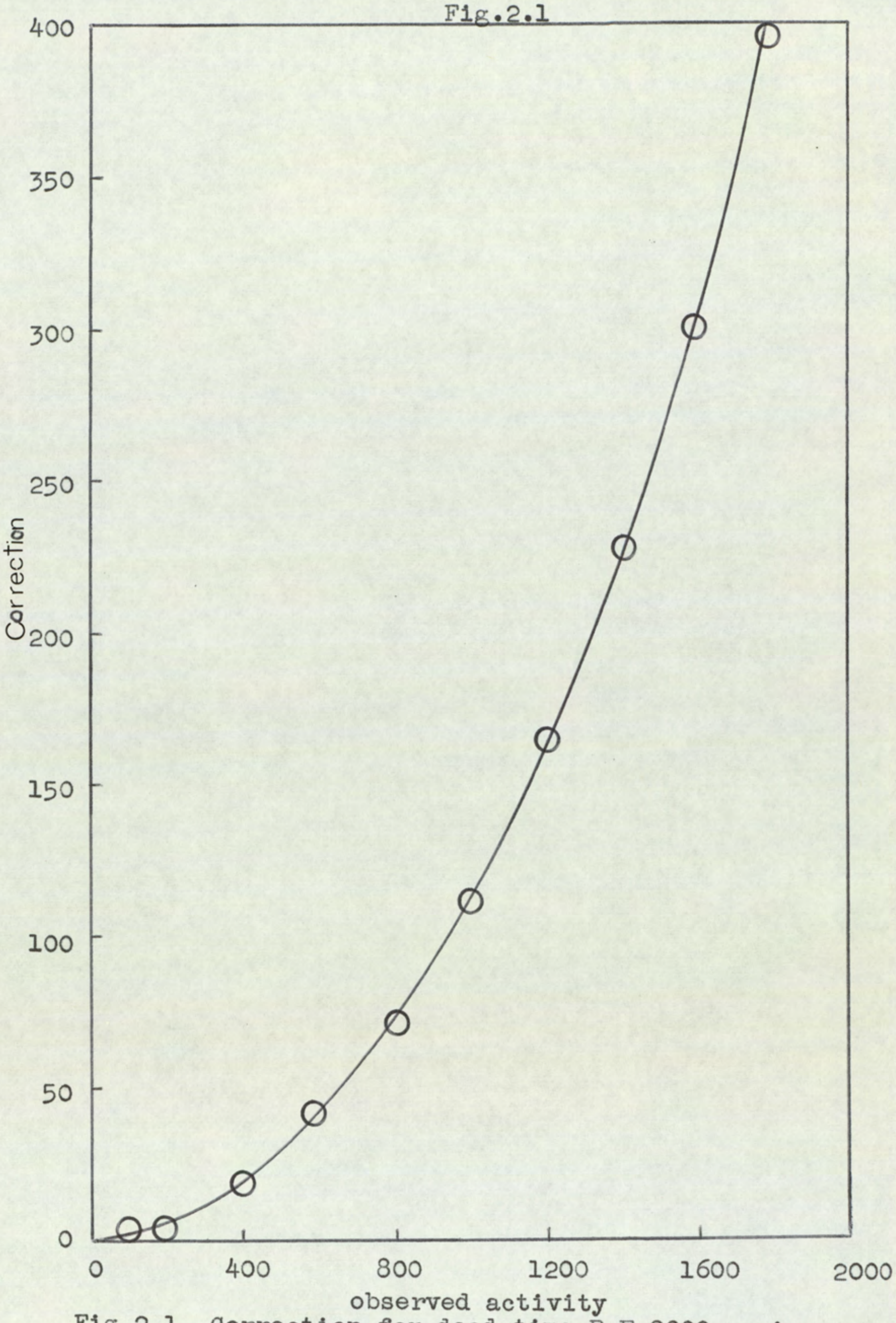


Fig.2.1. Correction for dead time, R.E.9000 series.

Method. A calibration curve was prepared according to the method of Snell.[7] Varying volumes of standard 10^{-3} M sodium salicylate were added to 0.2 ml 1:10 acetic acid and 0.3 ml freshly prepared 1% ferric chloride. The solution was made up to 10 ml and the optical density measured at 520 nm in a 2 mm cell against a reagent blank. A graph was drawn to show optical density versus concentration.

The reagent has no absorbance at 520 nm, and the acetic acid was also found to be unnecessary for the colour development. Future calibration curves were, therefore, prepared by simply adding 10^{-2} M ferric chloride to the salicylate so that the final concentration was 10^{-4}-5×10^{-4} M salicylate, and 2×10^{-3} M ferric iron. The Beer-Lambert law is obeyed to high optical densities and, therefore, 1 cm cells were used, so that 5×10^{-4} M salicylate corresponded to an optical density of 0.805.

The calibration curve is indicated in Fig. 2.2 and Table 2.4.

Table 2.4

Calibration Curve for the Determination of Salicylate with Ferric Iron

Molarity Salicylate $\times 10^4$	OD (1 cm)
1.0	0.160
2.0	0.325
3.0	0.475
4.0	0.640
5.0	0.805

Fig.2.2

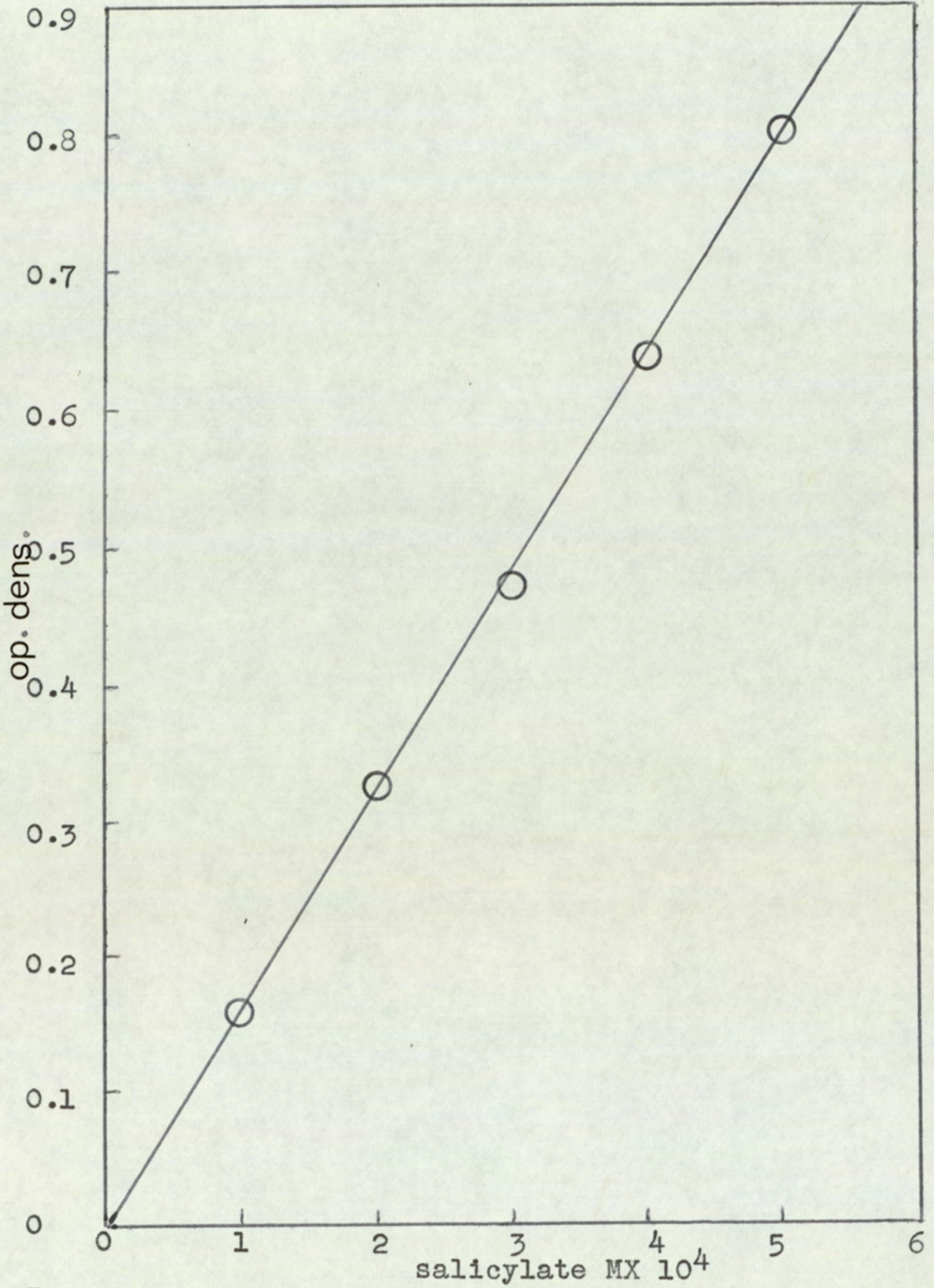


Fig.2.2. Calibration curve for the determination of salicylate with ferric iron.

As a further check, throughout the course of the work, a single standard concentration was usually included in any group of unknown samples.

CHAPTER 3

Aspects of Extraction Analysis using Substoichiometry as a Reaction Step in the Aqueous Phase

This chapter forms the basis of a publication by G. B. Briscoe and A. Dodson. Talanta 14, 1051, 1967.

3.1 Introduction

From Chapter 1 of this thesis, it will be realised that the majority of work completed to date on substoichiometry, and indeed aspirations for the future of the technique, centre around solvent extraction of metal chelates. The immediate limitation imposed by the theory is the need for a strong readily extractable chelate. Such species are formed generally with those cations of high valency where the chelation not only serves to neutralise the electronic charge but also saturate the co-ordination requirements of the metal.

With the rare earths this is often not the case. The most widely used solvent extraction procedures for rare earths employ polar solvents and ion association complexes. This is taken further nowadays with the increasing use of so called liquid ion exchange systems. These require special treatment in the context of the present work and are discussed in Chapters 4 and 5.

One would expect rare earths to be extracted by those chelating agents having -OH as the reacting group and this is the case. Acetylacetone and substituted acetylacetones are useful extractants. Thenoyltrifluoroacetone is popular, being more efficient than acetylacetone itself. Some extraction constants have been determined and are summarised in Table 3.1, which is taken in the main from the monograph 'Radiochemistry of the Rare Earths, Scandium, Yttrium and Actinium'.[4] The rare earths extract between about pH 3.5-4.5, varying with reagent concentration and metal, etc., but clearly are of no use in direct substoichiometry which would demand a threshold pH greater than the stability of the reagent will allow.

Thus for gadolinium extraction, using an equal volume of 10^{-5} M reagent and supposing 50% substoichiometry, the threshold pH must be greater than 10.3, even assuming the reagent was not dissociated. At this pH the reagent decomposes to trifluoroacetic acid and acetylthiophene.

Similar difficulties are encountered with, for example, 8-hydroxyquinoline and cupferron, where solubility problems add further limitations. Consequently the search for substoichiometric procedures must be taken into other fields.

Discounting less popular techniques such as substoichiometric precipitation of electrophoresis, etc., the obvious choice is to use ion exchange resins as proposed by the original authors[8] early in the development of the technique. This has been investigated and is reported in Chapter 6.

This present chapter deals with a similar idea in which the substoichiometric step is carried out in the aqueous phase by EDTA, followed by separation of the unreacted metal by chelate extraction with, in this case, thenoyltrifluoroacetone in xylene or toluene.

Unlike the direct solvent extraction, optimum conditions have to be calculated for the equilibrium condition of two reactions, the complexation and the separation. Further, the EDTA reaction requires to be buffered and consideration must be given to possible interference from this source.

An equilibrium theory based on the mass action law was developed to show how these optimum conditions can be achieved. The accompanying laboratory work was conducted along the lines of a model analytical method for rare earths by isotope dilution analysis, although it is realised that EDTA is completely non-specific and the method somewhat unrealistic unless preceded by a suitable preliminary separation based upon the nature of the other metals present.

3.2 Theory

There are two reactions to consider:

(1) Rare earth (M) + thenoyltrifluoroacetone (HA)

(2) Rare earth (M) + EDTA (Y)

$$M + 3HA_o \longrightarrow MA_{3\,o} + 3H \qquad (1)$$

$$M + Y \longrightarrow MY \qquad (2)$$

Electrical charges are again omitted for simplicity in writing. The subscript o denotes solution in organic solvent immiscible with water.

This theory makes use of the idea of conditional equilibrium constants similar to those proposed by Ringbom.[9] Accounts of these are available in many present day undergraduate texts, but since it is not always made obvious how easy it is to apply the ideas to solvent extraction and ion exchange as well as complexometry, it is worthwhile setting out the fundamental concepts in detail for this general case. Repeated reference will be made to conditional constants in this text.

The equilibrium concentration, $[X]$, of species X can be replaced in equilibrium equations by $[X']$, the total concentration of X present in all its forms. Equations become modified by an α coefficient

$$\alpha = \frac{[X']}{[X]} \tag{3}$$

To return to equations (1) and (2), the equilibrium constants are the extraction constant K_1,

where
$$K_1 = \frac{[MA_3]_o [H]^3}{[M]\,[HA]_o^3} \tag{4}$$

and the stability constant K_2,

where
$$K_2 = \frac{[MY]}{[M]\,[Y]} \tag{5}$$

Now instead of K_2 we write K_3

$$K_3 = \frac{[MY]}{[M]\,[Y']} \tag{6}$$

where $[Y'] = [H_4Y] + [H_3Y] + [H_2Y] + [HY] + [Y]$
for EDTA.

Thus
$$\alpha_{Y(H)} = \frac{[Y']}{[Y]}$$

$$K_2 = \frac{[MY]\,\alpha_{Y(H)}}{[M]\,[Y']} \tag{7}$$

Combining (4) and (7)

$$K_4 = \frac{K_1}{K_2} = \frac{[MA_3]_o[H]^3[Y']}{[MY]\;[HA]_o\alpha_{Y(H)}} \qquad (8)$$

This equation can represent the equilibrium condition for the substoichiometric separation which we require.

Consider the case of half the metal complexed with EDTA, i.e. so called 50% substoichiometry. When both phases have equal volume

$$[MY] = [MA_3]_o$$

and equation (8) simplifies to

$$K_4 = \frac{[H]^3[Y']}{[HA]_o^3\alpha_{Y(H)}} \qquad (9)$$

the equation is 'conditional' with respect to the EDTA, but still contains the expression $[HA]_o$. This can be calculated from the known total acid concentration added by the equation

$$\log [HA]_o = \log C_{HA} - \log \left[1 + p_{HA}^{-1}(1 + K_{HA}\ H^{-1}) \right]$$

but it is more consistent with the above equations to calculate a further α coefficient $\alpha_A = 1 + \frac{1}{p_{HA}} + \frac{K_{HA}}{p_{HA}[H]}$

$$= \frac{C_{HA}}{[HA]_o}$$

where C_{HA} is the sum of all concentrations of acid in both phases.

Fig.3.1

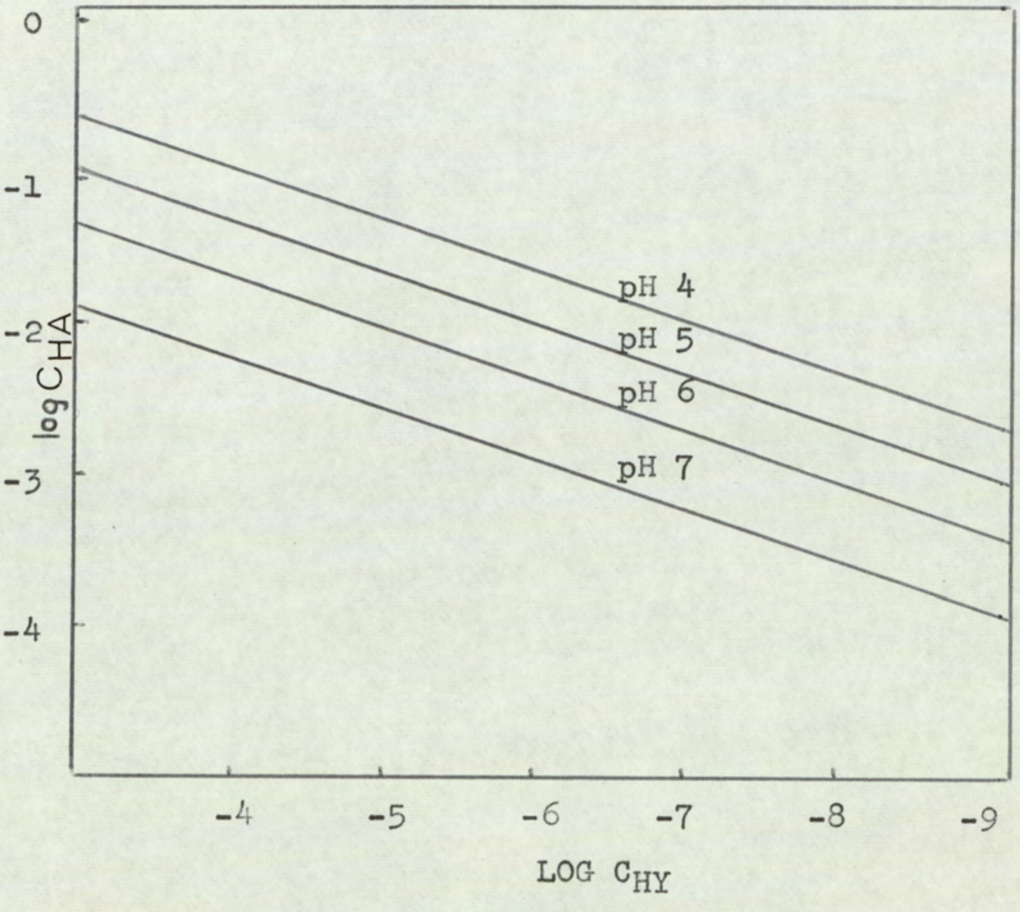


Fig.3.1. Influence of pH on the maximum permitted concentration of thenoyltrifluoroacetone which may be used to remove terbium from terbium-EDTA complex.

Thus equation (9) becomes

$$K_4 = \frac{[H]^3 [Y'] \alpha_A^3}{C_{HA}^3 \alpha_{Y(H)}} \qquad (10)$$

For successful substoichiometry, all the EDTA reagent must be consumed in the reaction with the metal. Practically this is considered true if $[Y'] < 0.001\, C_{HY}$, where C_{HY} is the concentration of EDTA that would be present if no reaction occurred.

Thus

$$K_4 = \frac{[H]^3 10^{-3} C_{HY} \alpha_A^3}{C_{HA}^3 \alpha_{Y(H)}} \qquad (11)$$

From this equation can be calculated a value C_{HA}, which represents the maximum concentration of HA_o which may be used to remove free metal from a solution in which a substoichiometric reaction with EDTA is taking place, without breaking down more than 0.1% of the EDTA complex. Provided $C_{HA} \gg [MA_3]$, the change in concentration will be negligible.

At constant pH, log C_{HA} plotted versus log C_{HY} will be linear and of slope $-\frac{1}{3}$. Such curves are easily calculated from available data, and are shown in Fig. 3.1. Only one metal, terbium, is shown, and the influence of pH is clearly illustrated.

A second graph, Fig. 3.2, shows how the lines are affected by the range of K_1/K_2 values throughout the metal series. The equilibrium constants for these reactions vary throughout the series in common with many rare earth properties. There are, however, several distinct ways in which the constants vary with atomic number,[2] and the trends are different in these two cases

Fig.3.2

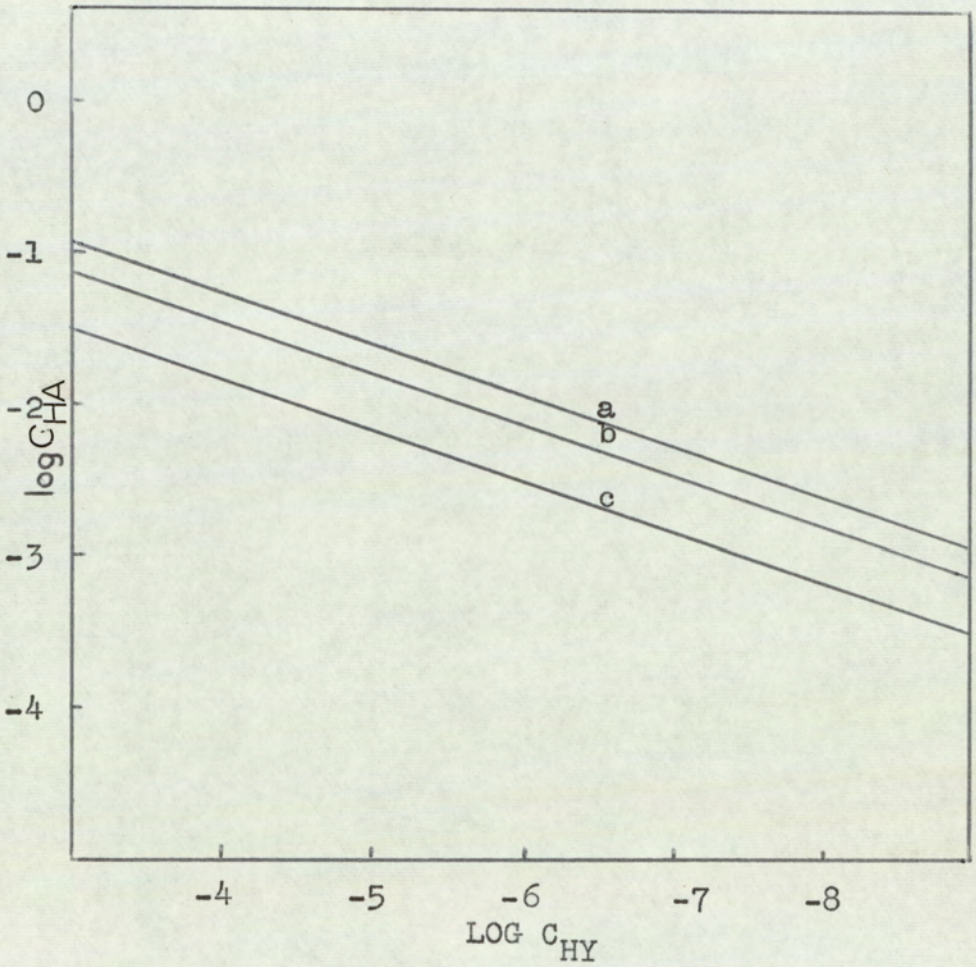


Fig.3.2. Influence of rare earth metal at pH 6 on the maximum permitted concentration of thenoyltrifluoroacetone used to remove free metal from the metal-EDTA complex.
a) For lutetium. b) For lanthanum. c) For gadolinium.

resulting in a maximum value of K_4 for gadolinium, at the centre of the series. The effect of this is seen in Fig. 3.2 and Table 3.1. In these calculations, K_1 is taken from results of Bronaugh and Suttle already cited[4] and K_2 from the appendix in Ringbom's book.[9] No account has been taken of ionic strength of the solution. There will be some effect, but for the purpose of our illustrations it is not important, nor indeed for our model analysis which is conducted at high ionic strength and for which these working values of K_1 and K_2 predict results quite satisfactorily.

Table 3.1

Constants for the Reaction of EDTA and Thenoyltrifluoroacetone with Rare Earths From Refs 4 and 9

Metal	$-\log K_1$	$\log K_2$	$-\log K_1/K_2$
La	9.89	15.50	25.40
Ce	8.82	15.98	24.80
Pr	8.23	16.40	24.63
Nd	7.96	16.61	24.57
Sm	7.06	17.14	24.20
Eu	7.02	17.35	24.37
Gd	6.96	17.37	24.33
Tb	6.89	17.90	24.79
Dy	6.64	18.30	24.94
Ho	6.42	18.74	25.16
Tm	6.34	19.32	25.66
Yb	6.11	19.51	25.62
Lu	6.17	19.83	26.00

The minimum excess concentration of HA_o can be calculated from equation (4), assuming that extraction is complete if $q > 1000$. This concentration is also best illustrated in graph form and Fig. 3.3 illustrates the case for terbium.

It is now possible to combine the information available concerning the maximum permissible and minimum required HA_o concentration. This can also be shown graphically, Fig. 3.4, and the result indicates a working range of HA_o concentration, at any pH, which can be used to remove excess of metal from the solution in which substoichiometry has taken place without affecting the EDTA complex. Calculations are in the experimental section.

This theory will hold provided that equations (4) and (8) are known to be obeyed in the concentration range under consideration.

The first can be verified by measuring q, the distribution ratio at constant pH, for varying HA_o concentration, see 3(v) and Table 3.8. A similar experiment can be used for equation (8), 3(vi). Consider the case when all of the EDTA present is just sufficient to complex all of the metal, but the HA_o concentration is sufficient to partly break down this complex at equilibrium. Then any free EDTA or MA_3 will be the result of this breakdown. Hence

$$[MA_3]_o = [MY] \text{ if } V_o = V_a$$

Rearranging equation (8)

$$\frac{K_4 \alpha_{Y(H)}}{[H]^3} = \frac{[Y']^2}{C_{HY} - [Y'] \; [HA]_o^3}$$

Fig.3.3

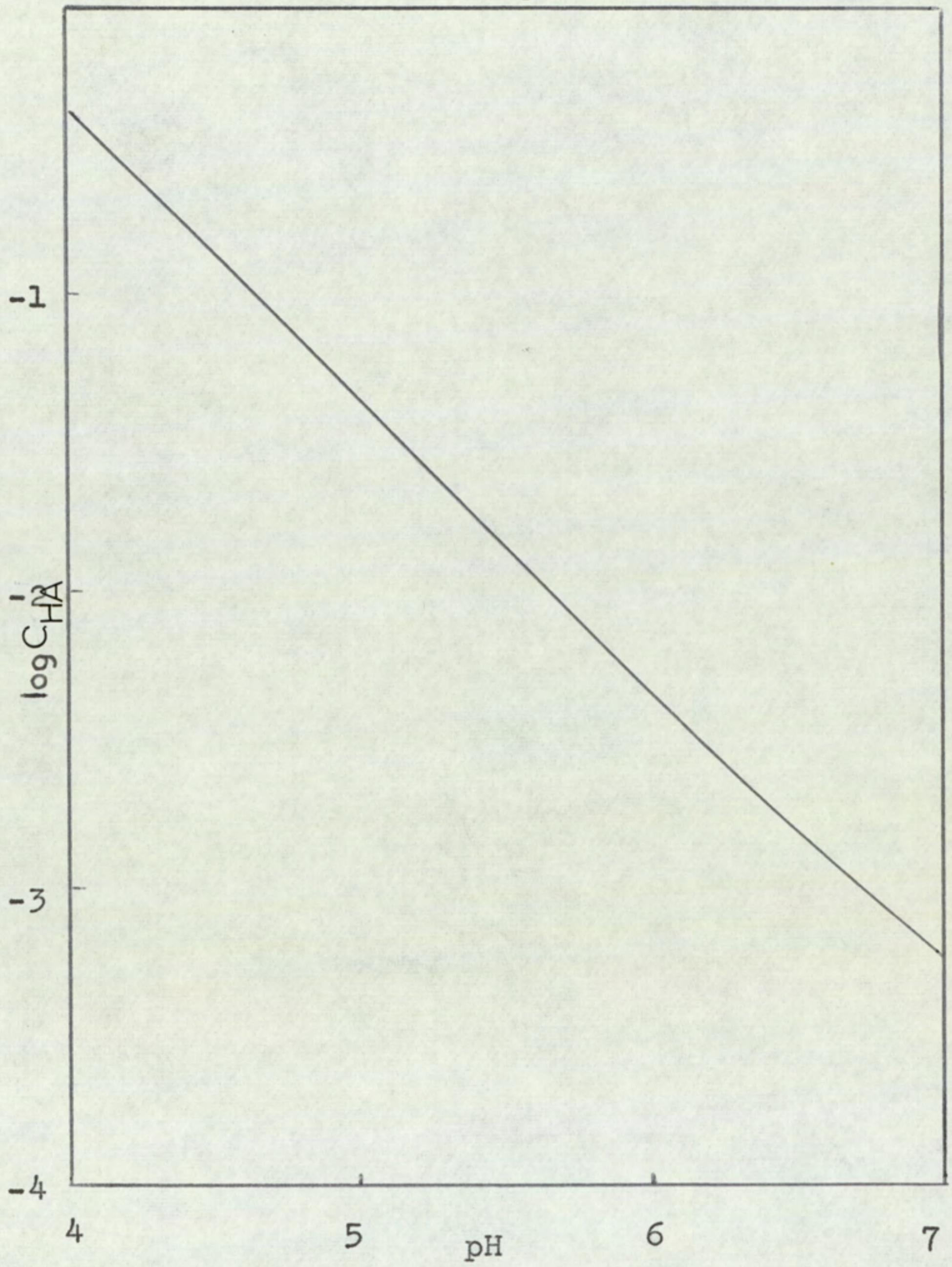


Fig.3.3. The minimum excess concentration of thenoyltrifluoroacetone required for the extraction of terbium at various pH values.

Hence $\log \frac{[Y']^2}{C_{HY} - [Y']}$ i.e. $\log \frac{[MA_3]^2}{[MY]}$ versus $[HA]_o$

should be linear and of slope 3.

Introducing the α_A term

$$\frac{K_4 \alpha_{Y(H)}}{[H]^3 \alpha_A^3} = \frac{[MA_3]_o^2}{[MY]\, C_{HA}^3} \qquad (12)$$

A typical result is shown in Fig. 3.5, from experiment 3(vi).

The equations presented in this section are based as stated on a condition of 50% substoichiometry. All concentrations calculated later in the chapter are also based on this figure. It is easily seen, however, that the degree of substoichiometry will affect the maximum value of the HA_o concentration. At only 10% substoichiometry $[MA_3]_o/[MY] = 9$, and all values calculated for HA_o concentration will be three times greater. Similarly, at $[MA_3]_o/[MY] = {}^1/9$, i.e. 90% substoichiometry, they will be lowered by a factor of three, which would for example make the separations much more difficult or impossible to achieve.

3.3 Choice of Buffer for this Reaction

The EDTA reactions described above need to be buffered, and, therefore, all of these reactions have been studied in buffered solution. The commonly used buffers for rare earth EDTA titration are acetate and more recently hexamine at about pH 5-6.

Hexamine is said to form complexes with rare earths[10] but these are weak and not thoroughly studied. Acetate on the other

Fig.3.4.

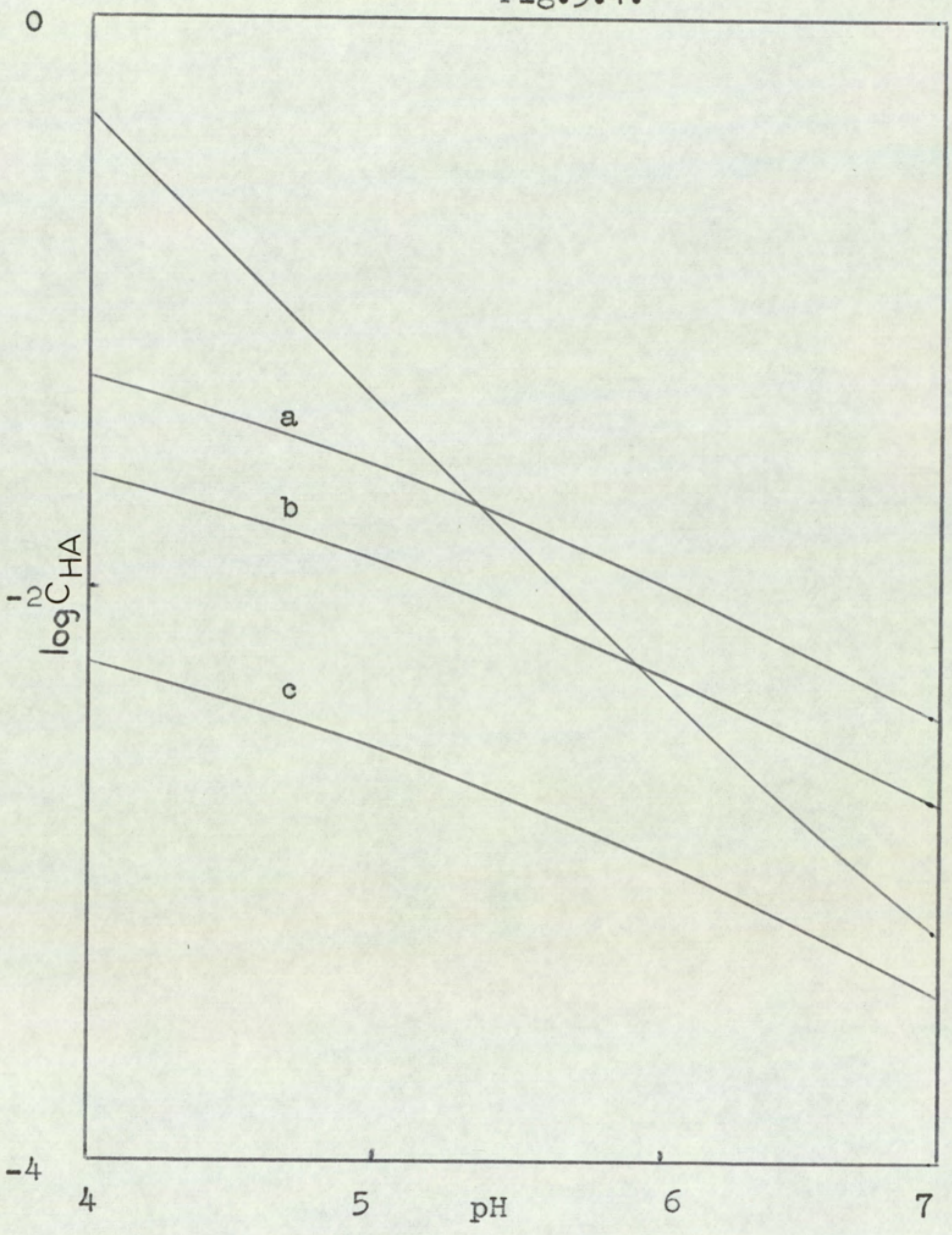


Fig.3.4. The working range of thenoyltrifluoroacetone concentration for the extraction of excess terbium from terbium-EDTA complex.
a) C_{HY} 10^{-5}M b) C_{HY} 10^{-6}M c) C_{HY} 10^{-8}M.

hand forms stable complexes of the type MA^{2+} MA_2^+, etc., and is likely to affect experimental q values in a far more serious way than, for instance, the ionic strength effect which has so far been ignored. Hexamine was, therefore, chosen as buffer for this study. It was adjusted to the correct pH with nitric acid. Only laboratory reagent grade hexamine was available, which is purported to contain traces of lead. The lead content was determined by extractive titration with dithizone and found to be present in concentration too low to affect either the theoretical verification or the model analysis. Whilst this extraction clearly indicates a means of purification, it was decided not to undertake the work unless interference became serious. Further study was made of this buffer system for ion exchange purposes and is reported in Chapter 6.

3.4 Time to Reach Equilibrium

Thenoyltrifluoroacetone (TTA) extracts rare earths very quickly.[4] This was confirmed using the hexamine buffer, quantitative extraction requiring less than 60 sec, 3(i) and Table 3.4. The reaction between metal EDTA complex in water and TTA in xylene was, however, very slow, even at pH 6 where there is considerable dissociation, 3(ii) and Tables 3.5 and 3.6. Equilibrium is virtually reached after a little over 1 h. Consequently reaction times of 2 h were chosen for the verification experiments.

Reaction equilibrium in the substoichiometric separation was reached as quickly as the direct extraction, under conditions where good substoichiometry was possible, 3(iv) and Table 3.7.

Fig.3.5

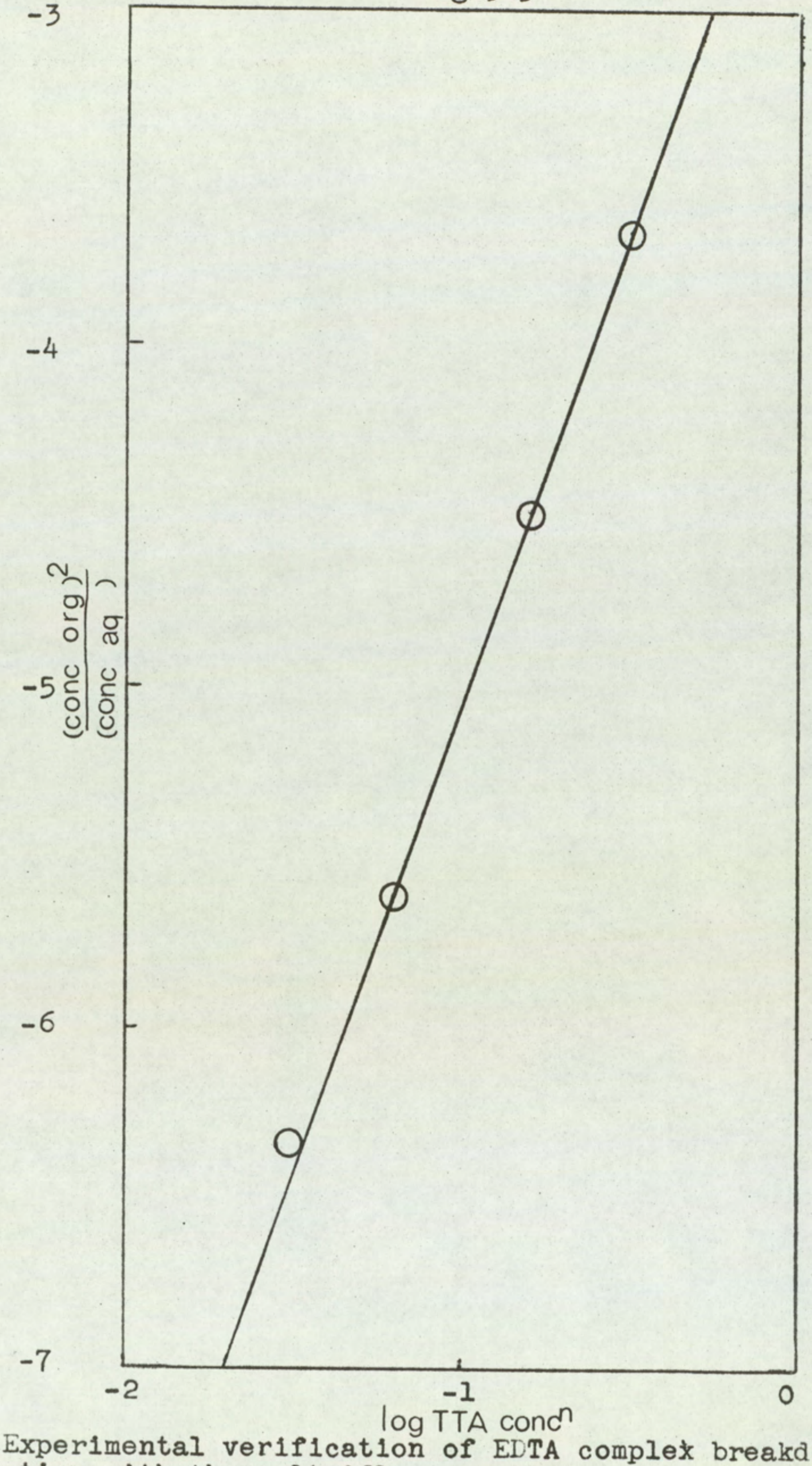


Fig 3.5.Experimental verification of EDTA complex breakdown on extraction with thenoyltrifluoroacetone.

3.5 A Consideration of Reagents Other Than EDTA and Thenoyltrifluoroacetone

The equilibrium equations set out above indicate that the factors affecting the choice of reagent are the stability constant of the aqueous complex, the extraction constant, and the pH.

(a) The Stability Constant

The stability constants of the polyaminocarboxylic acids vary considerably for any one rare earth. However, the acid dissociation constants also vary, and the net result is that the conditional stability constants are very similar to each other except at high pH. Only minimal advantage is, therefore, gained by using these other complexes (see Table 3.2). Those of DTPA afford the best alternative, but are less fully understood.

Table 3.2

Conditional Stability Constants of Some Rare Earth Complexes with Polyaminocarboxylic Acids at pH 5

Calculated from Figures given by Ringbom[9]

	NTA		EDTA		HEDTA		EGTA		DTPA	
log $\alpha_{Y(H)}$	4.8		6.6		5.3		8.5		9.3	
	log K	log K/α	log K	log K/α	log K	log K/α	log K	log K/α	log K	log K/α
La	10.4	5.6	15.5	8.9	13.8	7.5	15.5	7.0	19.4	10.1
Ce	10.8	6.0	16.0	9.4	14.5	9.2	15.7	7.2	19.4	10.1
Gd	11.5	5.7	17.4	10.8	15.4	10.1	16.9	8.4	22.5	13.2
Tb	11.6	6.8	17.9	11.3	15.5	10.2	17.3	8.8	22.7	13.4
Yb	12.4	7.6	19.5	12.9	16.2	10.9	17.8	9.3	22.6	13.3

(b) The Extraction Constant

The minimum concentration of HA is dependent on the one third power of the extraction constant. Thus for extractants having equal dissociation constant and partition coefficient values, a 1000 fold change in the extraction constant will be required to bring about a 10 fold change in the value of $[HA]_o$. The value of $K_4\alpha_{Y(H)}/\alpha_A^3$ is seen, therefore, to be an involved relationship and the effects of changing from one reagent system to another cannot easily be generalised. In a series such as the acetylacetone homologues, most of the dissociation constants are available and all are similar. The extraction of metals has, however, received a more qualitative treatment and only a few constants are known. Acetylacetone itself is, of course, a liquid and often used undiluted.

3.6 The Case of Cerium

Early work with this system was conducted using labelled cerium metal. This was abandoned because of suspected oxidation at the pH value chosen, which is not typical of the group. Reproducibility curves were prepared at pH 6 in hexamine buffer. The organic phases were highly coloured (yellow) in metal concentrations of 10^{-3} M, but the resulting reproducibility curves did not show signs of this complex breakdown even in TTA solution several times stronger than that predicted as permissible from the theory. This has not been investigated further at this stage.

3.7 Reproducibility Curves (Experimental Section 3(viii))

A graph showing the amount of metal separated in substoichiometry against the total concentration present in the system, has been called a reproducibility curve. Such curves are commonly used to indicate the success of the separation. Correct substoichiometry gives a horizontal line when the metal is in excess. Reproducibility curves were prepared in the present study using EDTA as reagent and usually terbium as the metal. Fig. 3.6 shows the type of graph obtained when EDTA is 10^{-5} M. These conditions are suitable for substoichiometry. Fig. 3.7 shows the same experiments at greater dilution. Substoichiometric separation is not suitable under these conditions. The curves have the shape corresponding to breakdown of the EDTA complex as described above. It must be realised, however, that this is not the only explanation, since too low a concentration of HA would give a similar curve, also shown in Fig. 3.7. Further complications due to the non-specific nature of EDTA could also arise, as the concentration of metal falls, and that of any impurity becomes relatively larger. If there is a foreign metal present capable of complexing with EDTA, the amount reacted depends on the amount of rare earth present, and on the relative stability constants. Such behaviour would also be reflected in a sloping reproducibility curve, but provided the concentration of metal sought was approximately known, and the standard chosen accordingly, the resulting comparison could possibly be subject to only small errors.

The theory shows clearly that, as the concentration falls, the working range of extractant concentration becomes very small

Fig.3.6

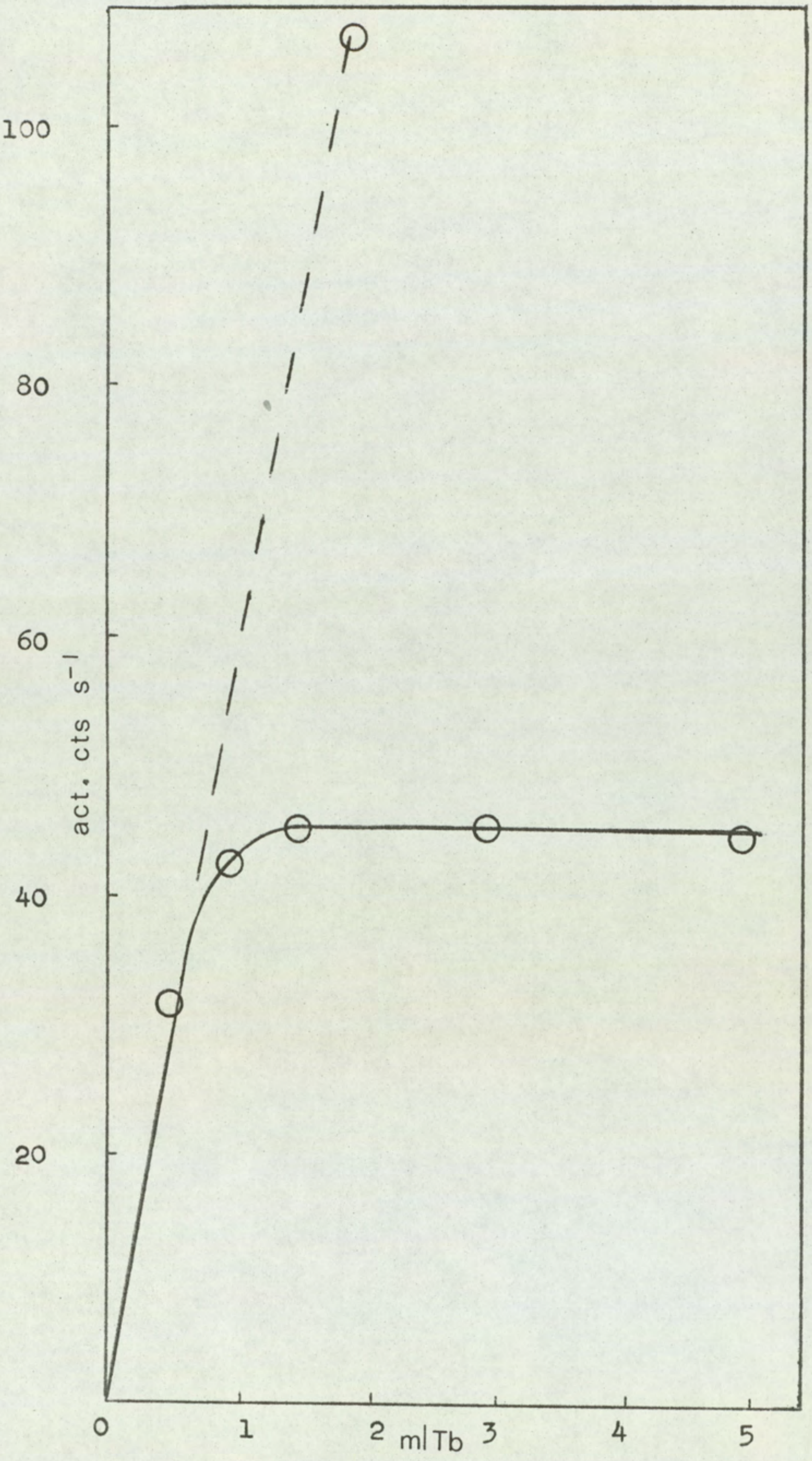


Fig.3.6. Reproducibility of substoichiometry.
Reproducibility curve for the substoichiometric reaction of terbium with EDTA.

at workable pH values, and the required equilibrium becomes more difficult and finally impossible to achieve. This is a major limitation of the technique as an analytical method. In such low concentration, K_4 values need to be known more accurately and an important advantage of substoichiometry, namely simplicity, is lost.

Preliminary extraction overcomes many of the interference difficulties and could be used prior to this stage.

None of the present work indicated that the reaction between rare earth metal and EDTA was slow. Nevertheless, there is doubt as to the speed of these reactions and the possibility of the EDTA reaction not achieving equilibrium needs to be considered. It could, however, only be improved by heating and this is not advised. Little difficulty due to hydrolysis occurred in the hexamine buffer even with terbium and ytterbium at pH 6. However, loss by hydrolysis or adsorption at these dilutions was a constant pitfall throughout all this research and was generally worsened by the action of heat.

It is worthwhile remembering at this stage, in the light of the theory presented, that it is the concentration of C_{HY} (EDTA) that influences the working range of HA_o concentration and, therefore, a slight degree of extra flexibility is gained by altering the degree of substoichiometry, as discussed in 3.3, where this is possible.

The precision of this process was determined at the concentration represented in Fig. 3.6 and the standard deviation found to be 1.95%, 3(vii). This is in accordance with the analysis of the

Fig.3.7

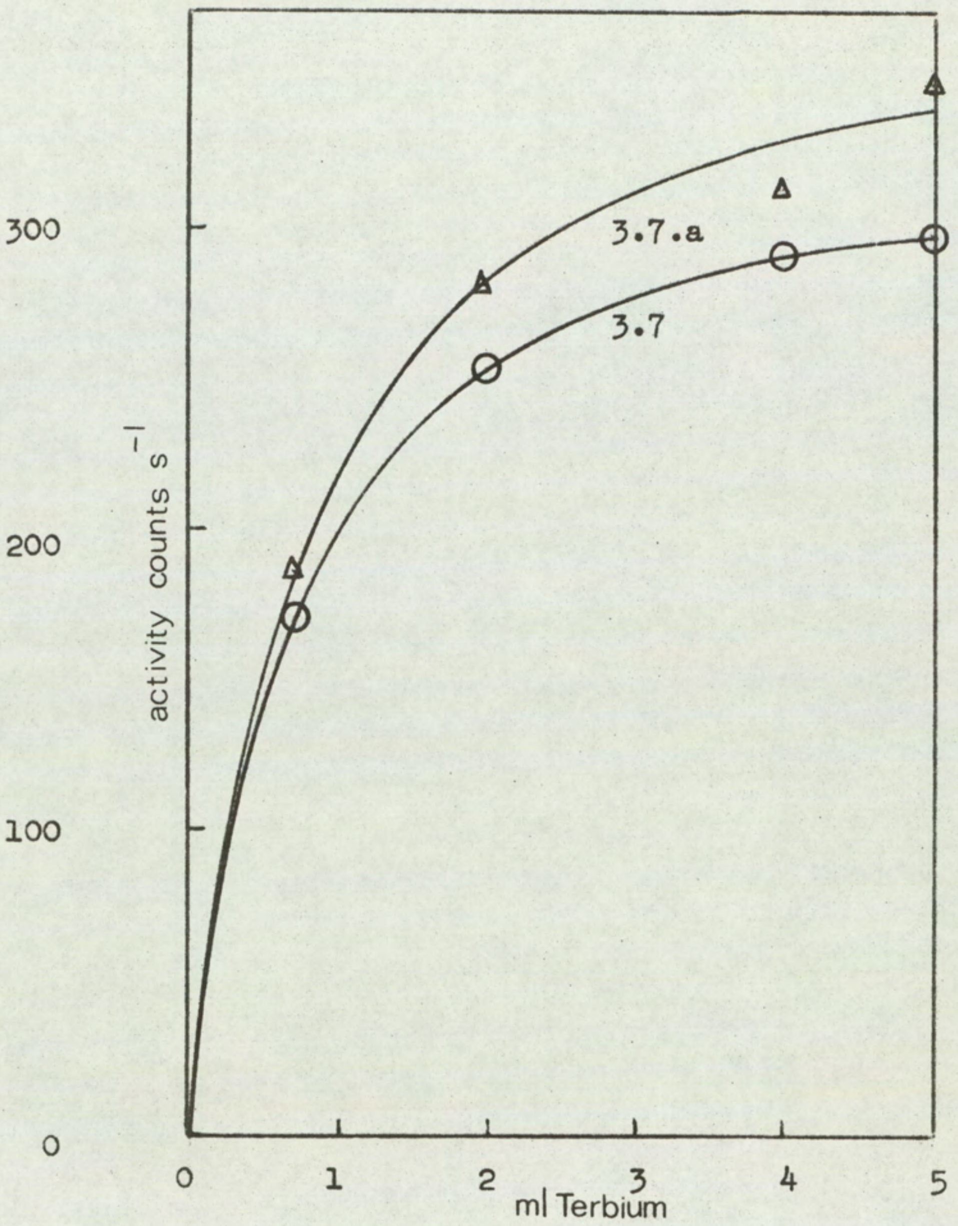


Fig.3.7. Examples of unsatisfactory reproducibility curves.

3.7 Extractant too concentrated.

3.7.a. Extractant too dilute.

test solutions presented below and compares favourably with other substoichiometric methods for isotope dilution analysis at this concentration.

All of these points of discussion lead to conclusions similar to those drawn by the original authors of substoichiometry, namely that production of a good reproducibility curve is justification for the comparisons required in the isotope dilution analysis. If the sloping part of the curve has the correct slope, and passes through the known point, representing activity in excess reagent, then the EDTA complex is being completely retained in the aqueous phase. If the plateau of the curve is horizontal, then a constant amount is retained when the metal is in excess and substoichiometry is working satisfactorily.

3.8 Model Analyses

To complete the development of the method, a number of test solutions were analysed by isotope dilution. The heavy metals, terbium and ytterbium, were used, although active ytterbium was not available and ^{170}thulium was used to label this metal. These metals both have the same K_4 value. Pure inactive thulium was not available.

Both 'standard' and 'sample' solutions were prepared by diluting analysed concentrated solutions of the metals. The ytterbium solution contained 38 μg/ml and the terbium solution 17 μg/ml. The concentration of EDTA used for the substoichiometry was 10^{-5} M, and each test solution contained 2 ml of standard plus 2 ml of sample where appropriate in a total volume of 10 ml. The TTA solution concentration was calculated from the theory. After extraction, aliquots were counted and the metal concentration estimated using the substoichiometric formula

$$x_{\text{sample}} = x_{\text{standard}} \left(\frac{\text{activity standard}}{\text{activity sample}} - 1\right)$$

Results are given in Table 3.3

Table 3.3

Model Analyses of Heavy Rare Earth Metals

Yb			Tb		
Taken $\mu g\ ml^{-1}$	Found $\mu g\ ml^{-1}$	Stand. Dev. $\mu g\ ml^{-1}$	Taken $\mu g\ ml^{-1}$	Found $\mu g\ ml^{-1}$	Stand. Dev. $\mu g\ ml^{-1}$
38.14	37.85	0.51	17.10	16.82	0.55
	38.77			17.75	
	38.46			17.42	
	38.81			17.52	
	37.85			16.87	
	38.46			16.26	
	37.33				
	37.96				
	38.66				

It can be concluded from these results that the substoichiometric isotope dilution analysis is satisfactory, and can be applied as the basis of a method to determine rare earths at concentrations of about 10^{-5} M. The precision as indicated here is tolerable, but depends markedly on the extractions of both sample and standard. Thus for a single sample, as many standard extractions as possible should be performed.

3.9 Experimental

General

Experimental work relevant to the discussion is presented here, together with calculations required for the preparation of figures, for the text, from literature data.

It will be realised that much of the extraction work was repetitive and could possibly be generalised. Nevertheless, key experiments have been described fully each time, so that maximum value can be realised from the cross references between the sections of the discussion, e.g. 3.4, and experimental, e.g. 3(i).

Results are presented in the form of small tables within each experiment. In the cases where the cross references are likely to be used, results are presented in a more formal manner and the table identified in the normal numbering sequence.

The order of experiments is somewhat different to the discussion sections to which they refer. Verification of theory, presented first in the discussion, logically follows experiments to ascertain time for equilibrium to be reached, etc. The calculations already mentioned are given at the start.

Calculations Required for the Preparation of Figs. 3.1, 3.2, 3.3, 3.4

Calculation of α_A for Thenoyltrifluoroacetone, and the Excess Concentration Required for the Extraction of Terbium Ions into Xylene

Constants used: partition coefficient into xylene 33.2

dissociation constant $10^{-6.23}$

$$\alpha_A = 1 + \frac{1}{33.2} + \frac{10^{-6.23}}{33.2\,[H]}$$

pH	α_A	C_{HY} based on Equation (4)
4	1.03	$10^{-0.3}$
5	1.03	$10^{-1.3}$
6	1.05	$10^{-2.3}$
7	1.20	$10^{-3.2}$
8	2.80	$10^{-3.85}$
9	Reagent decomposes	

Maximum Permitted Values of Thenoyltrifluoroacetone Concentration, During Substoichiometry with Terbium and EDTA, i.e. C_{HA} (for TTA), C_{HY} (for EDTA)

Calculated from

$$K_4 = \frac{[H]^3 \cdot 10^{-3} \cdot C_{HY} \cdot \alpha_A^3}{C_{HA}^3 \cdot \alpha_{Y(H)}} \qquad (10)$$

$K_4 = 10^{-24.8}$

α_A as above

$\alpha_{Y(H)}$ from reference 9, as given.

As these graphs are parallel and linear for C_{HY} versus C_{HA}, only selected points are given here.

pH	$\alpha_{Y(H)}$	C_{HY}	C_{HA}
4	$10^{8.6}$	10^{-4}	$10^{-0.93}$
		10^{-5}	$10^{-1.27}$
		10^{-6}	$10^{-1.60}$
5	$10^{6.6}$	10^{-3}	$10^{-0.93}$
		10^{-4}	$10^{-1.27}$
		10^{-5}	$10^{-1.60}$
6	$10^{4.8}$	10^{-4}	$10^{-1.60}$
		10^{-5}	$10^{-2.00}$
		10^{-6}	$10^{-2.43}$
7	$10^{3.4}$	10^{-3}	$10^{-1.90}$
		10^{-7}	$10^{-3.25}$

For other metals as in Fig. 3.2, these results are modified according to the relative values of the known constants as in Table 3.1.

3(i) Time to Reach Equilibrium in the Reaction Between Rare Earth (Terbium) and Thenoyltrifluoroacetone (TTA) in Xylene (From Section 3.4)

Solutions: 10^{-4} M terbium in 10^{-1} M $HClO_4$ was neutralised to pH 3 with NaOH solution

1 M hexamine buffer pH 6

10^{-2} M TTA in xylene.

Method. A mixture of 5 ml of metal and 5 ml of buffer was shaken for varying times at room temperature, with 10 ml of TTA solution. The phases were separated and centrifuged to remove traces of other layer. A 5 ml aliquot of each layer was counted.

Results

Table 3.4

Time to Reach Equilibrium

Time of shaking		Total activity counts s^{-1}	Organic phase activity counts s^{-1}	% Extraction
sec	15	1957	1832	93.7
	30	1972	1964	99.5
	60	1953	1956	99.9
min	3	1972	1970	99.9
	5	3302	3300	99.9
	15	3434	3430	99.9
	30	3472	3470	99.9

Conclusion. Extraction is complete within one minute.

3(ii) Time to Reach Extraction Equilibrium in the Reaction Between Rare Earth (Terbium) EDTA Complex and Thenoyltrifluoroacetone (TTA) in Xylene

Solutions: 1.13×10^{-3} M terbium solution in HNO_3 plus
2.84 ml of 10^{-2} M EDTA, neutralised, and made
to 50 ml

1 M hexamine buffer pH 6

5×10^{-2} TTA in xylene.

Method. Equal volumes of each solution were mixed and 10 ml of mixture shaken for varying times at room temperature with 10 ml of 5×10^{-2} M TTA in xylene. After separation and centrifuging the activity of 5 ml of each phase was counted and the percentage of the total activity present in the organic phase was determined. The pH of the aqueous phases was measured.

The experiment was repeated using completely fresh solutions and the two sets of results combined.

Results

Table 3.5

The Extraction of Terbium-EDTA Complex with TTA

Time of extraction min	Total activity counts s^{-1}	Activity in organic phase counts s^{-1}	% extracted	pH
1	1445	52.2	3.61	5.9
5	1418	60.6	4.27	5.9
10	1449	69.4	4.79	5.9
15	1438	70.3	4.92	5.9
20	1418	87.3	6.16	5.9
30	1438	87.8	6.05	5.9
40	1450	94.2	6.15	5.9
60	1435	101.3	7.05	5.9
120	1450	108.7	7.15	

Conclusion. The extraction tends toward equilibrium at extraction times greater than 1 h.

3(iii) A variation of this experiment at lower pH, and using toluene, gave similar results.

Method. A solution of 10^{-3} M terbium was buffered to pH 4.5 by adding solid hexamine. It was then titrated with 10^{-2} M EDTA. Equal volumes of the neutralised solution and TTA in toluene were shaken together. The layers were separated by centrifuging. A 2 ml aliquot of each phase was counted and the pH of aqueous phases measured. Again the percentage metal in the organic layer was calculated. The results are given in Table 3.6.

Results

Table 3.6

The Extraction of Terbium-EDTA Complex with TTA in Toluene

Time min	Organic phase counts s^{-1}	Aqueous phase counts s^{-1}	% extracted	pH
10	2505	751.8	23.0	4.55
20	2096	1065	33.6	4.55
30	2094	1248	37.5	4.55
40	2044	1446	41.6	4.55

These results fit an identically shaped curve to those of Expt. 3(ii).

Conclusion. Reaction just begins to approach equilibrium in 1 h.

3(iv) Time to Reach Equilibrium under Conditions of Substoichiometry

Solutions: 10^{-4} M terbium solution partly neutralised with NaOH

10^{-4} M EDTA solution

1 M hexamine buffer pH 6

6×10^{-3} M TTA in xylene.

Method. Aqueous phase mixtures consisting of 2 ml terbium, 1 ml EDTA, and 10 ml of buffer were prepared. Each aqueous phase was extracted with 10 ml of 6×10^{-3} M TTA in xylene. The phases were centrifuged and separated, and 5 ml aliquots of each were counted. The results are tabulated in 3.7.

Results

Table 3.7

Time to Reach Equilibrium in Substoichiometry

Time min	Activity aqueous phase counts s^{-1}	Activity organic phase counts s^{-1}	% extracted
1	610.9	788.7	56.2
5	591.6	790.3	57.1
10	597.1	777.6	57.0
15	577.0	806.1	58.2

Conclusion. As expected, the extraction is completed in less than one minute.

3(v) The Variation of Extraction of Terbium at Constant pH with Varying Concentrations of TTA (From Section 3.2)

The reader will be aware that many experiments have been conducted from which these data could be compiled. Here is reported a single experiment in which reagent concentrations were maintained at little more than trace level so that the characteristics of the reaction are made clear.

Solutions: 10^{-5} M terbium solution in water
1 M hexamine buffer pH 6
10^{-4} to 10^{-3} M TTA in xylene.

Method. The terbium solution was buffered by adding 9 ml of hexamine reagent to 1 ml of metal solution. It was then shaken with 10 ml of TTA for 45 min. After separation and centrifuging, 5 ml aliquots were counted, and the pH of each aqueous phase measured. The distribution ratio was calculated and plotted versus $[HA]_o$ on logarithmic paper.

Results

Table 3.8

Variation of q with Extractant Concentration

M TTA	Activity organic phase counts s^{-1}	Activity aqueous phase counts s^{-1}	pH	q	log K
1.24×10^{-4}	8.0	335.1	6.0	0.024	-7.9
3.10×10^{-4}	63.5	271.5	6.0	0.234	-8.1
6.2×10^{-4}	226.5	115.6	6.0	1.96	-8.1
1.24×10^{-3}	346.9	23.9	6.0	14.5	-8.1

Calculations. Extraction constant K $= \dfrac{q[H]^3}{[HA]_o^{\ 3}}$

or at constant pH

$$\log q = \text{const.} + 3 \log [HA]_o$$

The value of K is calculable from the intercept, but is better obtained from each point. The graph is linear, and of slope 2.90. Assuming a slope of 3.0, the values of K are as shown in column 6 of the Table 3.8 above.

Conclusion. The reaction can be represented as $M^{3+} + 3TTA_o$, and the extraction constant is $10^{-8.1}$ under these conditions.

3(vi) Observations on the Equilibrium TTA_o + TbEDTA, that is the Breakdown of Terbium EDTA by TTA.

Solutions: An equivalent mixture of terbium and EDTA was prepared by mixing 25 ml of 1.13×10^{-3} M in dilute HNO_3 with 2.84 ml of 0.99×10^{-2} M EDTA, neutralising to pH 4.5 and making to 50 ml.

1 M hexamine buffer pH 6

TTA, varying concentrations, in xylene.

Method. The metal solutions were buffered with an equal volume of hexamine buffer. A number of 10 ml aliquots were taken. Each was shaken with 10 ml of organic phase for 2 h. After shaking, the phases were centrifuged and separated, and 5 ml aliquots were counted. The pH of each aqueous phase was measured.

A 'blank' extraction was performed for only 30 secs to see if any free metal was present which would extract in this short time.

The concentrations of metal in each phase were calculated by comparison of activity with that of the standard solution. To verify the equilibrium constant of the reaction, equation (8) of section 3.2, the ratio $\frac{(\text{concentration of organic phase})^2}{(\text{concentration of aqueous phase})}$ was calculated and plotted logarithmically versus the concentration of TTA in the organic phase. The results are given below and illustrated in Fig. 3.5.

Table 3.9

Results of Experiment 3(vi)

Activity organic phase counts s^{-1}	Activity aqueous phase counts s^{-1}	$\frac{(\text{conc. org.})^2}{(\text{conc. aq.})}$	M.TTA	$-\log K_4$*
67	1553	4.67×10^{-7}	0.0313	24.6
150	1508	2.41×10^{-6}	0.0626	24.8
483	1163	3.22×10^{-5}	0.157	24.9
983	703	2.23×10^{-4}	0.313	24.9
43	1370			

pH of solutions 5.95.

*Calculated for slope 3.0, $\alpha_A = 1.05$ at pH 6, $\alpha_{Y(\bar{H})} = 10^{4.8}$ at pH 6. Mean value 24.8.

Activity of standard solution 1.13×10^{-5} M, 6987 counts s^{-1}.

Theory value of -log K_4 from figures previously quoted, 24.8.

Value calculated from actual intercept of line slope 2.8, 25.0.

Results after Correcting Organic Phases for Blank Activity

Activity organic phase counts s^{-1}	Activity aqueous phase counts s^{-1}	$\frac{(\text{conc. org.})^2}{(\text{conc. aq.})}$	M.TTA	-log K_4
24	1553	5.96×10^{-8}	0.0313	28.5
107	1508	1.22×10^{-6}	0.0626	27.5
440	1163	2.69×10^{-5}	0.157	26.6
940	703	2.03×10^{-4}	0.313	26.0

Clearly these results do not represent the constant K_4, as above, but indicate a pre-equilibrium state of the extraction.

Conclusion. The 'blank' is suspected to be due to complex breakdown even in this short time of shaking. The results are in good agreement with those expected and verify the reactions to be as presumed in the theory.

3(vii) Precision of the Separation Process

The following experiment was conducted to test the reproducibility of the substoichiometric separation conducted in this way.

Solutions: The terbium solution was buffered and reacted with EDTA by making the following mixtures:

1 M hexamine buffer pH 6	7.5 ml
10^{-4} M terbium	1.5 ml
10^{-4} M EDTA	1.0 ml
Organic phase	
10^{-2} M TTA in xylene	10.0 ml

Method. Extraction was continued for 5 mins. After centrifuging and separating, both phases were filtered through dry filter paper in case they should be still contaminated with opposite phase. A 5 ml aliquot of aqueous phase was taken for counting. The mean activity was calculated and the precision expressed as the standard deviation about the mean.

Results

Activity counts s^{-1}	Activity counts s^{-1}
905.07	868.97
906.84	895.66
910.50	880.54
909.40	928.91
912.52	888.18
910.86	921.83

Mean Result 903.27

Standard Deviation about Mean 17.65 = 1.95%

Conclusion. The degree of reproducibility is indicated by a standard deviation of 1.95% of the mean, on twelve results.

3(viii) Reproducibility Curves to Test Substoichiometry (Section 3.7)

Solutions: 10^{-4} M terbium

10^{-4} M EDTA

1 M hexamine buffer pH 6

10^{-2} M TTA in xylene.

Method. The following metal solutions were prepared and mixed with 1.0 ml EDTA; x ml terbium plus 9 - x ml buffer, where x = 0.5, 1.0, 1.5, 3.0, 5.0.

Each was shaken for 5 min with 10^{-2} M TTA in xylene. After separation and filtering, 5 ml aliquots were counted. One point was repeated using more concentrated EDTA so that excess reagent was present, and thus no metal was extracted. This was also recorded in the reproducibility graph, indicating the correct slope of the first part.

Results

x	Activity separated by EDTA counts s^{-1}
0.5	31.8
1.0	42.3
1.5	45.4
3.0	55.5
5.0	43.8
Excess pt 2.0	107.7

Conclusion. The reproducibility curve is that shown in Fig. 3.6, and is satisfactory in all ways for the purpose of substoichiometry.

Reproducibility Curve for 10^{-6} M Metal

When C_{HY} concentration falls to 10^{-6}, the concentration ratio of C_{HA} (max.) becomes equal to C_{HA} (min.) and a very interesting case arises. This experiment shows a variety of reproducibility curves indicating how substoichiometry becomes impossible to achieve under these conditions.

Solutions: 10^{-5} M terbium and 10^{-5} M EDTA, by dilution of those solutions in the experiment above. Specific activity was increased. Several concentrations of organic phase reagent were used (see Table 3.10).

Table 3.10

Results from 3(viii) Showing Activities in counts s^{-1} Representing Unsatisfactory Reproducibility Curves

C_{HA} x	1.4×10^{-3}	3.6×10^{-3}	7.03×10^{-3}	10^{-2}
0.7	188.0	166.6	169.9	172.7
2.0	285.0	272.5	260.5	256.6
4.0	316.7	313.5	287.8	292.6
5.0	351.2	324.9	307.8	297.0
2.0 Excess pt		803	781	

Plotted as Fig. 3.7.

Conclusion. None of these curves is satisfactory for substoichiometry, although the range of extractant concentration spans the optimum value. Fig. 3.7 and 3.7a are typical shapes of poor reproducibility curves.

The Reactions of Cerium in this Extraction

This experiment was among the earlier part of this investigation. It shows atypical behaviour in the light of the above theoretical predictions.

Solutions: 10^{-1} M hexamine buffer pH 6

10^{-3} M cerium

10^{-3} M EDTA.

Method. The EDTA solution was buffered by adding 1 ml to 5 ml of the hexamine reagent. Cerium was added, 1, 2, 3, 4, 5, 6 ml and each aqueous phase extracted with 10^{-1} M TTA in toluene for 5 min. The phases were centrifuged and parted. All the aqueous phase was made to 25 ml. The organic phases were coloured yellow/orange. The activity of 5 ml of aqueous phase was counted and is shown below. An excess EDTA point was also determined.

Results

ml Ce	Activity 5 ml counts s^{-1}
1	111.5
2	149.5
3	155.6
3 excess	319.5
4	154.0
5	152.9
6	160.9

Conclusion. This forms a perfectly good reproducibility curve, although there has apparently been aerial oxidation of the Ce to Ce IV and the TTA used is of a concentration which should have caused partial breakdown of the substoichiometric complex.

In all of these poor reproducibility curves, even those where conditions are barely less than satisfactory, substoichiometry is clearly not possible, despite only a short time of shaking, which should favour the extraction of free metal rather than breakdown of EDTA complex.

3(ix) Model Analyses (From Section 3.8)

Ytterbium

Solutions: 'Test solution' containing 38.14 μg ytterbium per ml.

Standard ytterbium containing 38.43 μg ml, labelled with ^{170}thulium.

10^{-2} M TTA in xylene. This concentration was chosen from the possible range $10^{-2.3}$-$10^{-1.7}$ M.

Standard 10^{-4} M EDTA.

1 M hexamine buffer.

Method. To each of a number of separating flasks was added 5 ml of buffer. Then a 2 ml aliquot of standard labelled solution was added followed by 2 ml of water (standards), or 2 ml sample (samples). A substoichiometric amount of EDTA, 2 ml, was pipetted into each flask, and the excess metal removed by shaking for 5 min with an equal volume of the organic phase. After separating and filtering each aqueous phase through a dry filter paper, the activity of 5 ml was determined.

Six samples were analysed with one standard and three with a second standard. The results are combined below. The amount of metal in the test solutions was calculated using the substoichiometry formula

$$x \text{ sample} = x \text{ standard } \left(\frac{\text{activity standard}}{\text{activity sample}} - 1\right)$$

where x = weight of metal.

Results

Standard activity counts s^{-1} (As)	Sample activity counts s^{-1} (A)	$\frac{As}{A} - 1$	Yb found μg ml
88.61	44.65	0.985	37.85
	44.18	1.009	38.77
	44.27	1.001	38.46
	44.08	1.010	38.81
	44.64	0.985	37.85
	44.27	1.001	38.46
86.55	43.90	0.971	37.33
	43.52	0.988	37.96
	43.14	1.006	38.66

Mean result, Yb = 38.24 μg ml.

Standard deviation about mean, 0.51 μg ml.

Terbium

Solutions: Test solution of terbium containing 17.1 μg ml.

Standard terbium solution containing 25.4 μg ml, labelled with ^{160}terbium.

Other solutions as for ytterbium.

Method. The method used was identical to the ytterbium experiment except that only 1 ml EDTA was used in the substoichiometric step.

Results

Standard activity counts s^{-1} (As)	Sample activity counts s^{-1} (A)	$\frac{As}{A} - 1$	Tb found µg ml
135.61	81.58	0.662	16.82
	79.79	0.699	17.75
	80.41	0.688	17.45
135.59	80.19	0.690	17.52
	81.45	0.664	16.87
	82.68	0.640	16.26

Mean result, Tb = 17.11 µg ml.

Standard deviation about mean, 0.55 µg ml.

CHAPTER 4

The Rare Earth Salicylates and Considerations of These Complexes for Solvent Extraction of Traces of Rare Earth Metal

4.1 Introduction

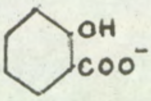
Among the most commonly used reagents for the solvent extraction of rare earth metals are tributylphosphate, 2-diethylhexylphosphoric acid, etc. These are unsuitable for direct substoichiometry as stated earlier. They are equally unsuitable, because of the high acidity required, for the separation as used in the EDTA-TTA work. It is interesting to examine other possible reagents of this type, not only to discover whether they can be of specific use, but also whether substoichiometric separations are possible at all in such mixtures.

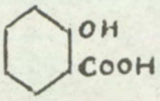
There are some promising ligands among carboxylic acids which have received only a little attention. These are generally less useful as extractants than the very weak acids. It was decided to examine the salicylic acid system in some detail. Preliminary experiments had shown that substoichiometry was a possibility with this reagent.

Salicylic acid in iso-amyl alcohol (amyl alcohol) has been reported as a suitable extractant for lanthanum and cerium.[11,12] These are incomplete studies and provide little quantitative data other than minimum pH for good extraction. Sudarikov[12] proposes that the reaction is

$$\mathrm{MSal}^{2+} + 2\mathrm{HSal} \longrightarrow \mathrm{MSal}_{3\,o} + 2\mathrm{H}^{+}$$

based on the pH observations

where Sal^- = 

HSal = 

Other work has been published by Russian authors among whom the name of Ermolenko predominates. Much of it relates to complexation at high pH when the phenol dissociates, and is primarily intended for use as a possible eluent in ion exchange. The results will be cited below where appropriate.

4.2 Choice of Solvent

From a study of the available literature, it seemed clear that the salicylate system was complicated and somewhat difficult to investigate experimentally. Salicylic acid is only slightly soluble in water, about 0.01 M depending on conditions, but is much more soluble in organic solvents. In collecting information in his book, Stary[13] quotes the partition coefficient as 3 for chloroform/water and 320 for hexone/water. The rare earth salicylates, $MSal_3$, also have low solubility in water.[14,15,16] They are apparently soluble in oxygenated solvents,[11,12] but both chloroform and hydrocarbons are unsuitable. Amyl alcohol and hexone have been chiefly used in this work. A small number of experiments were performed with ethyl orbutyl acetate.

A number of important conclusions can be drawn from these observations and before continuing we must discuss in more detail some aspects of solvent extraction outlined in earlier chapters.

4.3 Solvent Extraction in Oxygenated Solvents

Extractable chelates are usually encountered with three or four valent metal ions in which the six or eight fold co-ordination is fully satisfied. These are soluble in non-polar solvents and the accepted equilibrium theory holds true.

There are instances when the rare earths exhibit higher co-ordination numbers than six. If the electronic charges are satisfied, the additional co-ordination sites are occupied by water molecules. Such a complex is not soluble in non-polar solvents but is often soluble and extractable into polar solvents which can replace the water in the co-ordination sphere of the central ion. Oxygenated solvents behave in this way and there are strong suggestions that this is the case with the rare earth salicylates. For instance, whilst the salicylates are not extractable, the ternary complexes of salicylate and, for example, phenantholine $MSal_3.phen_2$ do extract into benzene.[17] Closely associated is the fact that amyl alcohol alone will extract rare earths as inorganic association complexes, from concentrated solutions of some anions.[18] In their standard work on solvent extraction[19] Morrison and Frieser class carboxylic acids including salicylic acid under ion association extraction. Also similar are complexes with extractants already mentioned, e.g. $La(NO_3)_3.3TBP$.

It will be appreciated that these extraction systems are very involved and more difficult to predict than the case of strong chelate extraction into non-polar solvents.

4.4 The Solubility of Salicylic Acid and Sodium Salicylate in Amyl Alcohol

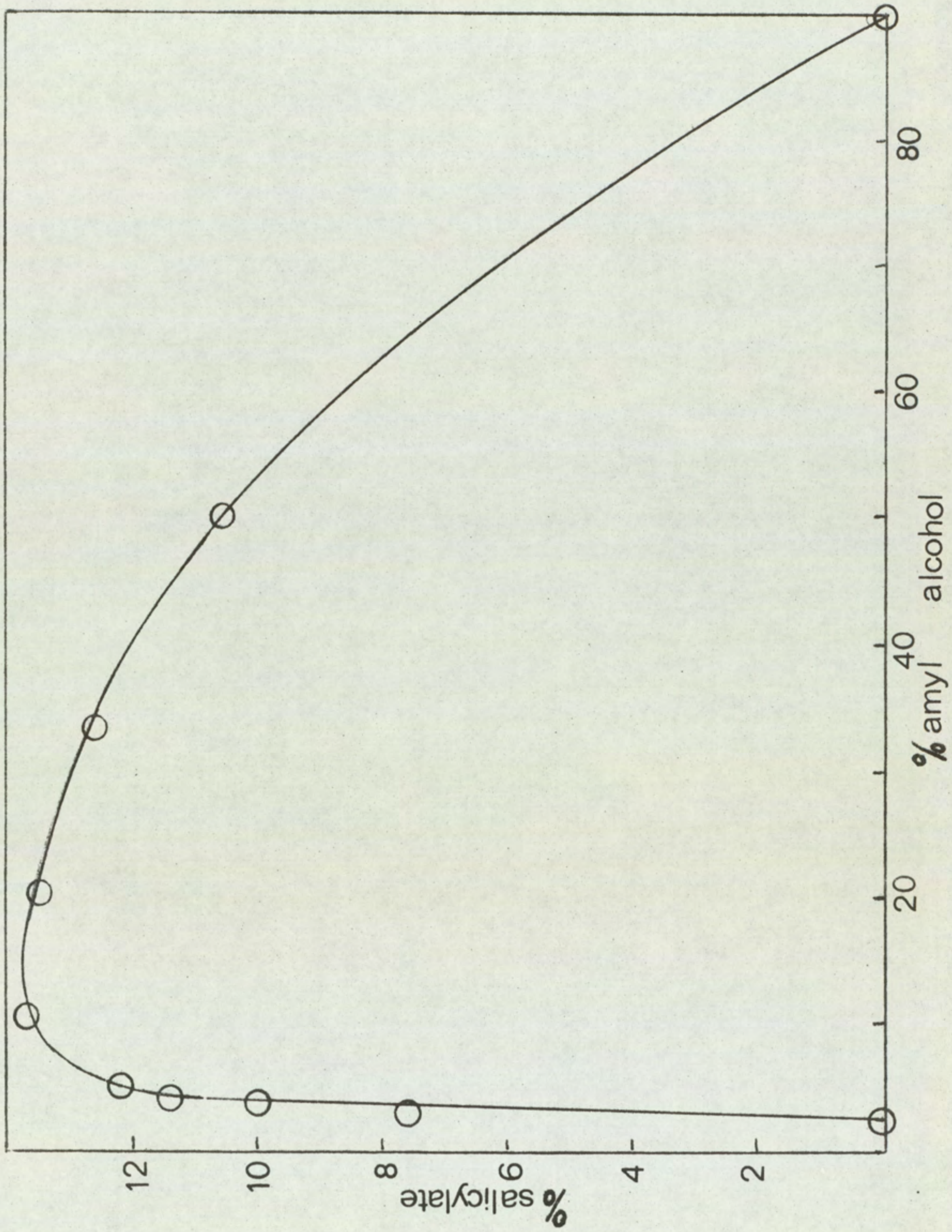
Polar solvents mix with water to a large extent, and many of the complications mentioned in 4.3 are a result of the effects of solutes and reagents on the mutual solubility of the two phases.

The distribution of salicylic acid between water and amyl alcohol has been measured, 4(i), both directly and in buffered solution containing enough free salicylate ions, it is assumed, to suppress further dissociation so that free unionised acid could be measured titrimetrically in both phases. The distribution coefficient varied from 92 to 130 depending on conditions.

The partition of sodium salicylate between amyl alcohol and water has also been examined in experiment 4(ii). The phase diagram for the system water, amyl alcohol, sodium salicylate is shown in Fig. 4.1. The vertical (salicylate) scale has been extended to emphasise the unsymmetrical nature of the curve in water rich mixtures. The implication of this curve is that over a wide range of strong sodium salicylate concentrations, the mixture is homogeneous. An alternative way of showing the same result is given in Fig. 4.2. This indicates the amount of amyl alcohol which a sodium salicylate solution, whose original molarity is shown, will tolerate before separating into two layers. It can readily be seen that amyl alcohol can only be used for extraction from salicylate less than about 1 M. Above 1.5 M, the mixture rapidly becomes one phase with increasing salicylate concentration. The same effect, less pronounced is observed with ethyl acetate, but hexone does not have this disadvantage. The graph for the hexone, sodium salicylate system, 4(ii), is also shown in Fig. 4.2.

A further conclusion, or alternative interpretation is that under conditions when two phases exist, some of the sodium salicylate will extract into the organic phase, and the amount extracted will depend upon the original concentration. This dependency can be followed quite easily by, for example, having sodium salicylate labelled with ^{22}sodium, 4(iii).

Fig.4.1. The phase diagram for water, amyl alcohol, and sodium salicylate



^{22}Sodium was available during this research as the metal in magnesium target material, from which it readily dissolves into hot water. This procedure results in highly active ^{22}NaOH of negligible concentration. Thus ^{22}sodium salicylate could be made very simply by isotopic exchange by using this 'active water' to make up strong sodium salicylate solutions, which were then diluted to the required concentration with water. The results are presented in Fig. 4.3. More tedious methods involving salicylate determination gave the same results, 4(iii).

The presence of free salicylic acid in the organic layer tends to inhibit this extraction but not markedly. The effect is shown in Fig. 4.4 but is discussed in more detail later in the chapter.

4.5 Considerations in the Design of Experiments to Study Rare Earth Salicylate Extraction

Salicylic acid, like other carboxylic acids, does not bring about extraction until the pH is such that it is appreciably ionised in the aqueous phase. Thus the reaction is best expressed as

$$M + nSal \longrightarrow MSal_{n\,o}$$

In this way the effect of pH change can be viewed as competition in the reaction of salicylate for the available cations M and H.

In order to learn as much as possible from the reaction, it must be studied over a wide range of salicylate concentrations.

The extraction is suppressed by increasing ionic strength (μ) but as the salicylate needs to be in large excess over the metal to effect a marked extraction, the chosen value of μ must also be large in order to be constant. This in turn leads to the

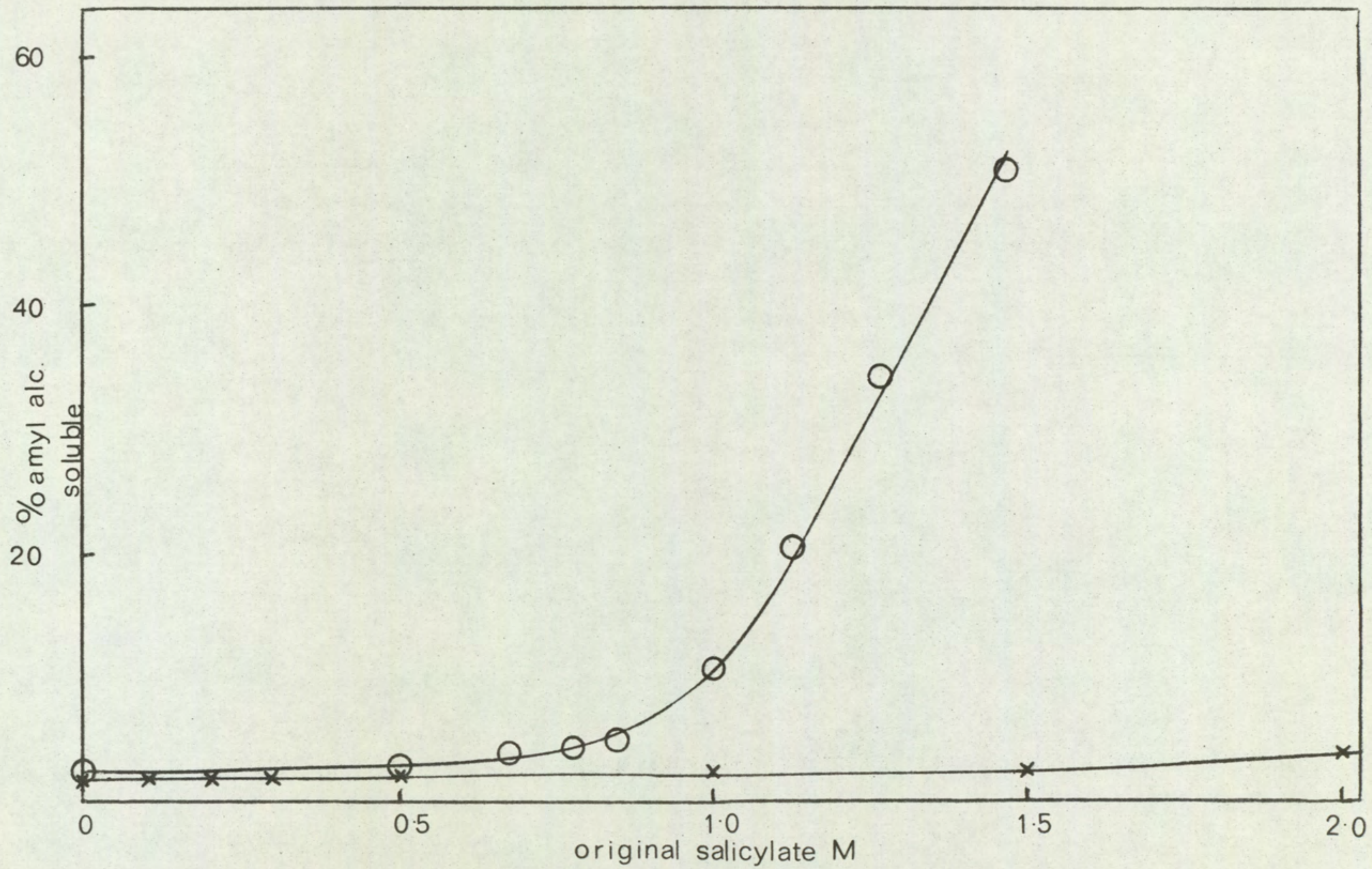


Fig 4.2 Alternative presentation of Fig 4.1

distribution ratio (q) becoming very small in practical terms at low salicylate concentrations. Thus the reaction can only be studied over a narrower concentration range than is desirable. Further, one has to be careful when adding supporting ions that other complexes are not formed which will affect the extraction. This is not always easy to detect. Valuable information as far as practical experiments are concerned, can be obtained by studying this extraction at varying ionic strength, i.e. with only sodium salicylate and rare earth present in the aqueous phase. Although it is difficult to transfer such data for use in another experiment, the results for analytical purposes are quite rewarding.

The variations of q with ionic strength can be partly interpreted in the light of the extended Debye Hückel equations, for example, the Davies modification[20]

$$-\log f \;=\; Az^2 \left(\frac{\mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}} - C\mu\right) \qquad (1)$$

A and C are constants and f is the mole fraction activity coefficient which is related to the other commonly used activity coefficients γ (molal), and y (molar) as follows:

$$y = \frac{m\, d_o \gamma}{C}$$

where m = moles Kg

C = moles litre

and d_o = density of solvent.

$$f = \gamma \left[\; 1 + 10^{-3}\; v.W_A.M \;\right]$$

where W_A = mol. wt of solvent

and v = moles of ions from 1 mole of solution.

Fig.4.3.a

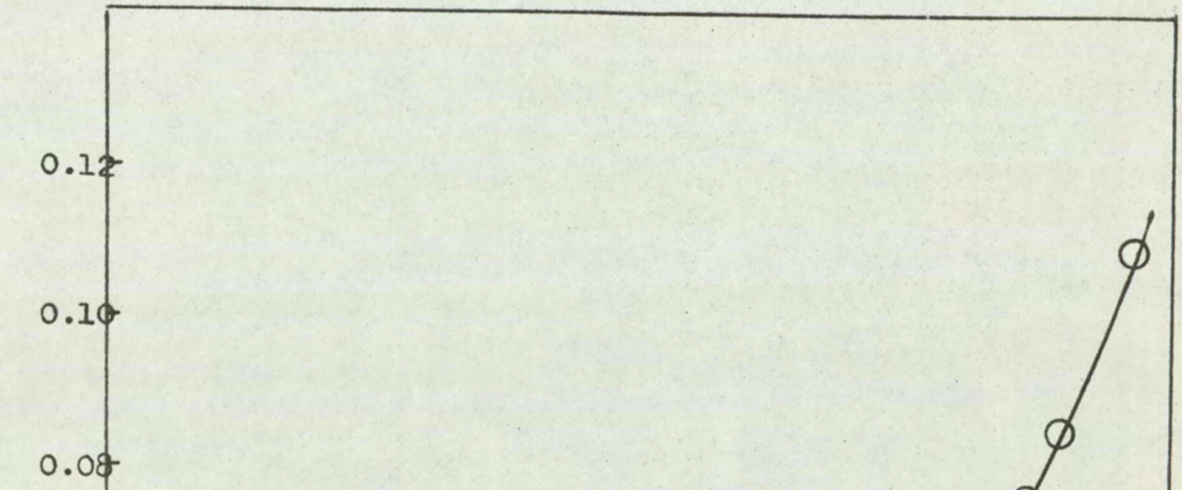


Fig.4.3.a. The partition of sodium salicylate into amyl alcohol

Fig 4.3b

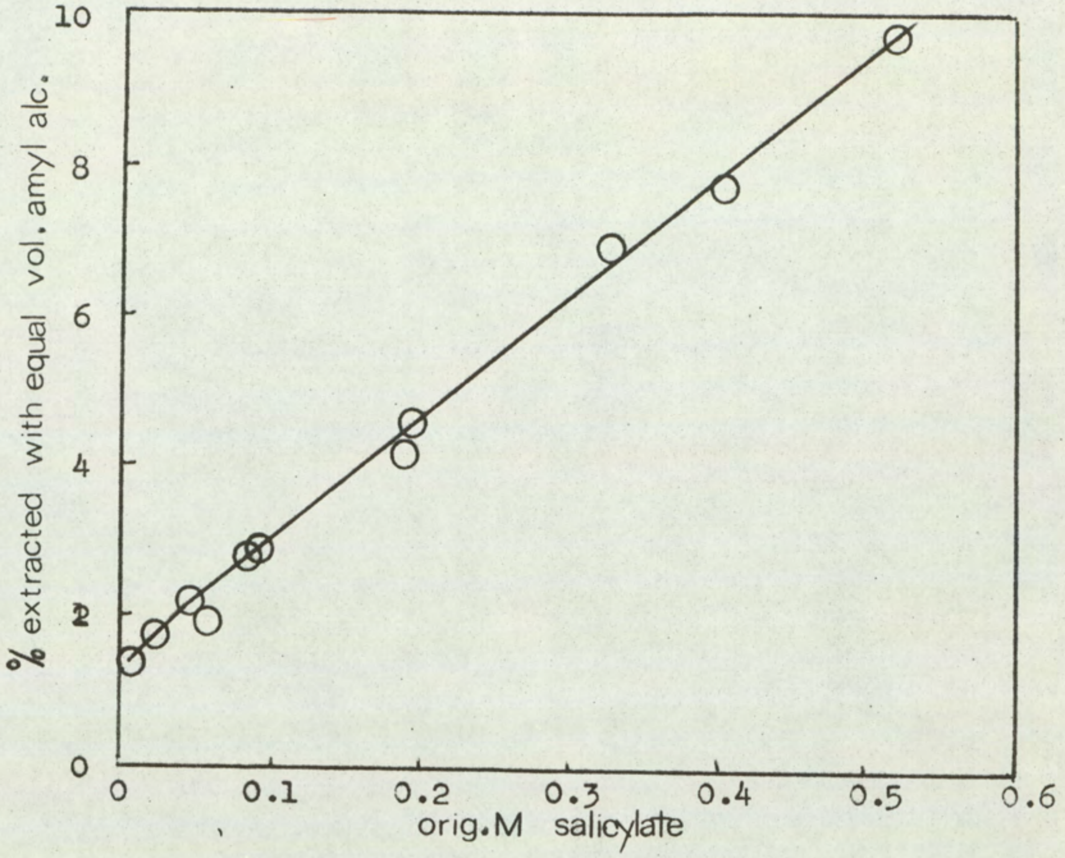


Fig.4.3b. The partition of sodium salicylate into amyl alcohol

Fig.4.4

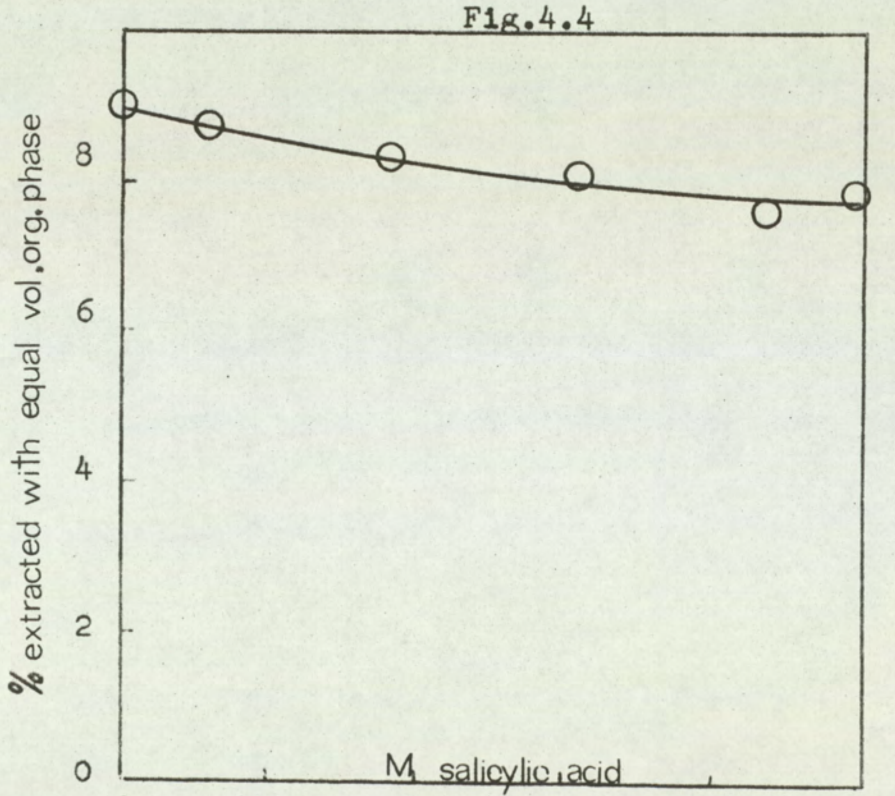


Fig.4.4 The effect of salicylic acid on the partition shown in 4.3

Clearly these are almost identical for dilute aqueous solutions.

The rare earth metals are known to obey the Davies equation and provided we assume that the activity of the extracted species is constant at a constant solvent composition, it is straightforward to illustrate that they do so in this case. Table 4.1, expt 4(iv), gives details of the comparison of distribution ratios of cerium from .05 M sodium salicylate over a limited range of ionic strengths, to those corrected to ionic strength zero by means of the Davies equation, using A = 0.5, C = 0.3, which are commonly used approximations. At higher values of μ the agreement falls off as shown in the last figure of Table 4.1 because the assumptions made above are no longer true, and density corrections need to be applied.

Table 4.1

The Variation of Distribution Ratio of Cerium Salicylate with Ionic Strength

μ	$\gamma_{CeSal.}\gamma^2_{Sal}$	q observed	q calculated
0.082	0.264	13.28	50.3
0.110	0.226	11.78	52.0
0.138	0.206	10.77	52.3
0.166	0.192	10.10	52.6
0.194	0.180	9.25	51.4
0.614	0.175	7.00	40.0

The aqueous species has been taken as $CeSal^{2+}$ in accordance with the stability constant results of Cefola, Tompa et al.[21] which reproduces results from Tompa's own doctoral dissertation. This is justified by results in this present study.

This raises a further point, namely that there is little available material on the nature of the aqueous rare earth salicylate complexes other than the paper cited above and the conductimetric work of Ermolenko.[14,15,16,22] These complexes are difficult to investigate due to solubility problems and often lack of sensitivity in the commonly used methods of constant determination. Cefola[21] used a potentiometric method and although difficulties are mentioned, no primary results or calculations are given. Ermolenko developed a theory of his own in connection with his conductimetric titrations. A recent spectrophotometric study[23] is probably better than either but is very lengthy.

To maintain the theme of this research, distribution methods were considered but proved impossible due to tertiary complex formation. A digression was made to carry out a potentiometric titration study, which provided little valuable information due to the lack of sensitivity for the weak complex formation, and the serious interference of rare earths and supporting electrolyte to the behaviour of the chosen glass electrodes.

One final question in the choice of experimental conditions is outstanding. Substoichiometry with aminocarboxylic acids or similar reagents was always maintained as the possible goal in this work; and such reactions require a buffered solution. It was decided to study the extraction system also in a buffer for which salicylate alone is available. Other complexing agents were not tolerable and mixtures of hexamine, as used previously, with amyl alcohol and salicylate were equally odious. Free salicylic acid was, therefore, included in the organic phase in this work wherever possible. This provided a satisfactory if not first class buffer in the aqueous phase. Unforeseen complications arose from this technique which are explained below. Fortunately they proved to be resolvable.

4.6 The Distribution of Rare Earths between Sodium Salicylate and Polar Solvents (From Experiment 4(vi) and Following)

When a tervalent rare earth metal is extracted upon reacting with a monovalent ligand, the equilibrium has been described by

$$E = \frac{[MA_3]_o}{[M][A]^3} \qquad (2)$$

$$E = \frac{q}{[A]^3} \qquad (3)$$

A logarithmic plot of q versus $[A]$ is linear and of slope 3. If MA and MA_2 exist in the aqueous phase, then the slope is lessened and changes continuously in a manner determined by the relative sizes of the stepwise formation constants of these complexes. There are a number of well-established methods adequately reviewed in standard texts, for extracting approximate values of these constants from the curves.

The time required for equilibrium to be reached in the salicylate extraction was determined by measuring q for gadolinium at various time intervals, 4(v). As expected, equilibrium is reached quickly, effectively within a few seconds of the phases being mixed. In the subsequent experiments extraction times of 2-10 minutes were used, depending upon the allocation of time for other commitments within the experiment.

Fig. 4.5 shows the log plot of q versus salicylate concentration for the extraction of lanthanum into hexone at $\mu = 0.1$ maintained by addition of $NaClO_4$, 4(vi). The solutions were buffered by having approximately equal concentrations of salicylate (aqueous) and salicylic acid (organic). Lanthanum concentration was negligible and each solution was labelled with a suitable active tracer as described in Chapter 1. The experiment was also conducted with cerium, praseodymium and neodymium. Fig. 4.6 shows the same curve for the extraction of terbium into amyl alcohol. All solutions in this experiment were maintained at $\mu = 0.6$, thus enabling salicylate of higher concentration to be used. Cerium, neodymium and ytterbium were also examined in this way, 4(vii).

Before making any quantitative assessment of these results it is important to ascertain the nature of the reacting species which so far have been assumed to be $MSal_3$, $MSal_2$, etc. The need for high concentration of reagents in this type of extraction has already been stressed. It occurs in both conventional ion association such as $HFeCl_4$ into ether and also with other carboxylic acids. In this present situation, almost the maximum salicylate concentration permitted by the phase diagram is needed to obtain q values approaching 100. The fall in q at high salicylate concentration is important and must be explained. It occurs with hexone, not illustrated, as well as amyl alcohol and

Fig.4.5

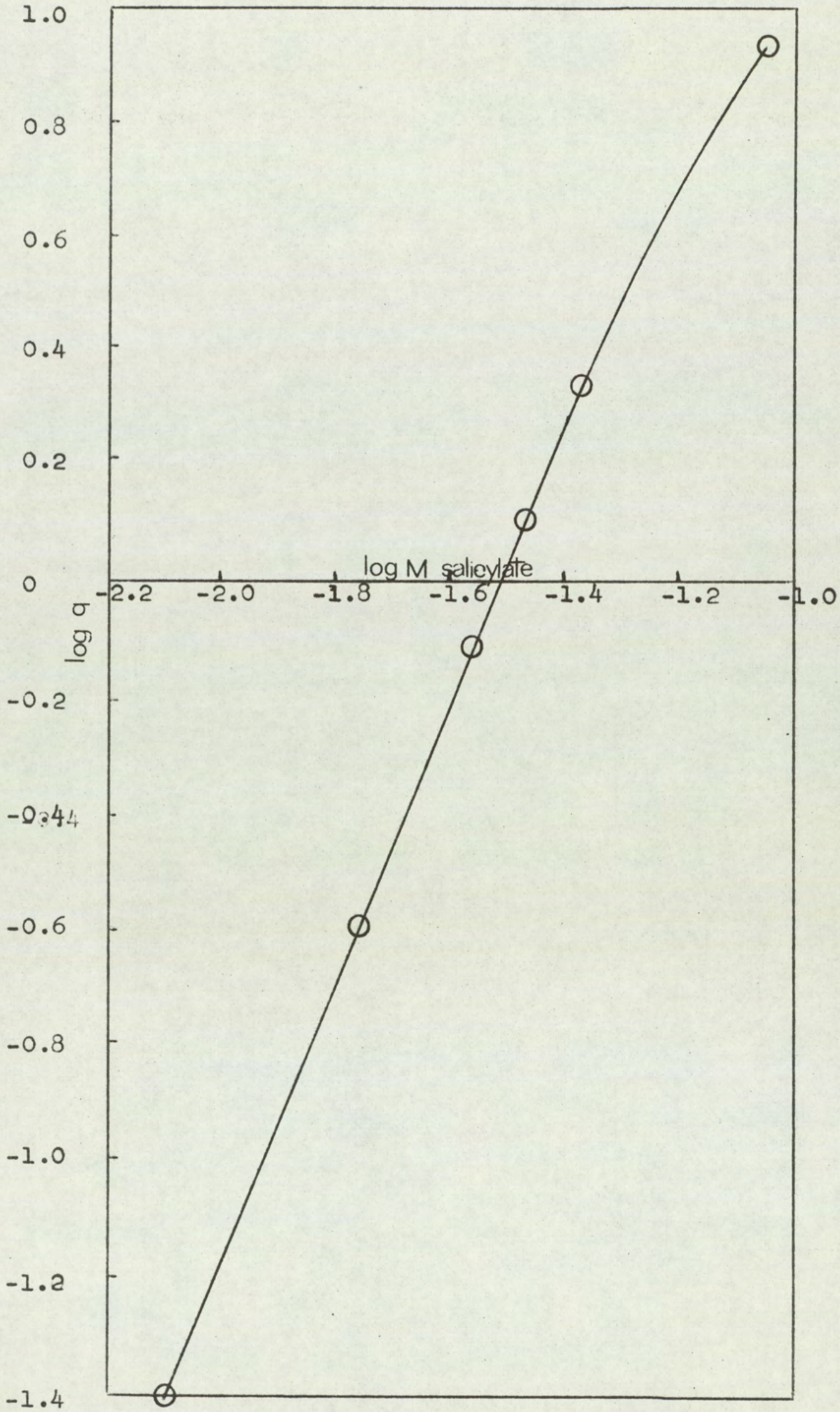


Fig 4.5. The extraction of lanthanum into hexone.

is, therefore, not simply an effect of the rapidly increasing mutual solubility of reagents.

Ermolenko[16] has shown that the $MSal_3$ complex becomes less soluble in increasing salicylate concentrations. Therefore, there is no formation of $MSal_4^-$ ions which might bring about the effect.

It is important to realise that in buffering the extraction in the way chosen, the composition of the organic phase changes markedly at these high concentrations. The extraction has been studied in constant salicylate concentration at various concentrations of free acid in the organic phase. Thus the alteration in the solvent effect can be examined and at the same time the presence or absence of addition complexes $MSal_3.HSal_x$ detected, 4(viii). Such complexes are indicated by an increase of q as salicylic acid increases at constant salicylate concentration. Thus

$$E_{HSal} = \frac{q}{[HSal]} \qquad (4)$$

If no addition complexes occur, then q will be constant and increase of acid will move the reaction toward a more acid extraction in accordance with the mass action law.

Fig. 4.7 shows the results of the extraction of some rare earths from the buffer at various pH values. There is no evidence of addition complexes, but instead q rises with increasing pH passing through a maximum at about pH 5-6.

It seems reasonable to discount the possibility of either extractable hydroxy complexes or non-extractable acid complexes in view of the foregoing arguments about fully chelated $MSal_3$ extraction. The effect of altering solvent composition must be given full attention.

Fig.4.6

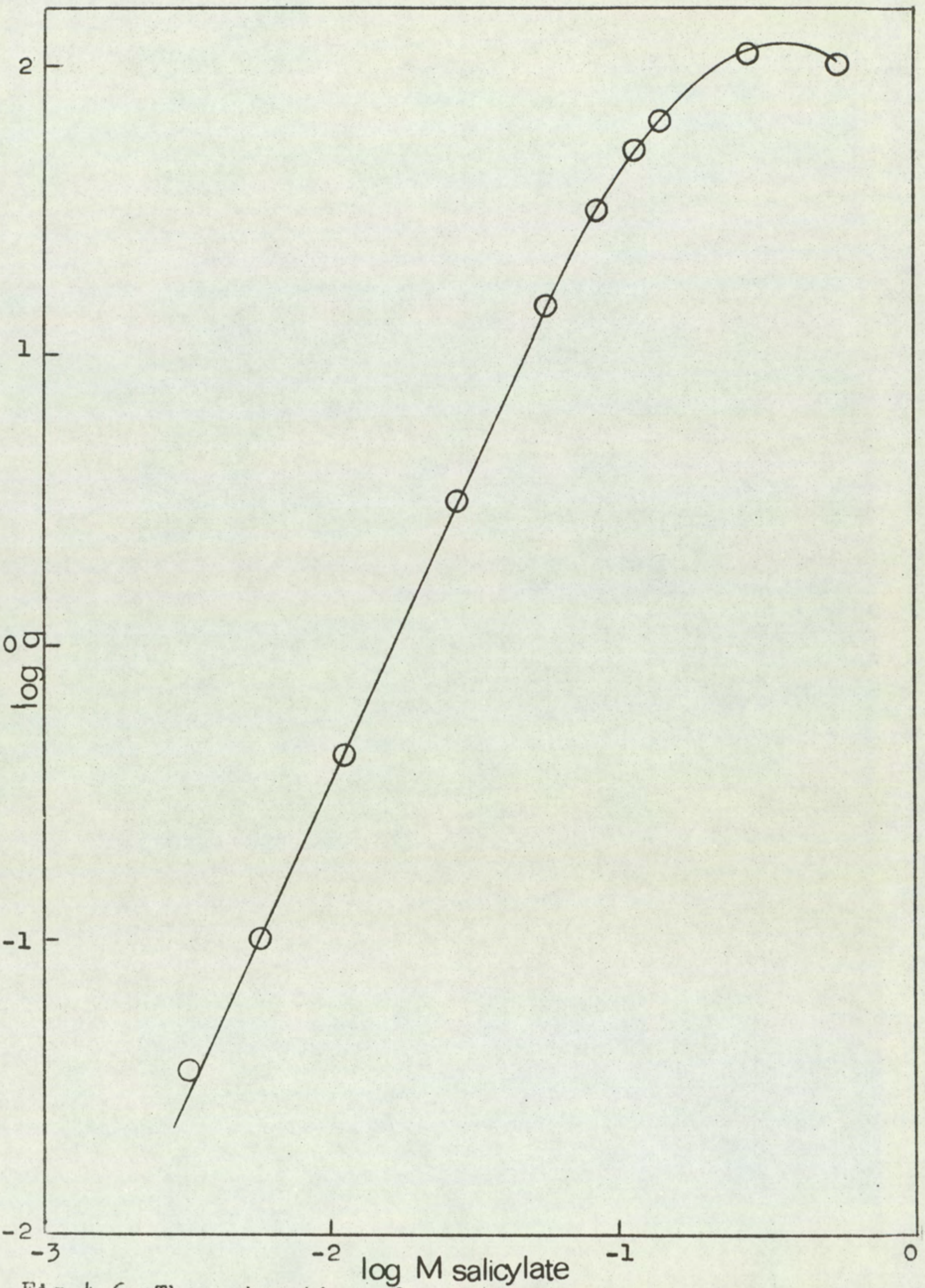


Fig.4.6. The extraction of terbium into amyl alcohol

The molarity of 'pure' amyl alcohol saturated with 10% water at 25°C is 8.5 M. The molarity in a 1 M solution of salicylic acid is reduced to 7.5, Fig. 4.8.

Experiments were conducted to establish the effects of diluting the extractant with an inert solvent, 4(xi) and 4(x). These proved surprisingly difficult to do. Hexone-chloroform and hexone-xylene mixtures, for instance, are very difficult to separate cleanly from sodium salicylate, and also develop a curdy precipitate at the interface. Amyl alcohol chloroform at pH 6 separates well and successful experiments can be achieved. The distribution of cerium varies as the concentration of extractant varies, as shown in Fig. 4.9.

A comprehensive study of this effect has not been made. Such a study is a major project in its own right and would extend the bounds of the present problem too much. Even so, one can conclude that the extraction depends upon the effective concentration of the solvent, and is quite possibly stoichiometric to give $MSal_3.3$ solvent, especially in the case of amyl alcohol. An addition complex of this kind provides adequate explanation for the increase in q as $HSal_o$ decreases as seen in the pH dependency curves. Below salicylic acid concentration of 0.1 M the effect is negligible.

Above pH 5 the extraction falls again as the pH increases. Sudarikov[12] proposed that lanthanum and cerium were extractable up to pH 10 whilst scandium in comparison was stripped back at these pH values. The rare earths shown here do not extract at high pH. With cerium, the extraction is difficult to control due to the tendency to oxidise in air under alkaline conditions. Lanthanum was not studied at high pH while our supply of short lived

Fig 4.7

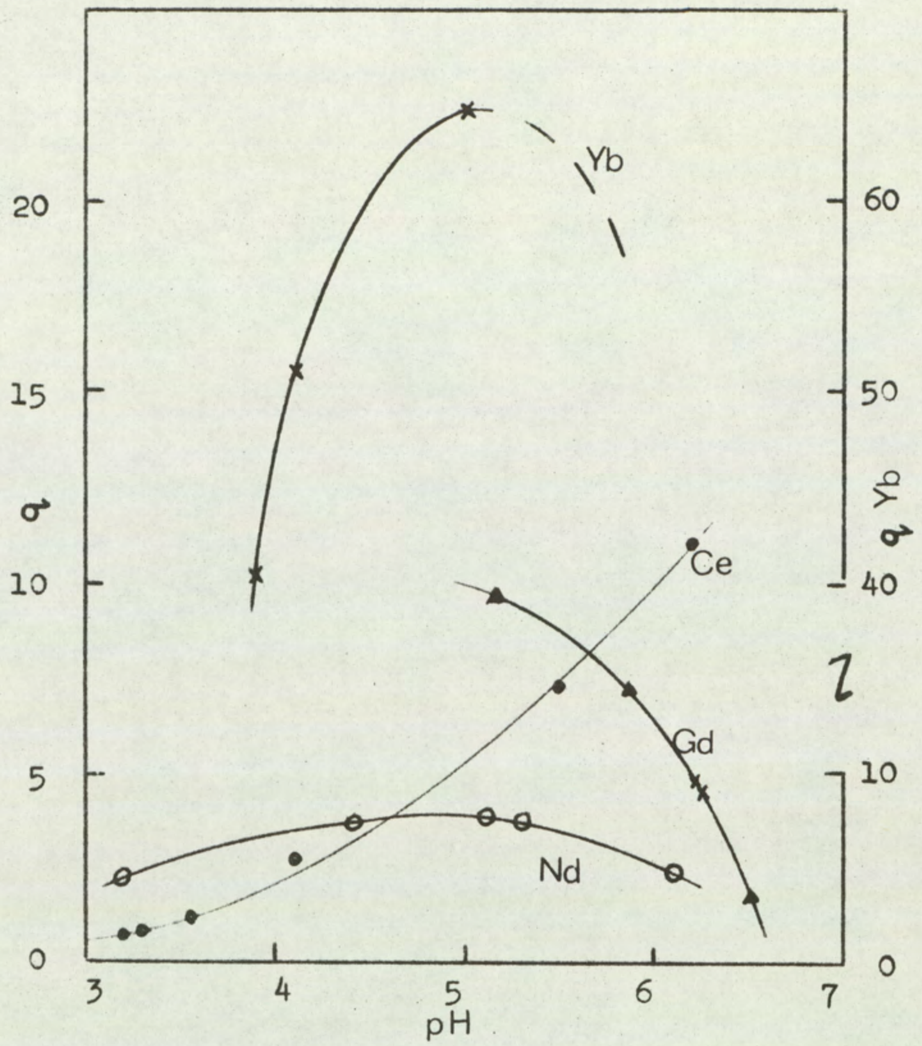


Fig.4.7. The extraction of rare earths at various pH values.

Fig.4.8

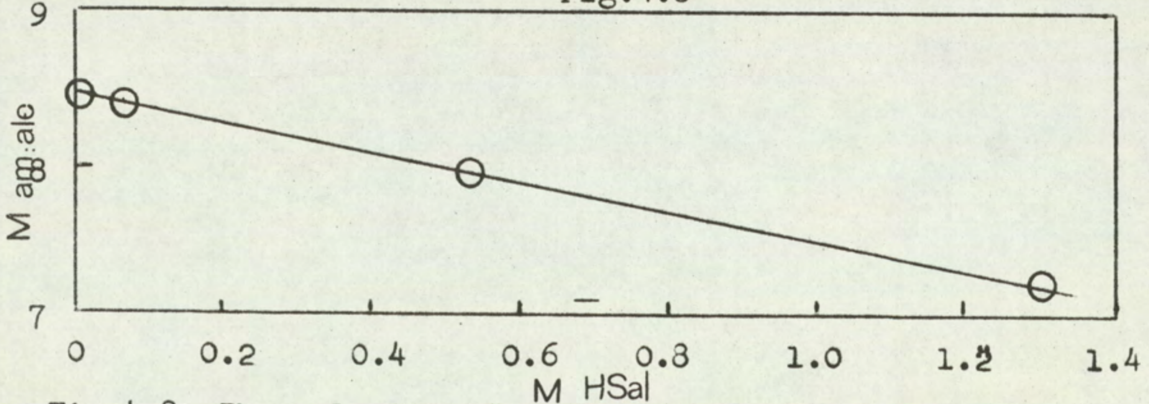


Fig.4.8. The molarity of amyl alcohol in a solution of salicylic acid in this solvent.

^{140}lanthanum was available, but neodymium and particularly the heavy rare earths all strip back as the acidity falls. Loss by adsorption has been a common observation with rare earth solutions at low acidity. In some cases where adsorption took place during extraction, apparently sensible q values were obtained with the remaining metal in solution, but in general the measurement of distribution and the preparation of extraction curves was not possible unless buffer was present to minimise this loss. The light rare earths are least affected and with especial care can be extracted up to pH = 6.5.

There is little doubt that hydrolysis causes the back stripping. Ermolenko[22,24] has proposed hydroxy salicylate complexes $M(OH)Sal_2$ and $M(OH)_2Sal$ but has not measured their stability. Information on the $M(OH)_x$ complexes is equally scarce.

4.7 Calculation of Extraction Constants (From Experiments 4(vii) and 4(vii))

The diminished extraction at high acid concentration in unbuffered solution is inseparable from the effect of the formation of the higher aqueous complexes, MSal and $MSal_2$, in buffered extraction as shown for instance in Fig. 4.6. At lower concentrations when the acid effect is slight, extraction constants can be calculated, remembering that actual analytical conditions might force one to work at higher concentrations, and reservations must be applied. Thus if the curve is taken to be linear and slope 2

$$E' = \frac{[MSal_3]_o}{[MSal]\,[Sal]^2}$$

can be easily determined.

fig.4.9

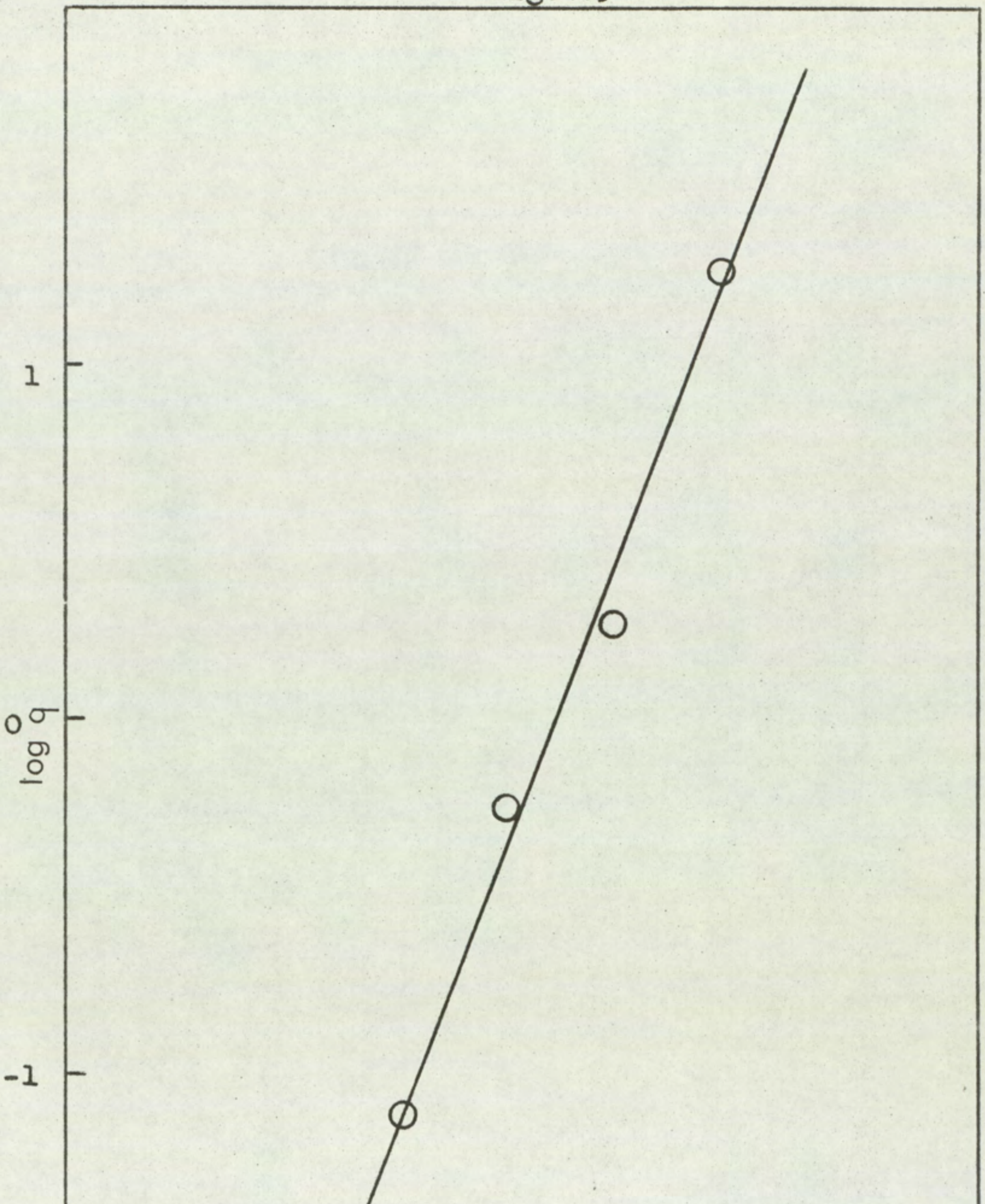


Fig.4.9. The distribution of cerium salicylate into amyl alcohol/chloroform mixtures.

If the slope is $>$ 2, then approximate values of $\beta_1 = \frac{[MSal]}{[M][Sal]}$ can be obtained using the limiting value method of Leden,[25] that is,

when
$$q = \frac{[MA_3]}{[M] + [MA] + [MA_2] + [MA_3]}$$

the equation can be rewritten

$$\frac{[A]^3}{q} = \frac{1 + \beta_1[A] + \beta_2[A]^2 + \beta_3[A]^3}{p_\circ \beta_3}$$

where p = partition coefficient of MA_3

and β_n = stepwise formation constants.

Let $p\beta_3 = f$

then

$$\frac{[A]^3}{q} = f^{-1} + f^{-1}\beta_1[A] + f^{-1}\beta_2[A]^2 + f^{-1}\beta_3[A]^3 = F_0$$

Similarly

$$\frac{F_0 - f^{-1}}{[A]} = f^{-1}\beta_1 + f^{-1}\beta_2[A] + f^{-1}\beta_3[A]^2 = F_1$$

$$F_2 = \frac{F_1 - f^{-1}\beta_1}{[A]} = f^{-1}\beta_2 + f^{-1}\beta_3[A]$$

f and β_n can be determined from limit F as $[A] \longrightarrow 0$ and so on.

If one further assumes that any line of slope $>$ 2 is a straight line, this graphical presentation is made even simpler and extrapolation is avoidable if the equations are rearranged thus

$$\frac{[A]^3}{q} = f^{-1} + f^{-1}\beta_1 [A]$$

$$1 = f^{-1} \frac{q}{[A]^3} + f^{-1}\beta_1 \frac{q}{[A]^2}$$

which has the form

$$1 = K_1 \left(\frac{1}{Z}\right) + K_2 \left(\frac{1}{B}\right)$$

Z and B can be plotted as co-ordinates and the straight line joining them will intersect at (K_1, K_2), i.e. at $(f^{-1}, f^{-1}\beta_1)$.

In the two cases cited here, i.e. extraction into hexone at $\mu = 0.1$ and amyl alcohol at $\mu = 0.6$, these approximations could be made. The values of β_1 obtained in this way are subject to large errors, as the graphs differ from slope = 2 only very slightly indicating that the metal salicylate clearly predominates over free metal. In the hexone extraction of light rare earths, only lanthanum and cerium show significant amounts of M^{3+}. Praseodymium and neodymium give a graph of slope not sufficiently > 2, Table 4.2.

At higher $\mu = 0.6$, whilst cerium and neodymium have slope very close to 2.0, terbium and ytterbium are steeper and could possibly be calculated in the above manner but the variation of $q/(\mathrm{Sal})^2 = E'$ is so slight that the calculations have no real meaning. The average values of E' are presented in Table 4.3.

Table 4.2

The Extraction of Light Rare Earths into Hexone at $\mu = 0.1$ ($NaClO_4$). From Experiment 4(vi)

Metal	β_1 approx.	$E = \frac{[MSal_3]_o}{[M][Sal]^3}$	$E' = \frac{[MSal_3]_o}{[MSal][Sal]^2}$
La	55	9.61×10^4	1.75×10^3
Ce	60	2.15×10^5	3.48×10^3
Pr	-	-	2.88×10^3
Nd	-	-	2.63×10^3

Table 4.3

The Extraction of Rare Earths into Amyl Alcohol at $\mu = 0.6$ ($NaClO_4$). From Experiment 4(vii)

Metal	$E' = \frac{[MSal_3]_o}{[MSal][Sal]^2}$
Ce	2.05×10^3
Nd	4.43×10^3
Tb	3.93×10^3
Yb	3.34×10^3

The reproducibility of these results depends on the reproducibility of the separation procedure following the mixing of the two layers. These extractions were conducted at constant temperature and special care was taken to avoid contaminating each phase with the other.

Despite this, it was observed that there was always more variation in the aqueous phase than in the organic phase. On a sample of six tests, the standard deviation of the organic layer activity, ^{170}terbium, was 1.40%, and that of the aqueous layer 3.08%. In each case the total activity measured was sufficient for counting errors to be negligible. There was also negligible error in the salicylate determination by the method given in 1(ii). The actual concentration of salicylate and salicylic acid was 3.6×10^{-3} M giving $E' = 4.72 \times 10^{3}$. Clearly lack of reproducibility stems from contamination in the aqueous phases.

4.8 Extraction from Other Media (From Experiment 4(xiii))

As mentioned previously, extraction has also been conducted in chloride media and with salicylate only present.

Chloride complexes are reported in the Chemical Society monograph on stability constants.[26] Data are few and obtained in varying conditions. In view of the uncertainty, it is unwise to speculate on how such complexes will affect an extraction of this type. The experiment can be conducted without difficulty. Fig. 4.10 shows a comparison of the extraction of terbium from chloride and perchlorate at similar high ionic strength. Because of slight differences in the experiments, μ is not exactly equal in the two cases, but the difference is not important since the

Fig.4110

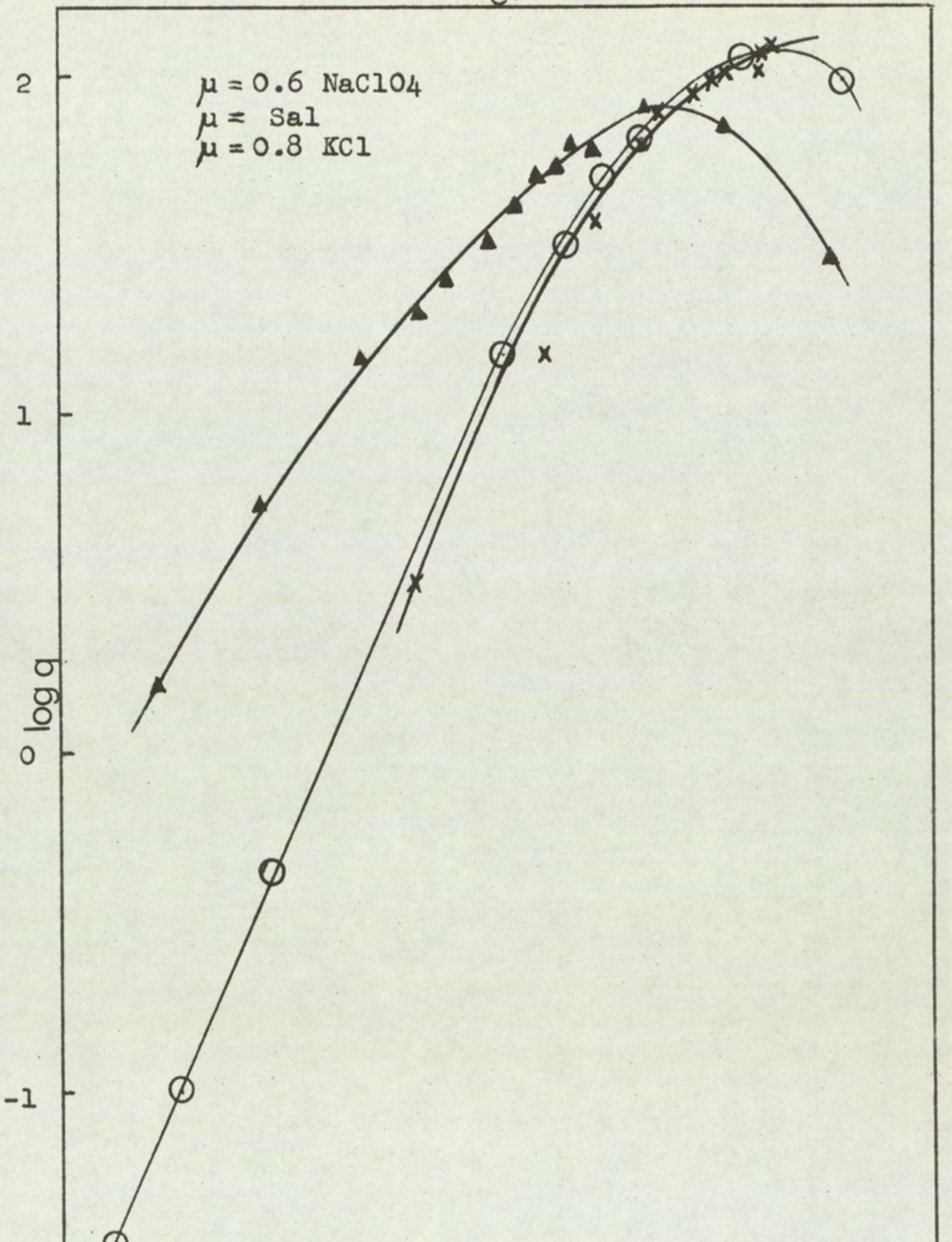


Fig.4.10. Comparison of the extraction of terbium from chloride and perchlorate medium.

effects of changes at this concentration are slight. The chloride has little effect on the extraction over the salicylate concentration range used. Also shown is the extraction curve when only salicylate and metal are present in the aqueous phase. The effect of changing ionic strength is indicated by the more pronounced change of slope. There is a clear order of magnitude difference in q at low salicylate, from that at high ionic strength. Both curves at constant ionic strength rise above the varying ionic strength curve. This is unexpected behaviour and not readily explained. A more usual curve was obtained with ytterbium and is shown in Fig. 4.11.

A comparison of several heavy rare earths is given in Fig. 4.12, showing extraction from salicylate only.

Lanthanum and praseodymium were also extracted from chloride at constant ionic strength 0.5. Parallel extraction curves were obtained and are shown in Fig. 4.13. The slope changes from 3.0 to 2.0 as the salicylate concentration is increased. The results demonstrate that chloride complexes are formed, although this is not obvious from the terbium experiment at higher salicylate concentrations, Fig. 4.10. Comparing the praseodymium result with the closely grouped results for other metals in perchlorate solution, described in 4.6 and Experiment 4(vii), extraction is suppressed and in low concentrations of salicylate, so is the formation of the salicylate complex.

The slope of the extraction curve is close enough to 2.0 and 3.0 over a range wide enough to make good estimations of average values of E and E' from this chloride medium. Variation in chloride concentration used was too slight to accurately estimate

Fig.4.11

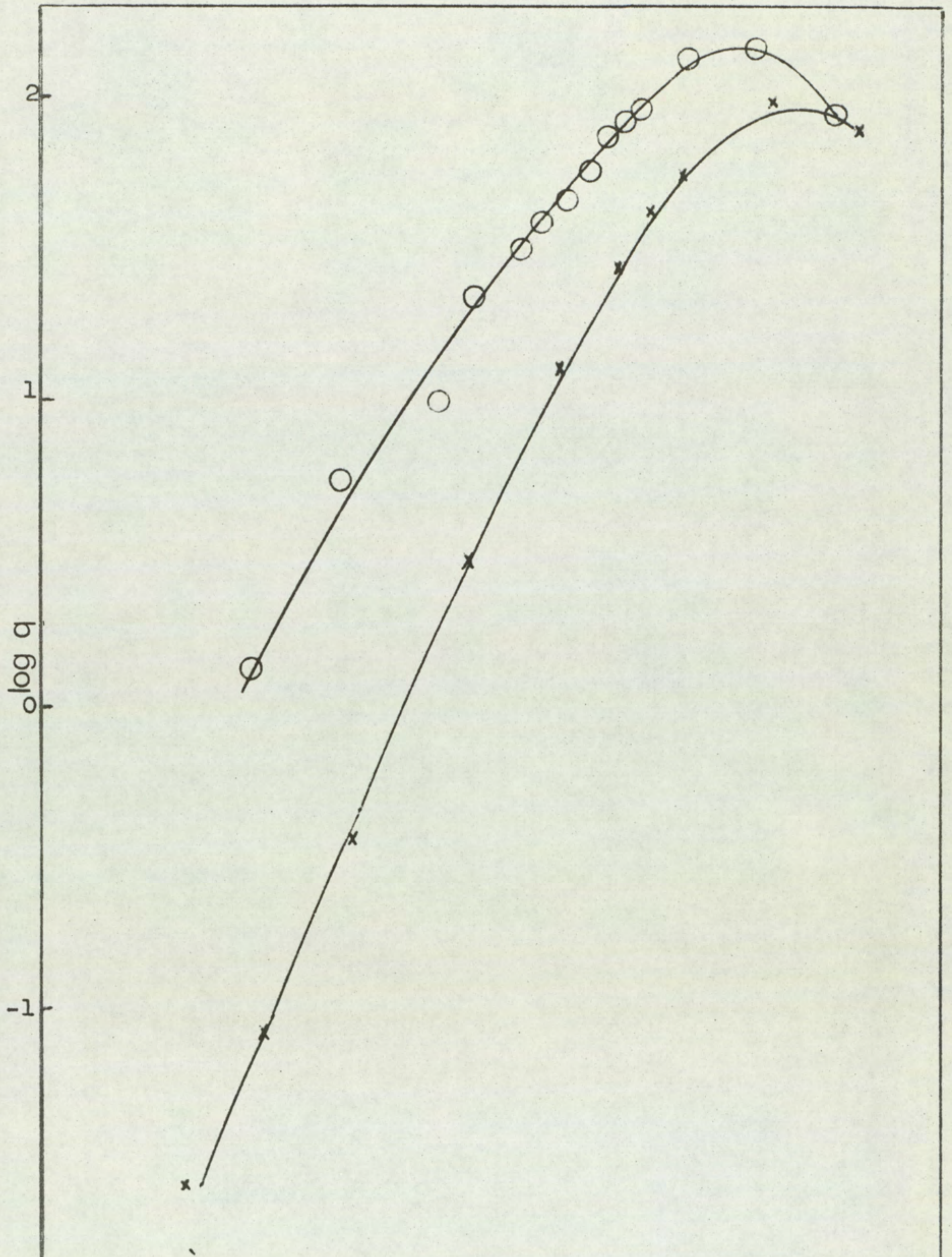


Fig.4.11. Comparison of the extraction of terbium at variable and constant ionic strength.

the chloride constants, although from a comparison of the results for β_1 with Table 4.1 the value of β_{MCl} is approximately 2.6 for both lanthanum and praseodymium, in keeping with the observations of other authors.[26] Results are summarised in Table 4.4.

Table 4.4

Extraction from Chloride Solution

	E'	E	β_1
La	1.36×10^3	3.18×10^4	23.4
Pr	2.81×10^3	8.08×10^4	28.8

4.9 Experimental

General

Unless stated otherwise, all solutions in extraction experiments are pre-saturated with the opposite phase.

4(i) The Distribution Coefficient of Salicylic Acid between Amyl Alcohol and Water at 25°C

(a) Direct Extraction

Solutions: 1.0 M salicylic acid in amyl alcohol
10^{-1} M NaOH standard.

Method. A 10 ml portion of salicylic acid in amyl alcohol was mixed with 150 ml of water and extracted for 2 minutes. The aqueous phase was filtered, and a 100 ml aliquot titrated with 0.1 M NaOH. The organic phase was separated and centrifuged, then 5 ml was titrated with the same NaOH. A blank titre was conducted in each case.

Fig.4.12

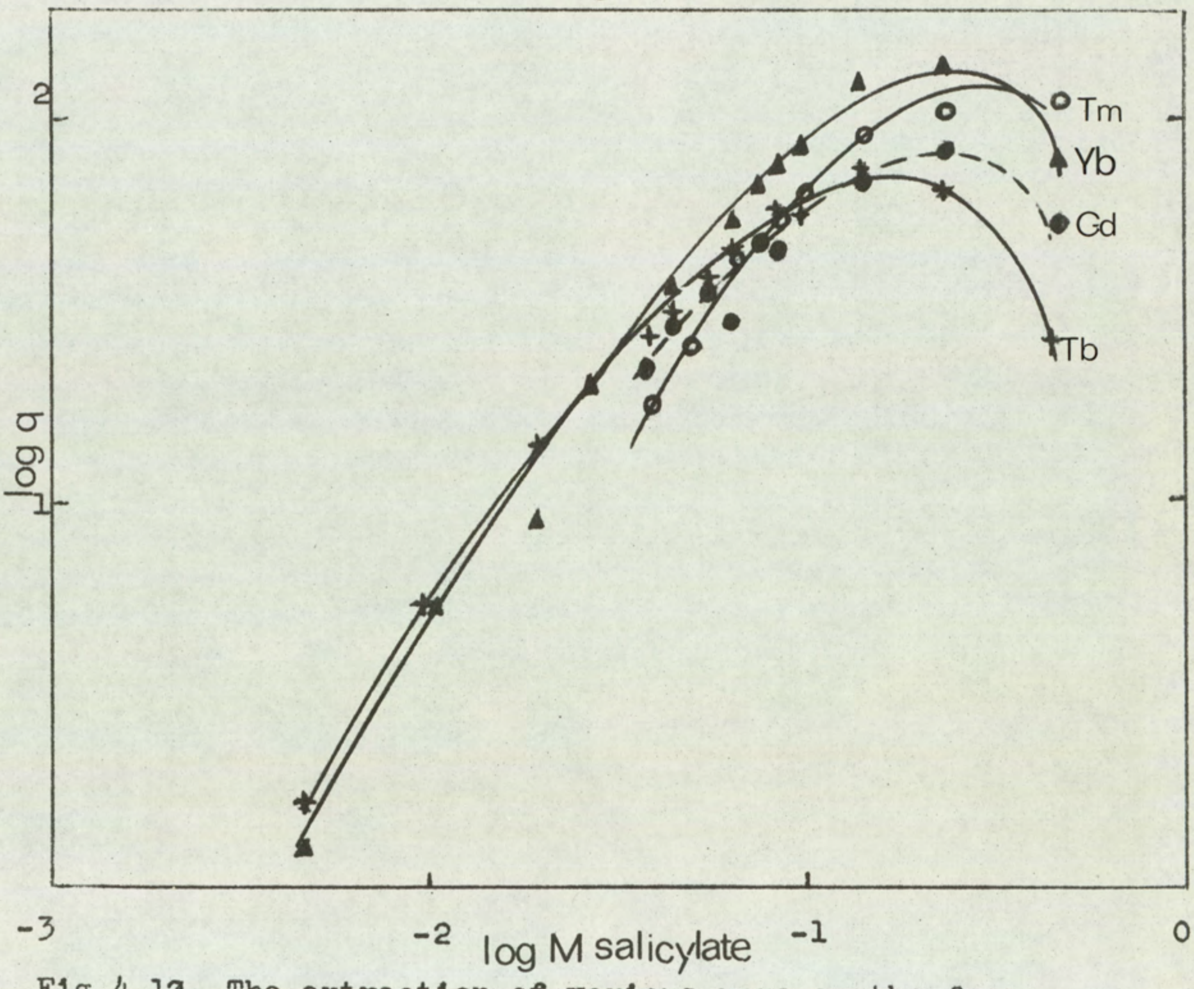


Fig.4.12. The extraction of various rare earths from sodium salicylate.

Results

Molarity NaOH = 0.082 M

Blank Titres Nil

Dissociation constant taken as $10^{-2.96}$

Aq. titre ml	Org. titre ml	Molarity aq. phase	Molarity aq. undiss.	Molarity org. phase	Dist. Coeff.
11.85	55.3	9.7×10^{-3}	7.25×10^{-3}	9.1×10^{-1}	126
10.70	54.6	9.5×10^{-3}	6.9×10^{-3}	8.9×10^{-1}	129

(b) Indirect Determination

Cerium solution is included in the experiment so that variation of distribution ratio could also be observed.

Solutions: Saturated salicylic acid in amyl alcohol

5×10^{-2} M sodium salicylate of ionic strength 0.2 M ($NaClO_4$)

5×10^{-5} M labelled cerium in water

Standard NaOH.

Method. A mixture of 10 ml salicylate and 1 ml metal were extracted with the following organic phases for 30 minutes.

	ml sat. HSal	plus	ml amyl alcohol
1	2		8
2	4		6
3	6		4
4	8		2
5	10		0

.Fig.4.13

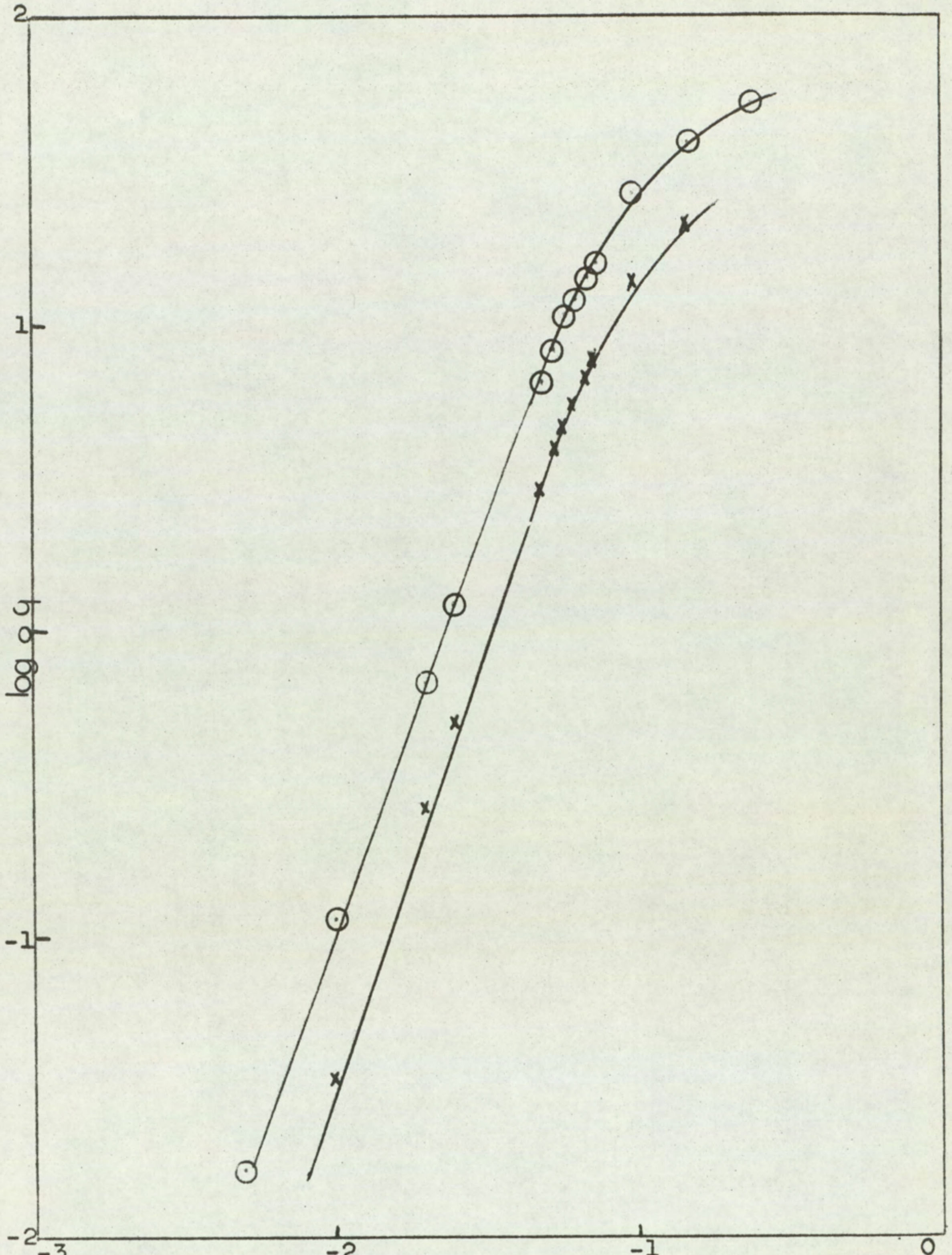


Fig.4.13. The extraction of lanthanum and praseodymium salicylates from chloride medium.

The layers were centrifuged apart and the organic phase removed. The aqueous phase was filtered to remove alcohol. An aliquot of each was titrated with standard NaOH.

(a) Organic layer 0.51 M NaOH

(b) Aqueous layer 0.015 M NaOH.

Assuming dissociation is suppressed by the 0.05 M salicylate, the distribution coefficient is given by the ratio of the molarities of acid as determined.

Org. titre ml	Aq. titre ml	Molarity org.	Molarity aq.	Dist. Coeff.
1.10	0.85	0.332	2.6×10^{-3}	129
1.85	1.70	0.560	5.1×10^{-3}	108
2.80	2.70	0.845	8.1×10^{-3}	103.5
3.80	3.80	1.15	1.15×10^{-2}	100
4.65	5.05	1.40	1.52×10^{-2}	92.2

Taking $pk_{HA} = 2.96$ (average of a number of quoted values), the pH theoretical can be calculated and compared with the observed.

pH_{THEORY}	pH_{OBSERVED}
4.28	4.28
3.985	3.98
3.78	3.75
3.63	3.60
3.51	3.48

4(ii) Determination of Phase Equilibrium for the System Water, Amyl Alcohol, Sodium Salicylate. (Fig. 4.1, 4.2 from Section 4.4)

Solutions: 2.0 M sodium salicylate in water

Distilled water

Amyl alcohol.

Method. Mixtures of sodium salicylate and water were titrated with amyl alcohol until cloudy. The end point was usually easy to see. The temperature of the solution in the burette was approximately 25°C and that in the titration vessel maintained at 25°C. At this temperature the density of the sodium salicylate solution was measured and the salicylate content determined by evaporating to dryness and weighing. The experiment was duplicated.

Results

Density amyl alcohol 0.800 g ml^{-1}

Analysis of salicylate solution:

weight of 5 ml	5.630 g
weight on drying	1.630 g
∴ weight of water	4.00 g.

ml Sodium salicylate	ml water	ml Amyl alcohol	% Sodium salicylate	% water	% Amyl alcohol
0	10	0.30		97.1	2.9
5	15	0.80	7.66	89.3	3.04
5	10	0.80	10.02	86.0	4.0
5	8	0.80	11.42	84.1	4.48
5	7	0.85	12.24	82.6	5.16
5	5	1.60	13.68	75.5	10.88
5	4	3.10	13.45	66.0	20.55
5	3	5.35	12.62	54.2	34.18
5	2	9.80	10.54	38.8	50.66

The Phase Equilibrium of Sodium Salicylate-Water Hexone Mixtures (Fig. 4.2)

The experiment was performed exactly as above.

Density of hexone 0.83 g ml^{-1}. Other weights as above.

Results

ml Sodium salicylate	ml Water	ml Hexone	Wt % Hexone
0.2	19.8	0.46	1.81
0.5	19.5	0.46	1.86
1.0	19.0	0.46	1.85
2.0	18.0	0.48	1.94
3.0	17.0	0.52	2.07
5.0	15.0	0.59	2.32
10.0	10.0	0.67	2.57
15.0	5.0	0.70	2.59
20.0	0.0	1.00	3.57

4(iii) The Distribution of Sodium Salicylate between Amyl Alcohol and Water

Sodium salicylate solutions $>$ about 0.2 M can be analysed quite satisfactorily by simply evaporating under an infra red lamp and weighing the solids. This is rapid and reproducible. It is unsufficiently accurate for low concentrations. In this experiment dilute solutions were labelled with ^{22}sodium and detected by gamma scintillation.

^{22}Sodium was available as metal in magnesium target material. It was removed by water and was thus present as highly active NaOH of negligible concentration. It was used to prepare ^{22}sodium salicylate by isotopic exchange, i.e. on dilution of inactive salicylate of high concentration.

Solutions: Labelled sodium salicylate

Amyl alcohol.

Method. Equal volumes of sodium salicylate and amyl alcohol were shaken together for 15 minutes. The temperature was maintained at 25°C before shaking and during separation, which took several minutes. Temperature control was not exercised during shaking but changes were slight since room temperature was 24°C. The layers were centrifuged apart and aliquots of each taken for salicylate determination.

Results

Concentrated Solutions

Original sodium salicylate M	Added wt. g 5 ml sodium salicylate	Extracted wt. g 5 ml sodium salicylate	% extracted	Dist. ratio
0.058	0.0465	0.0009	1.9	0.0192
0.196	0.1564	0.0072	4.6	0.0483
0.353	0.2826	0.0196	6.95	0.0747
0.403	0.3216	0.0249	7.75	0.0840
0.519	0.4141	0.0401	9.75	0.108

Labelled Solutions

Standard: 1.00 x 10^{-1} M sodium salicylate = 5023 counts per second in the 5 ml aliquot.

ml 0.1 M sodium salicylate in aq. phase (total 10 ml)	Activity counts s^{-1} in 5 ml aliquot (aq.)	Activity counts s^{-1} in 5 ml aliquot (org.)	% Extraction	Dist. ratio
1	502.1	7.1	1.39	0.0141
2.5	1254.2	22.2	1.72	0.0177
5	2464.0	55.5	2.20	0.0225
8	3927.0	111.3	2.76	0.0284

These are shown in Fig. 4.3.

Variation of the Percentage Sodium Salicylate which Partitions into Amyl Alcohol as a Function of the Free Acid Concentration of the Organic Phase

Solutions: 4.73×10^{-1} M sodium salicylate labelled with ^{22}sodium

1 M salicylic acid in amyl alcohol, diluted further to give concentrations 0.125 M, 0.375 M, 0.625 M, 0.875 M.

Method. Equal volumes of each phase were shaken together for 15 minutes. The phases were centrifuged apart and separated, the aqueous phase filtered to remove traces of alcohol. The activity of 5 ml aliquots of each phase was measured.

Results

Molarity organic acid	Activity organic aliquot counts s^{-1}	Activity aqueous aliquot counts s^{-1}	Dist. ratio q	% Extracted
0.125	65.24	684.8	0.0955	8.7
0.375	62.72	691.9	0.0905	8.3
0.625	61.01	696.1	0.0877	8.1
0.875	58.36	700.1	0.0833	7.64
1.00	60.14	704.8	0.0851	7.85

Presented in Fig. 4.4.

Conclusion. The conclusions of these experiments are discussed in Section 4.4.

4(iv) The Effect of Ionic Strength on the Extraction of Cerium Salicylate into Amyl Alcohol. (From Section 4.5)

The general form of this extraction experiment was common to all the measurements of rare earth distribution ratios in the salicylate system. As the ^{22}sodium extraction has also been described in full, needless repetition will be avoided in the experiments that follow, and only important differences will be emphasised.

Solutions: Sodium salicylate solutions approximately 0.05 M in salicylate, all equal, of varying ionic strength adjusted with $NaClO_4$

5×10^{-5} M labelled cerium solution in water

5×10^{-2} M salicylic acid in amyl alcohol.

Method. Reaction mixtures were prepared by adding 1 ml of cerium solution to 10 ml of each of the salicylate solutions and these were extracted at 25°C with 10 ml of organic phase. The extraction flasks were allowed to stand in a water bath for a total of two hours to equilibriate, during which they were shaken for 15 minutes to mix the phases. Separation on standing is slow and incomplete. The phases were centrifuged apart and the aqueous phases further treated by filtering through a dry paper and discarding the last few drops. Aliquots of each phase, 5 ml, were taken and counted.

The salicylate content of the aqueous phase was determined by diluting to approximately 5×10^{-4} M and developing the colour of $FeSal^{++}$ (see Chapter 1). The optical density was measured at 520 nm and compared to a standard. The pH was also measured to ensure that the solution was sufficiently neutral for the salicylate to be fully ionised. The results have already been tabulated in Table 4.1.

Results

M sodium salicylate	M sodium perchlorate	Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q
0.054	0.028	5794	436	13.28
0.054	0.056	6124	521	11.74
0.054	0.084	6156	572	10.77
0.054	0.112	6073	602	10.10
0.054	0.140	6018	651	9.25
0.054	0.560	5839	834	7.0

Assuming the organic phase activity is constant and taking it to be 1, the effect on q would be due to the product of activities $_{\text{CeSal}}\;{}^{2}_{\text{Sal}}$, which is in theory calculable from, for instance, the Davies modification of the extended Debye Huckel equations

$$- \log f_z = 0.5\, z^2 \left[\frac{\mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}} - 0.3\mu \right]$$

where f_z = mole fraction activity coefficient

z = charge on species

μ = ionic strength

and the constants have been approximated to the values shown.

Thus calling $\gamma_{\text{CeSal}}\gamma^2_{\text{Sal}} = \gamma'$

$$- \log \gamma' = 3 \left[\frac{\mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}} - 0.3\mu \right]$$

μ	$\frac{\mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}} - 0.3\mu$	γ'	$q_{corr.} = q/\gamma'$
0.082	0.193	0.264	50.3
0.110	0.215	0.226	52.0
0.138	0.229	0.206	52.3
0.166	0.239	0.192	52.6
0.194	0.248	0.180	51.4
0.614	0.252	0.175	40.0

Conclusion. The ionic species present appear to obey the Davies equation.

4(v) Time Required to Reach Equilibrium in the Extraction of Rare Earth Salicylates

Solutions: 4×10^{-2} M gadolinium in water

5.7×10^{-2} M sodium salicylate in water

Amyl alcohol.

Method. A 1 ml aliquot of metal solution was added to 10 ml salicylate and extracted for varying times. The flasks were immersed in the water bath at 25°C, removed as required and shaken with 10 ml amyl alcohol also at 25°C.

Extraction was halted by quickly centrifuging followed by separation of the layers by pipette. A 5 ml aliquot of each phase was counted.

Results

Time of Extraction (minutes)	pH	Total activity of aq. phase counts s^{-1}	Total activity of org. phase counts s^{-1}	% Extr.
0.5	7.06	37.83	1460	97.5
1.0	7.14	38.80	1447	97.5
2.0	7.12	37.60	1464	97.55
5.0	7.11	38.78	1433	97.40
10.0	7.12	37.76	1460	97.45
30.0	7.14	37.10	1443	97.5

Conclusion. Extraction is rapid and equilibrium reached in 30 seconds.

4(vi) Extraction of Light Rare Earths as Salicylates into Hexone at Ionic Strength 0.10 M. (From Sections 4.6 and 4.7)

Solutions: Sodium salicylate of varying concentration of ionic strength 0.1 by suitably mixing 5×10^{-1} M sodium salicylate, 5×10^{-1} M $NaClO_4$ and diluting.

In each case, 200 ml of water was added to the following mixtures:

ml salicylate	50	25	20	15	10	5	2.5	0.5
ml $NaClO_4$	0	25	30	35	40	45	47.5	49.5

Rare earth metals, suitably labelled, were prepared in 0.1 M $NaClO_4$ solution either by dissolving irradiated oxides (see Chapter 2) or labelling inactive solutions with stock activities.

Praseodymium	irradiated Pr_6O_{11}	10^{-3} M Pr
Neodymium	irradiated Nd_2O_3	10^{-3} M Nd

Cerium	labelled with ^{144}Ce	10^{-3} M Ce
Lanthanum	irradiated La_2O_3	10^{-3} M La

10^{-1} M salicylic acid in hexone

Method. The following mixtures were made to determine the equilibrium conditions after extraction.

ml metal	ml salicylate	ml hexone	ml salicylic acid
1	10	0	10
1	10	5	5
1	10	6	4
1	10	7	3
1	10	8	2

Extraction and separation were carried out as described in 4(iv) and 4(v), shaking twice for two minutes each time and counting 5 ml aliquots. The praseodymium experiment was duplicated to give an idea of experimental error. The remaining results are for one extraction at each concentration.

Results

Praseodymium

Test	Activity counts s^{-1}	q	Activity counts s^{-1}	q	D
1 aq.	4.10	17.1	3.39	19.5	13.1
org.	70.22		66.30		
2 aq.	10.58	5.73	10.18	5.51	3.9
org.	60.64		56.11		
3 aq.	14.11	3.81	13.89	3.81	0.0
org.	53.88		49.14		
4 aq.	20.66	2.26	19.47	2.24	0.45
org.	46.65		43.50		
5 aq.	33.27	0.84	32.24	6.83	1.20
org.	28.04		26.68		

where $$D = \frac{q_2 - q_1}{q_2 + q_1} \times 100.$$

The margin of error is acceptable for this type of extraction.

	Sal. Det. OD 1 cm	Dilution	Final conc. $M \times 10^4$	Original conc. $M \times 10^2$
1	0.705	5 to 1000	4.50	9.00
2	0.677	5 to 500	4.32	4.32
3	0.534	5 to 500	3.40	3.40
4	0.426	5 to 500	2.71	2.71
5	0.268	5 to 500	1.71	1.71

Cerium

	Activity counts s^{-1}	q	Sal. det. OD 1 cm	pH	Sal. conc. M x 10^2
1 aq.	37.43	19.7	0.682	5.33	8.70
org.	727.27				
2 aq.	124.44	4.58	0.675	5.10	4.30
org.	569.48				
3 aq.	186.84	2.66	0.534	5.05	3.40
org.	498.42				
4 aq.	272.39	1.58	0.425	5.10	2.71
org.	430.16				
5 aq.	394.22	0.575	0.264	4.90	1.70
org.	226.37				
6 aq.	520.48	0.102	0.113	4.60	0.73
org.	53.09				

Lanthanum

	Activity counts s^{-1}	q	Sal. det. OD 1 cm	pH	Sal. conc. M x 10^2
1 aq.	69.57	8.62	0.707	5.30	8.75
org.	598.47				
2 aq.	182.42	2.26	0.342	5.10	4.22
org.	412.30				
3 aq.	251.19	1.31	0.275	5.05	3.40
org.	329.14				
4 aq.	306.86	0.78	0.221	5.15	2.73
org.	239.25				
5 aq.	405.00	0.26	0.140	5.00	1.73
org.	103.40				
6 aq.	474.18	0.039	0.064	4.85	0.79
org.	18.56				

Neodymium

	Activity counts s^{-1}	q	Sal. det. OD 1 cm	pH	Sal. conc. M x 10^2
1 aq.	100.36	16.28	0.715	5.2	8.83
org.	1628.27				
2 aq.	357.86	3.48	0.278	5.1	3.43
org.	1003.59				
3 aq.	459.39	2.04	0.225	5.3	2.78
org.	940.82				
4 aq.	1249.67	0.51	0.142	5.0	1.74
org.	640.42				
5 aq.	847.81	0.202	0.068	5.0	0.84
org.	171.52				

Recheck of OD of salicylate 5×10^{-4} M, OD 1 cm = 0.810.

Calculations According to Leden's Method

For convenience in tabulation,
salicylate concentration is abbreviated to A

Lanthanum

$A \times 10^2$	A^3	A^2	$\frac{A^3}{q} \times 10^5$	$\frac{A^2}{q} \times 10^4$	α_{MSal}	$E \times 10^{-4}$
8.75	6.59×10^{-4}	7.65×10^{-3}	7.77	8.87		
4.22	7.45×10^{-5}	1.77×10^{-3}	3.30	7.84	3.30	9.96
3.40	3.93×10^{-5}	1.15×10^{-3}	3.00	8.80	2.86	9.44
2.73	2.04×10^{-5}	7.47×10^{-4}	2.62	9.58	2.49	9.46
1.73	5.17×10^{-6}	2.99×10^{-4}	1.02	11.70	1.94	9.60
0.79	4.93×10^{-7}	6.24×10^{-5}	1.26	1.60	1.43	11.33

Plotting as co-ordinates: $f^{-1} = 1.05 \times 10^{-5}$ and $f^{-1}\beta_1 = 5.7 \times 10^{-4}$ from which $\beta_1 = 54.7$.

$$E \text{ mean} = 9.61 \times 10^4$$

$$\frac{E \text{ mean}}{\beta_1} = 1.75 \times 10^3 = E'$$

Cerium

$A \times 10^2$	A^3	A^2	$\frac{A^3}{q} \times 10^5$	$\frac{A^2}{q} \times 10^4$	α_{MSal}	$E \times 10^{-5}$
8.70	6.61×10^{-4}	7.60×10^{-3}	3.36	3.86		
4.30	7.91×10^{-5}	1.84×10^{-3}	1.73	4.00	3.59	2.67
3.40	3.93×10^{-5}	1.16×10^{-3}	1.47	4.37	3.05	2.07
2.71	1.99×10^{-5}	7.35×10^{-4}	1.26	4.66	2.64	2.10
1.70	4.90×10^{-6}	2.90×10^{-4}	0.854	5.04	2.02	2.38
0.73	3.90×10^{-7}	0.503×10^{-4}	0.382	5.00	1.44	3.77

Plotting as co-ordinates: $f^{-1} = 4.8 \times 10^{-6}$ and $f^{-1}\beta_1 = 2.9 \times 10^{-4}$ from which $\beta_1 = 60.4$

$$E = 2.15 \times 10^5$$

$$E' = 3.48 \times 10^3$$

For praseodymium and neodymium there was insufficient indication of free metal being present to do this calculation. Thus $q/A^2 = E'$ can be directly read from the logarithmic plot of q versus salicylate concentration.

Praseodymium

	q/A^2	
	Set 1	Set 2
1	2.11×10^3	2.40×10^3
2	3.08×10^3	2.96×10^3
3	3.29×10^3	3.06×10^3
4	3.08×10^3	3.05×10^3
5	2.88×10^3	2.85×10^3

Mean value of
$E' = 2.88 \times 10^3$

Neodymium

	$q/A^2 = E'$
1	2.09×10^3
2	2.92×10^3
3	2.63×10^3
4	1.60×10^3
5	2.88×10^3

Mean value discounting
result 4 = 2.63×10^3

4(vii) The Extraction of Some Rare Earths as Salicylates into Amyl Alcohol at Constant Ionic Strength 0.6 M ($NaClO_4$)

Solutions: 6.15×10^{-1} M sodium salicylate
6.15×10^{-1} M $NaClO_4$
5×10^{-5} M labelled rare earths in 0.6 M $NaClO_4$
6×10^{-1} salicylic acid in amyl alcohol.

Method. A series of solutions of salicylate were made by mixing the above solutions to give a number of differing salicylate concentrations at constant ionic strength.

The same dilutions were performed with the salicylic acid and amyl alcohol. The extraction was made with salicylic acid of approximately equal concentration to the salicylate and always in the same ratio.

1 ml of metal plus 10 ml salicylate were extracted at 25°C by the techniques already described in 4(iv), 4(v). The phases were separated and 5 ml aliquots taken for radioactivity determination, pH and salicylate concentration, by the colorimetric method using Fe^{3+}. A full calibration check was made on the salicylate determination and found to be identical to that made previously, 1(ii).

Dilutions of the aqueous phases for salicylate determination were as follows:

1	x 400	6	x 100
2	x 200	7	x 20
3	x 200	8	x 10
4	x 200	9	x 10
5	x 100	10	x 2

Results

Terbium

	Activity counts s^{-1}	q	Sal. det. OD 1 cm	Sal. conc. $M \times 10^2$	pH	$\frac{A^2}{q} \times 10^4$ (Leden)
1 org.	4983	97.5	0.444	54.4	4.80	
aq.	51.1					
2 org.	4980	112.0	0.404	27.0	4.38	
aq.	44.6					
3 org.	5067	63.8	0.223	13.70	4.80	
aq.	79.4					
4 org.	4970	48.9	0.175	10.70	4.86	
aq.	101.5					
5 org.	4881	30.95	0.266	8.15	4.87	2.14
aq.	157.8					
6 org.	4706	14.86	0.176	5.37	4.95	1.94
aq.	317.6					
7 org.	3674	3.20	0.440	2.70	5.26	2.28
aq.	1149					
8 org.	1328	0.433	0.357	1.09	5.43	2.75
aq.	3066					
9 org.	389.5	0.101	0.187	0.574	6.53	3.27
aq.	3838					
10 org.	142	0.0354	0.523	0.321	6.60	2.94
aq.	4012					

Conclusion. There is little evidence here of free metal in solution. Therefore, $E' = 3.93 \times 10^3$, β_1 not calculable.

A log plot of q versus salicylate concentration is given in Fig. 4.10, together with the results of 4(xii) and 4(xiv).

Neodymium

	Activity counts s^{-1}	q	Sal. det. OD 1 cm	Sal. conc. M x 10^2	pH	$\frac{A^2}{q} \times 10^4$ (Leden)
1 org.	125.5	42.5	0.412	50.50	4.80	
aq.	2.94					
2 org.	129.01	45.1	0.407	25.00	4.70	
aq.	1.98					
3 org.	124.5	46.65	0.203	12.50	4.75	
aq.	2.67					
4 org.	126.9	37.9	0.162	9.94	4.77	
aq.	3.74					
5 org.	124.3	23.07	0.245	7.52	4.80	2.45
aq.	5.39					
6 org.	120.8	12.24	0.163	4.97	4.80	2.02
aq.	9.83					
7 org.	95.83	2.89	0.403	2.47	4.92	2.11
aq.	33.15					
8 org.	32.70	0.42	0.334	1.02	5.17	2.47
aq.	78.50					
9 org.	10.23	0.105	0.108	0.515	5.35	2.52
aq.	97.62					
10 org.	5.93	0.043	0.478	0.292	6.10	1.98
aq.	137.8					

Conclusion. Again there is no free metal present.

$$E' = 4.43 \times 10^4$$

β_1 not calculable.

Ytterbium

	Activity counts s^{-1}	q	Sal. det. OD 1 cm	Sal. conc. M x 10^{2}	pH	$\frac{A^2}{q} \times 10^4$ (Leden)
1 org.	5147	76.2	0.440	54.00	4.72	
aq.	67.5					
2 org.	5198	96.3	0.440	27.00	4.60	
aq.	54.0					
3 org.	5215	55.5	0.221	13.60	4.65	
aq.	94.1					
4 org.	5174	41.9	0.175	10.70	4.60	
aq.	123.7					
5 org.	5018	27.1	0.267	8.20	4.60	2.48
aq.	185					
6 org.	4889	12.84	0.178	5.46	4.60	2.32
aq.	380.9					
7 org.	3445	2.89	0.435	2.66	4.68	2.45
aq.	1327					
8 org.	1274	0.356	0.355	1.09	4.64	3.31
aq.	3578					
9 org.	356.4	0.080	0.182	0.559	4.75	3.90
aq.	4431					
10 org.	121.4	0.026	0.510	0.302	4.80	3.51
aq.	4631					

Conclusion

$$E' = 3.34 \times 10^4$$

β_1 not calculable.

Cerium

	Activity counts s^{-1}	q	Sal. det. OD 1 cm	Sal. conc. M x 10^2	pH	$\frac{A^2}{q} \times 10^4$ (Leden)
1 org.	6665	61.7	-	-	4.68	
aq.	107.1					
2 org.	6651	61.8	0.440	27.00	4.70	
aq.	107.6					
3 org.	6510	32.6	0.225	13.70	4.70	
aq.	199.8					
4 org.	6496	23.75	0.174	10.70	4.70	
aq.	273.6					
5 org.	6296	15.00	0.261	8.0	4.73	4.27
aq.	419.4					
6 org.	5839	7.00	0.175	5.37	4.80	4.11
aq.	834.8					
7 org.	4090	1.66	0.442	2.70	4.83	4.39
aq.	2459					
8 org.	1154	0.228	0.364	1.12	4.79	5.48
aq.	5043					
9 org.	33.8	0.0587	0.194	0.580	4.96	5.72
aq.	5768					
10 org.	30.0	0.022	0.556	0.340	5.90	5.27
aq.	5913					

Conclusion

$$E' = 2.05 \times 10^4$$

β_1 not calculable.

4(viii) The Extraction of Rare Earths from the Chosen Buffer at Various pH Values. (From Section 4.6 and Fig. 4.7)

(a) The extraction of Ce from 0.01 M sodium salicylate into salicylic acid in amyl alcohol.

Solutions: A number of amyl alcohol solutions of salicylic acid were prepared as follows.

1 10 ml of M/1 HSal
2 8 ml of M/1 HSal + 2 ml amyl alcohol
3 5 ml of M/1 HSal + 5 ml amyl alcohol
4 1 ml of M/1 HSal + 9 ml amyl alcohol
5 0.1 ml of M/1 HSal + 10 ml amyl alcohol
6 10 ml pure amyl alcohol.

Method. Each solution was used to extract a mixture of 1 ml of 10^{-3} M cerium and 10 ml of 0.01 M sodium salicylate. The technique adopted was as for previous extraction experiments of this type and the phases were separated by centrifuging and filtering before counting a 5 ml aliquot of each. The pH of each aqueous phase was measured; two aliquots were diluted to about 5×10^{-4} M and the salicylate determined colorimetrically with FeIII. The results are tabulated below and expressed graphically, Fig. 4.7.

Results

Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q	pH	Sal. det. OD 1 cm Dil. x 50	Sal. conc. M
18.06	19.51	0.905	3.2		
18.37	19.88	0.905	3.3		
20.01	17.35	1.20	3.52		
21.61	10.20	2.95	4.15	0.331	0.0102
18.23	6.28	7.18	5.5	0.335	0.0102
18.58	5.62	11.0	6.2		

At the highest pH there is clearly some loss of metal and these figures are subject to larger errors than the others.

(b) The extraction of ytterbium from 10^{-1} M salicylate into salicylic acid in amyl alcohol.

This experiment is essentially the same as that above for cerium. As the stock active ytterbium was more dilute and of low specific activity, a 10 ml aliquot of metal was added to 1 ml of more concentrated salicylate about 0.8 M. The 0.8 M acid was omitted.

Results

Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q	pH	Sal. det. OD 1 cm Dil. x 250	Sal. conc. M
624.86	15.22	41.1	3.90		
623.85	12.21	51.1	4.15	0.292	7.1×10^{-2}
612.21	94.3	65.0	5.00	0.300	7.2×10^{-2}
546.92	61.90	8.83	6.25		
551.42	59.90	9.20	6.20		

Result also shown graphically in text, Fig. 4.7.

Conclusion. In the light of the pattern indicated by the cerium and the more serious effects observed with ytterbium at high pH, it was decided to test another lighter earth, neodymium in 10^{-2} M sodium salicylate and other heavy earths, thulium and gadolinium, at high pH.

Reaction mixtures were as before, i.e. 10 ml of salicylate, 1 ml of metal of negligible concentration, and salicylic acid in amyl alcohol having the following concentrations:

1 1 M
2 10^{-1} M
3 10^{-2} M
4 10^{-3} M
5 Pure solvent
6 10^{-2} M NaOH in amyl alcohol.

Not all of these solutions were used in the case of thulium and gadolinium.

Results

Neodymium

Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q	pH	Sal. det. OD 1 cm Dil. x 50	Sal. conc. M
342.52	148.54	2.30	3.22		
368.35	104.48	3.52	4.4		
379.90	95.24	3.99	5.13	0.432	0.0134
369.12	98.68	3.74	5.30		
314.01	137.77	2.27	6.10		
262.80	loss of metal		6.50		

Gadolinium

Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q	pH	Sal. det. OD 1 cm Dil. x 50	Sal. conc. M
118.82	12.44	9.55	5.15		
111.08	15.46	7.18	5.85	0.445	0.0138
66.72	40.97	1.63	6.50		
2.74	0.25	loss of metal	9.70		

Thulium

Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q	pH	Sal. det. OD 1 cm Dil. x 50	Sal. conc. M
211.82	10.04	21.2	5.15		
198.29	15.29	12.96	5.72		
160.79	20.49	7.89	6.00		
7.46	3.16	loss of metal	8.90	0.448	0.0140

Conclusion. Hydrolysis causes extraction to diminish at high pH. Loss of metal by adsorption created a serious problem in this experiment. A full discussion is given in Section 4.6 and Fig. 4.7.

4(ix) To Determine the Amyl Alcohol Molarity of Salicylic Acid Solutions

Method. The density of wet amyl alcohol at 25°C and that of a number of salicylic acid solutions in this solvent were determined by weighing known volumes measured at 25°C (water bath). The percentage of amyl alcohol and hence the molarity was calculated in each case taking the water content of the solvent to be 10.0%.

Results

	Observed Density	Molarity A.A.
Amyl alcohol saturated with H_2O	0.828	8.46
10^{-1} M salicylic acid solution	0.826	8.30
5.23×10^{-1} M salicylic acid solution	0.847	7.92
1.305 M salicylic acid solution	0.889	7.21

Density differences are slight until molarity of salicylic acid is about 0.5. The general trend is obvious from the graphical presentation of results, Fig. 4.8.

4(x) The Extraction of Rare Earth Metals with more Dilute Solutions of Amyl Alcohol (From Section 4.6 and Fig. 4.9)

Experiments were conducted to investigate the effects of diluting the amyl alcohol extractant with inert solvent. Among those used were benzene, xylene, carbon tetrachloride and chloroform. Hexone was diluted and checked in the same way. Extraction with diluted solvent proved to be very difficult. Conclusions could only be drawn from the experiments having amyl alcohol diluted with chloroform or carbon tetrachloride. In all the other cases separation of the layers was too awkward to be adequately achieved with the apparatus available. The chloroform amyl alcohol experiment is outlined below.

Solutions: Amyl alcohol in chloroform was prepared as follows:

1	10% by volume
2	20% by volume
3	40% by volume
4	80% by volume.

Method. A 10 ml aliquot of each organic phase was shaken in a pear-shaped flask for 30 minutes with 5 ml of 10^{-1} M sodium salicylate and 5 ml 5×10^{-4} M cerium. The phases were separated and 5 ml aliquots counted in order to measure q.

Results

Activity org. layer counts s^{-1}	Activity aq. layer counts s^{-1}	q	Amyl alcohol molarity	pH
78.0	977.2	0.078	0.92	6.9
375.7	693.3	0.542	1.84	7.0
731.2	329.7	2.22	3.68	7.1
914.9	50.94	17.9	7.36	6.85

Conclusion. These results show no evidence of metal loss even at this pH. A log plot of q versus amyl alcohol molarity, Fig. 4.9, is linear and of slope 2.65, and indicates possible co-ordination of the solvent.

4(xi) Reproducibility of the Extraction of Terbium Salicylate at High Ionic Strength (0.5 M $NaClO_4$)

Solutions: 5×10^{-5} M labelled terbium in 0.5 M $NaClO_4$

0.05 M sodium salicylate in 0.5 M $NaClO_4$

0.05 M salicylic acid in amyl alcohol.

Method. The following six identical solutions of terbium in 5×10^{-2} M sodium salicylate of ionic strength 0.6, were extracted as in 4(v). Equal volumes of each were taken for counting. The salicylate concentration of the aqueous phase was determined and the pH measured.

Results

Test	Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q	pH	Sal. det. OD 1 cm Dil. x 10
1	1723.1	281.9	6.11	4.79	0.285
2	1739.7	266.4	6.53	4.79	0.290
3	1726.6	291.2	5.39	4.82	0.290
4	1696.6	286.8	5.92	4.82	0.290
5	1692.9	287.0	5.90	4.80	0.290
6	1750.3	280.3	6.24	4.74	0.290

Mean 1721.5 282.3

Stand. Dev. 24.10 8.70

1.399% 3.084%

Conclusion. The largest part of the error arises from contamination of the aqueous phase.

4(xii) The Extraction of Rare Earths from Solutions Containing Only the Metal and Sodium Salicylate (From Section 4.8)

These experiments were similar to those already described for extraction at constant ionic strength. The only major experimental difference was that the salicylate concentration of each stock solution was accurately known at the start and was not determined again after extraction. In the case of the more concentrated solutions, however, a correction was made to account for any loss due to partition into the organic layer.

Solutions: Metal solutions - approximately 5×10^{-5} M in water.

Sodium salicylate solutions - a series ranging from 1 M to 6×10^{-3} M in water.

Salicylic acid - solutions having the same concentrations as above in amyl alcohol.

Method. The reaction mixture was 5 ml of metal and 5 ml of salicylate extracted with the appropriate acid solution, as previously described, so that the resultant pH of the aqueous phases were all equal, about 4.7.

After separation, 5 ml aliquots were taken and counted. The pH of each aqueous phase was measured.

Results

Ytterbium

Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q	Molarity salicylate added	Molarity salicylate equil.	pH
Set 1					
1822	21.37	85.3	0.503	0.458	4.53
1829	12.20	150	0.251	0.232	4.60
1823	13.10	133	0.151	0.140	4.63
1806	19.95	90.5	0.100	0.097	4.70
1806	22.10	81.7	0.090	0.088	4.72
1804	24.94	72.3	0.080	0.078	4.70
1790	30.45	58.8	0.070	0.068	4.70
1795	39.90	44.9	0.060	0.0585	4.69
1781	46.64	38.2	0.050	0.049	4.70
1751	57.26	30.6	0.040	0.039	4.76
1859	87.91	21.2	0.030	0.029	4.76
996.1	219.7	4.40	0.020	0.020	4.72
1197	225.6	5.30	0.010	0.010	4.75
663.5	513.6	1.29	0.005	0.005	4.72
Set 2					
576.0	32.60	17.68	0.027	0.025	4.73
561.2	39.71	14.14	0.024	0.024	4.75
566.1	46.91	12.06	0.0211	0.021	4.75
499.9	52.81	9.47	0.018	0.018	4.75
531.3	59.31	8.96	0.016	0.016	4.75
492.1	50.18	9.81	0.014	0.014	4.75
374.97	86.91	4.31	0.009	0.009	4.8
324.82	116.5	2.78	0.008	0.008	5.1

Terbium

Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q	Molarity salicylate		pH
			added	equil.	
5853.9	199.2	29.6	0.503	0.458	4.50
6156	86.53	71.5	0.251	0.232	4.55
6107	74.26	82.2	0.151	0.140	4.58
5911	96.89	61.0	0.100	0.097	4.67
5909	92.40	63.9	0.090	0.088	4.69
5830	107.3	54.3	0.080	0.078	4.72
5841	117.4	49.7	0.070	0.068	4.80
5763	139.9	41.2	0.060	0.0588	4.75
5767	175.6	32.85	0.050	0.049	4.77
5734	201.2	28.45	0.040	0.039	4.77
5579	278.8	20.3	0.030	0.029	4.80
5307	355.0	15.0	0.020	0.020	4.92
4087	739.0	5.56	0.010	0.010	5.09
2359	1440	1.64	0.005	0.005	5.70
1854	2187	0.85	0.004	0.004	5.65
1202	2078	0.38	0.003	0.003	5.59

These results are compared to Experiments 4(vi) and 4(xiv) in Fig. 4.10.

Gadolinium

Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q	Molarity salicylate added	equil.	pH
1075.6	17.95	59.8	0.503	0.458	4.53
1062	11.56	91.9	0.251	0.232	4.60
1063	13.70	77.5	0.151	0.140	4.66
1060	15.68	67.6	0.10	0.097	4.66
1068	21.94	48.7	0.09	0.088	4.66
1052	20.14	52.2	0.08	0.078	4.69
1043	31.40	33.2	0.07	0.068	4.70
1048	28.01	37.4	0.06	0.0585	4.71
1040	33.85	30.73	0.05	0.049	4.76
1026	43.37	23.67	0.04	0.039	4.75

Thulium

Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q	Molarity salicylate added	Molarity salicylate equil.	pH
2276	18.34	124	0.501	0.458	4.46
2312	19.90	116.2	0.252	0.230	4.52
2198	21.86	100.5	0.151	0.140	4.61
2201	32.21	68.4	0.10	0.097	4.64
2205	37.2	59.6	0.09	0.088	4.65
2201	41.47	53.1	0.08	0.078	4.67
2165	45.22	47.9	0.07	0.068	4.70
2131	79.77	26.72	0.05	0.049	4.73
2114	106.1	19.92	0.04	0.039	4.73
684.6	838.3	0.816	0.045	0.005	5.65
479.7	798.3	0.60	0.004	0.004	6.10
324.2	1006.8	0.319	0.003	0.003	6.00
121.6	803.5	0.151	0.002	0.002	6.35
19.21	1047	0.018	0.001	0.001	-

Conclusion. The results as above are shown graphically in Figs. 4.10, 4.11, 4.12, and are discussed in Section 4.8.

4(xiii) The Extraction of La and Pr from Chloride Solution (From Section 4.8)

These experiments had the same general form as those already outlined. The salicylate solutions were all made to constant ionic strength 1 M by diluting stock 1 M salicylate with 1 M KCl. In extraction this became diluted to 0.5 by the addition of 5×10^{-5} M metal in water. Thus ionic strength was constant and chloride variable. The extraction and separation were as already described in 4(v), and in common with 4(xiii) the salicylate at equilibrium was calculated.

It was found that in counting the ^{142}praseodymium either brehmstrahlung or photopeak radiation could be counted equally well.

Results

Lanthanum

Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q	Molarity salicylate		pH
			added	equil.	
5379.5	104.54	51.5	0.25	-	4.70
5270.4	247.84	21.3	0.175	-	4.74
5736.1	383.20	13.40	0.10	0.6077	4.76
4838.2	643.82	7.51	0.075	0.073	4.77
4719.4	743.87	6.34	0.070	0.068	4.77
4611.3	861.92	5.35	0.065	0.0635	4.78
4455.3	983.38	4.53	0.060	0.0585	4.78
4285.8	1191.4	3.58	0.055	0.054	4.79
4063.3	1434.5	2.83	0.050	0.049	4.79
1709.9	3618.3	0.47	0.025	0.025	4.80
1062.9	4244.0	0.25	0.020	0.020	4.80
177.14	5122.7	0.034	0.010	0.010	4.86
23.83	5274.1	0.604	0.005	0.005	4.84

Praseodymium

No allowance has been made for the decay of ^{142}praseodymium but related pairs were counted adjacently for only 200s. The activity is that of the 1.54 MeV gamma ray only.

Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q	Molarity salicylate		pH
			added	equil.	
354.3	6.79	52.12	0.25	-	4.73
357.7	9.41	38.0	0.175	-	4.78
344.9	13.20	26.12	0.10	0.097	4.77
334.1	21.73	15.38	0.075	0.073	4.80
333.9	26.15	12.78	0.070	0.069	4.84
323.9	28.72	11.28	0.065	0.064	4.82
325.5	32.13	10.13	0.060	0.0585	4.82
312.3	39.60	7.89	0.055	0.0545	4.82
301.9	47.72	6.31	0.050	0.049	4.83
177.4	158.7	1.12	0.025	0.025	4.96
129.1	210.4	0.614	0.020	0.020	5.15
29.3	297.2	0.099	0.010	0.010	5.48
5.59	317.9	0.017	0.005	0.005	5.30
0.66	321.0	0.002	0.0025	0.0025	6.30
0.235	327.9	0.0007	0.001	0.001	6.36

Calculations of extraction constants.

Concentration salicylate $M \times 10^2 (A)$	Praseodymium		Lanthanum	
	$\frac{q}{A^2} \times 10^3$	$\frac{q}{A^3} \times 10^4$	$\frac{q}{A^2} \times 10^3$	$\frac{q}{A^3} \times 10^4$
9.7	2.78		1.42	
7.3	2.89		1.41	
6.9	2.70		1.33	
6.4	2.76		1.31	
5.85	2.96		1.32	
5.45	2.66	4.76		2.21
4.9	2.63	5.35		2.40
2.5	1.80	7.18		3.00
2.0		7.68		3.13
1.0		9.90		3.40
0.5		1.36		3.18

From which:

$E'_{Pr} = 2.81 \times 10^3$ $\qquad$ $E'_{La} = 1.36 \times 10^3$

$E_{Pr} = 8.08 \times 10^3$ $\qquad$ $E_{La} = 3.18 \times 10^4$

$\beta_1 = 28.8$ $\qquad$ $\beta_1 = 23.4$

Approximate values of chloride stability constant.

$$M(Cl) = \frac{54.7^{+}}{23.4} = 2.32$$

$$\therefore \quad M(Cl) = \frac{1.32}{0.5^{*}} = 2.64$$

$^{+}$ From Table 4.1

* Approximate average chloride concentration.

Conclusion. Chloride complexes are formed which diminish the stability of the aqueous salicylate complexes, and consequently the extraction. The results are summarised in Table 4.3.

4(xiv) The Extraction of Terbium from Chloride Solution

Solutions: 5×10^{-5} M terbium in water

1 M sodium salicylate

1 M KCl

1 M salicylic acid in amyl alcohol

Amyl alcohol.

Method. A series of salicylate solutions were prepared by diluting the sodium salicylate with the KCl. Identical dilutions were made using the salicylic acid and amyl alcohol.

A mixture of 1 ml metal and 5 ml salicylate at each concentration was extracted at 25°C for 5 minutes, with an equal volume of acid solution of the same concentration. The phases were separated and analysed according to the methods described in 4(iv) and 4(v). The results are tabulated below and presented in Fig. 4.10 for comparison with extractions from other media.

Results

Activity aq. phase counts s^{-1}	Activity org. phase counts s^{-1}	q	Salicylate concentration M x 10
3.48	420.6	120.8	3.35
3.63	421.9	116	3.17
3.73	420.7	112.7	3.18
4.04	422.2	104.4	3.01
3.90	421.5	108.1	2.59
4.19	422.0	100.9	2.32
4.25	390.1	91.9	2.00
5.04	391.2	77.7	1.62
6.35	387.8	61.0	1.36
10.54	391.4	37.1	1.00
23.95	364.3	15.2	0.70
84.77	267.8	3.16	0.28

Conclusion. These values are slightly lower than those obtained in perchlorate solution. However, the difference is too slight to accurately estimate values of the chloride stability constants in this concentration of salicylate. The extraction curve is shown in Fig. 4.10.

CHAPTER 5

Substoichiometric Reactions in Salicylate Solutions

5.1 Theory

The previous Chapter describes the essential differences between solvent extraction into polar and non-polar solvents. This Chapter is concerned with substoichiometric reactions taking place under the first condition, and the added limitations compared with those outlined in Chapter 3, when considering possible analytical methods.

Firstly, it is essential to consider again the equilibria outlined in Chapter 3, with respect to the salicylate system. The equations can be expressed quite simply as follows.

The extraction reaction is

$$M + 3Sal^- \longrightarrow MSal_{3\,o} \qquad (1)$$

If the solvent effect is constant, the extraction constant is given by

$$E = \frac{[MSal_3]_o}{[M][Sal]^3} \qquad (2)$$

However, aqueous complexes are known to be formed and, therefore,

$$E_2 = \frac{[MSal_3]_o}{[M'][Sal]^3} \qquad (3)$$

$$E_2 = \frac{E}{\alpha_{M(Sal)}} \qquad (4)$$

As before, the competing reaction is

$$M + Y \rightarrow MY$$

The stability constant, previously called K_2 (Chapter 3) is given by

$$K_2 = \frac{[MY]}{[M][Y]} \tag{5}$$

Now $$K_2' = \frac{[MY]}{[M'][Y]} = \frac{K_2}{\alpha_{M(Sal)}} \tag{6}$$

and if this is made conditional with respect to pH, again using K_3 as in Chapter 3

$$K_3' = \frac{[MY]}{[M'][Y']} = \frac{K_2}{\alpha_{M(Sal)}\alpha_{Y(H)}} \tag{7}$$

Now $$\frac{E_2}{K_3'} = \frac{[MSal_3]_o[M'][Y']}{[M'][Sal]^3[MY]} \tag{8}$$

or $$E_x = \frac{[MSal_3]_o[Y']}{[Sal]^3[MY]} \tag{9}$$

which represents the conditional reaction in terms of pH of

$$MY + 3Sal \rightarrow MSal_{3_o} + Y$$

that is the breakdown of the required substoichiometric complex MY.

The previous Chapter shows that reaction (1) is not easy to predict, especially in the presence of other ions in noticeable concentration. However, under chosen conditions, the variation of extraction with salicylate concentration is not difficult to assess experimentally, as has also been shown.

5.2 Substoichiometric Reactions and the Extraction of Cerium III Salicylate

Consider the extraction of rare earth metals from solutions containing only salicylate buffered with salicylic acid. These results have already been quoted in Chapter 4 to demonstrate ionic strength effects. Particular attention is paid here to these conditions giving good extraction.

The equation relating q to % extraction is

$$\% \text{ Extraction} = \frac{100\,q}{\left(q + \frac{V_a}{V_o}\right)} \qquad (10)$$

Fig. 5.1 shows the % extraction as a function of q for various values of V_a/V_o, which is referred to as 'the volume ratio' in this text.

The extraction of cerium with salicylate concentration is shown in Fig. 5.2, from 5(i), for both hexone and amyl alcohol solvent. For cerium the alcohol is the best extractant, but this is not a general rule. The higher members are not only increasingly extractable but also increasingly soluble in hexone.

At volume ratio 1/10, the 99.9% extraction demanded by substoichiometry is achieved at salicylate concentration 0.4 M for amyl alcohol at pH 5. Using less free acid, this value can be

Fig.5.1

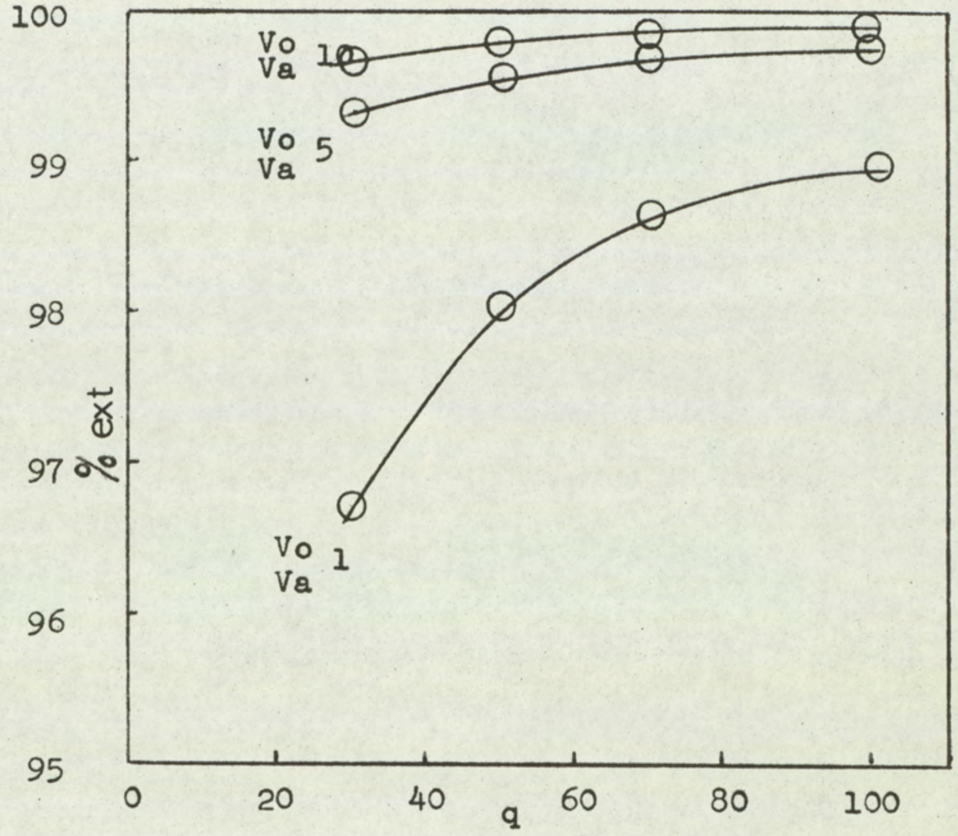


Fig.5.1. Percentage extraction for various values of q.

as low as 0.15 M. Using hexone, the extraction is not good enough for 99.9% removal even under the most concentrated conditions shown, until the volume ratio is 1/20.

In studying substoichiometry in the system EDTA-TTA, established data allowed the choice of reagent concentration to be made with some confidence. From this work it was concluded that the reaction between MY and TTA in xylene was slow to reach equilibrium and could easily be made negligible and thus ignored.

Clearly in the present study this does not apply. One has less freedom of choice in extraction conditions and the time to reach equilibrium will be shorter. Therefore, in contrast to the TTA experiments it was decided to measure directly the extent to which MY complexes were affected by the salicylate extraction system, under usable analytical conditions.

From a knowledge of the EDTA stability constants, and the approximate values of the salicylate stability constants, it is certain that rare earth metals are quantitatively complexed by an equivalent of EDTA even in the presence of a large excess of salicylate. It was observed that in 5 minutes the reaction

$$\mathrm{CeY} + 3\mathrm{Sal} \longrightarrow \mathrm{CeSal}_{3_o}$$

had proceeded far enough toward completion for the equilibrium

$$E_x = \frac{\left[\mathrm{CeSal}_3\right]_o \left[\mathrm{Y'}\right]}{\left[\mathrm{CeY}\right]\left[\mathrm{Sal}\right]^3}$$

to be readily identified in a plot of log q versus log $[\mathrm{Y'}]$. The time is arbitrary, and was chosen as being sufficient for

Fig.5.2

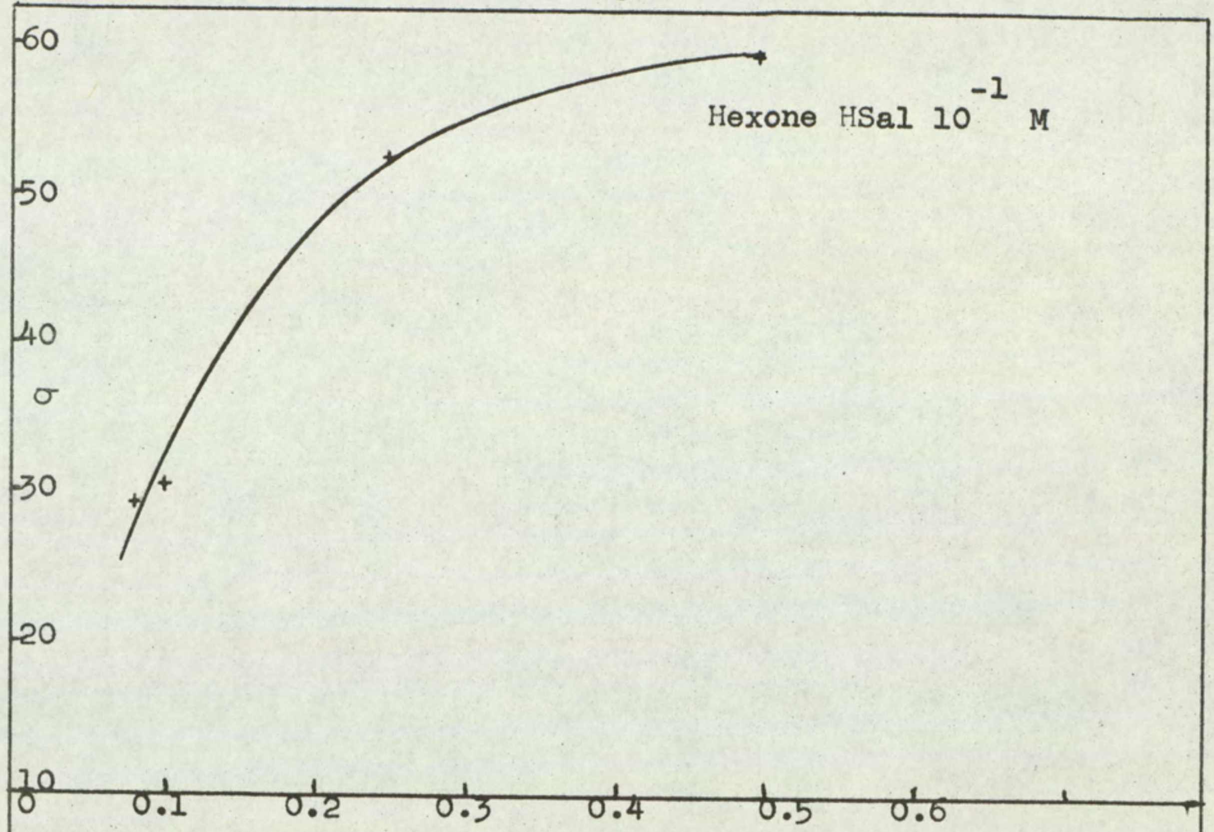
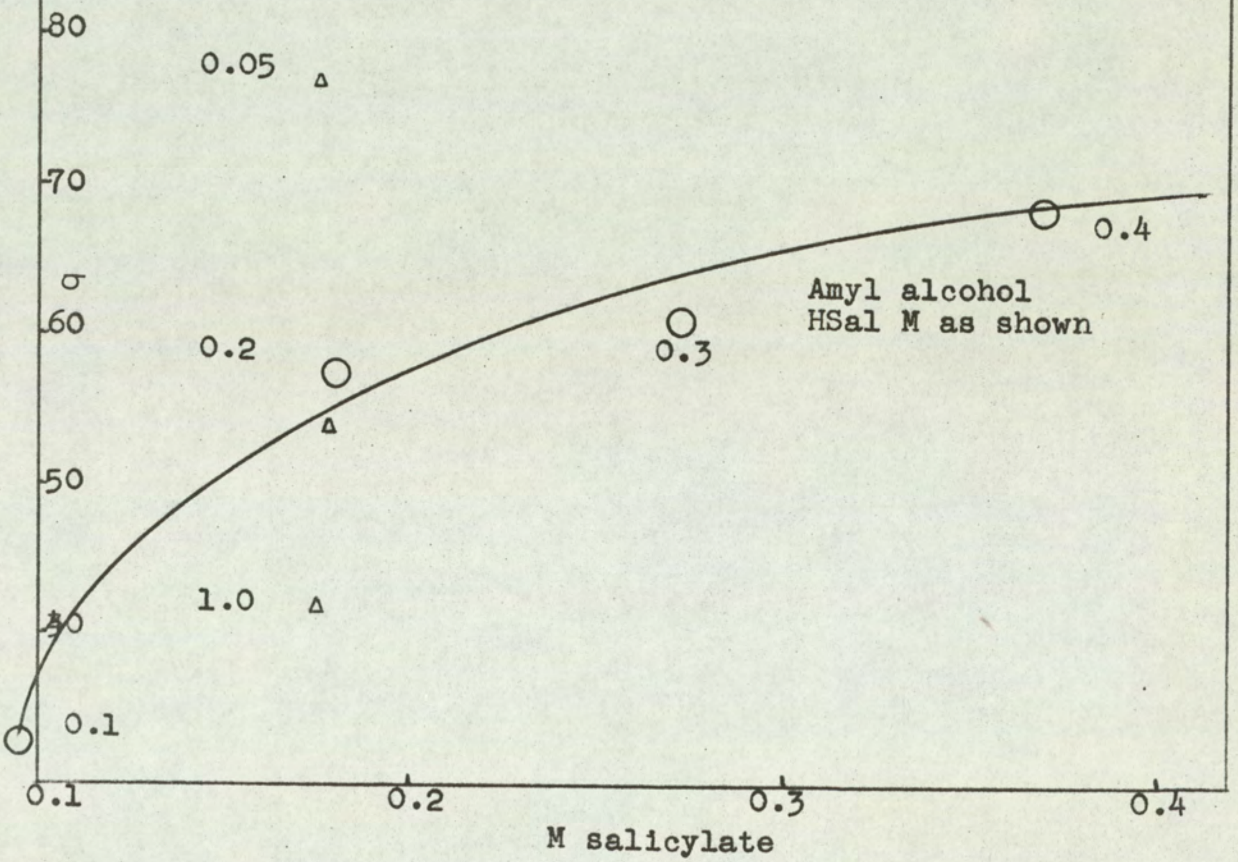


Fig.5.2 The extraction of cerium salicylate into amyl alcohol and hexone.



quantitative extraction as described above, and also practicable for inclusion in an analytical method. A number of experiments of this type were conducted. The best results were generally obtained when EDTA was used but DTPA also gave satisfactory results. Both hexone and amyl alcohol were used, 5(ii) and 5(iii). Results were best at low volume ratios and in buffered rather than unbuffered (nearly neutral) solution. Fig. 5.3 shows the plot of -log q versus -log $[Y']$ for the extraction of various concentrations of Ce-EDTA complex with 0.5 M sodium salicylate and a ten-fold volume excess of 0.1 M salicylic acid in hexone. The slope is -0.95, whereas theory gives -1.0. It is assumed that the predominant species in the aqueous phase at equilibrium is still MY, which the result apparently justifies.

What would be the effect of this operation on a previously satisfactory substoichiometric reaction between the metal and EDTA?

$$E_x = \frac{[MSal_3]_o [Y']}{[Sal]^3 [MY]} \qquad (9)$$

As $[MY]$ represents all of the metal in the aqueous phase

$$[MSal_3]_o \frac{V_o}{V_a} = [MY] \frac{(100 - S)}{S} \qquad (11)$$

where S is the percentage or degree of substoichiometry.

At S% substoichiometry

$$E_x = \frac{[Y'] V_a (100 - S)}{[Sal]^3 V_o . S} \qquad (12)$$

From the measured E_x can be calculated the maximum permitted concentration of salicylate to give a fixed minimum permissible ratio of $[Y']/[MY]$ and loss of MY, i.e. the species to be determined.

$$[\mathrm{Sal}]^3 = \frac{[Y']\, V_a(100 - S)}{E_x \cdot V_o \cdot S} \qquad (13)$$

which becomes

$$[\mathrm{Sal}]^3 = \frac{10^{-3}\, C_{HY} \cdot V_a(100 - S)}{E_x \cdot V_o \cdot S} \qquad (14)$$

when $[Y'] = 10^{-3}\, C_{HY}$.

The value of E_x for Ce-EDTA determined in 0.5 M salicylate is 7.3×10^{-6} for hexone, Fig. 5.3.

Values of $[\mathrm{Sal}]^3/C_{HY}$ calculated from Equation 14 are given in Table 5.1, for $V_o/V_a = 1$.

Table 5.1

Calculated Values of $[\mathrm{Sal}]^3/C_{HY}$

S	$\frac{100 - S}{S}$	$\frac{[\mathrm{Sal}]^3}{C_{HY}}$
10	9	$10^{3.09}$
50	1	$10^{2.14}$
90	0.11	$10^{1.18}$

Fig.5.3

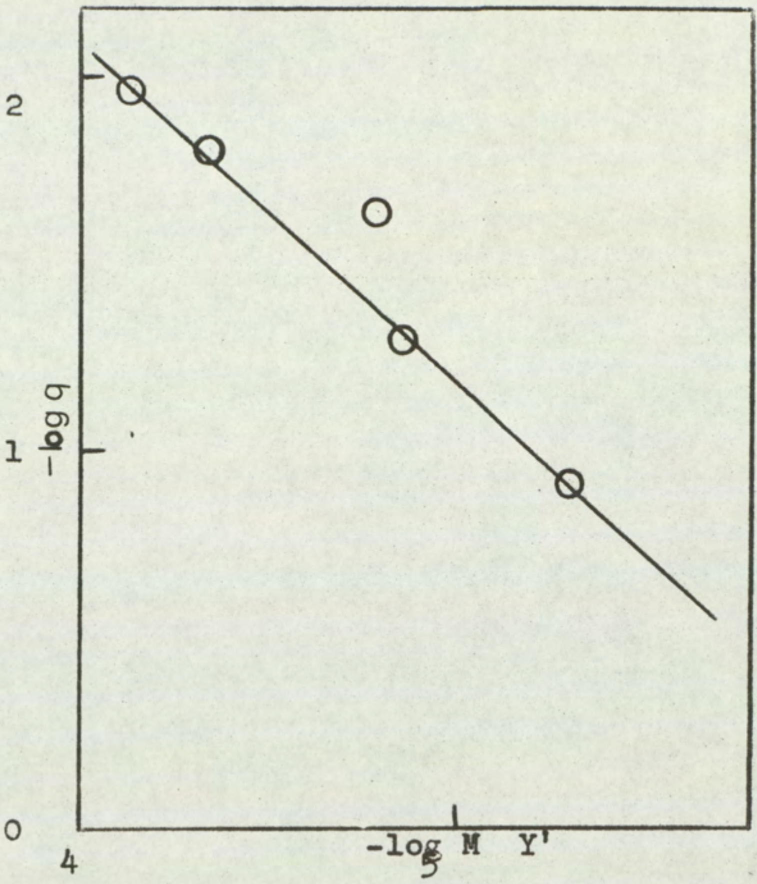


Fig.5.3. The breakdown of cerium-EDTA by salicylate. Extraction into hexone.

Fig.5.4

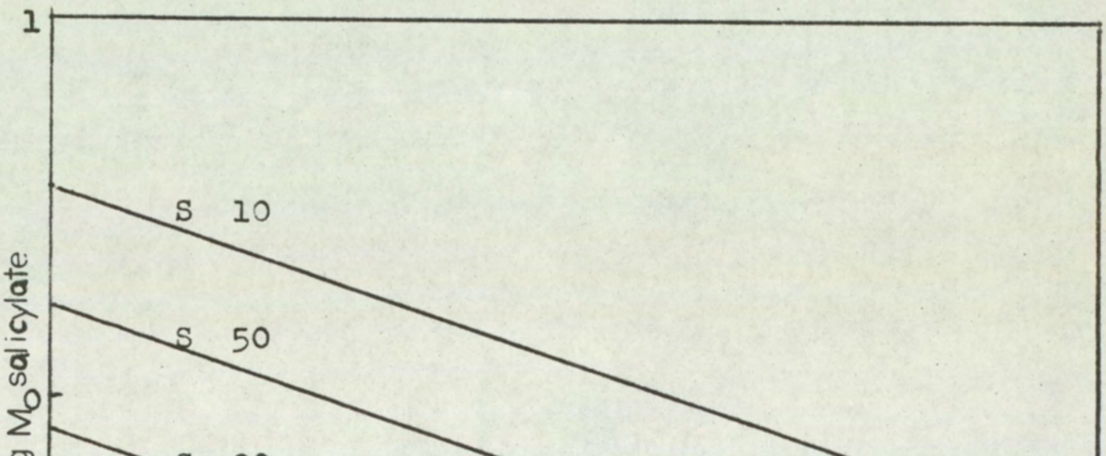


Fig.5.4. Values of salicylate concentration permissible in substoichiometry.

Table 5.2

Values of log [Sal] Calculated from Equation 14

log C_{HY}	log [Sal] S = 10	 S = 50	 S = 90
-4	-0.30	-0.62	-0.94
-3	0.03	-0.29	-0.61
-2	0.37	0.05	-0.27
-1	0.70	0.38	0.06

These values are shown in Fig. 5.4.

If the salicylate extraction is improved by increasing V_o/V_a to 10, log [Sal] is lowered by 0.33 which is almost equal to the decrease (0.32) in log [Sal] which is brought about by increasing S from 10 to 50 or 50 to 90. If V_o/V_a is increased to 100, the decrease in log [Sal] is equivalent to increasing S from 10 to 90 and so on.

It will be seen from Fig. 5.4 that the degree of substoichiometry has a slight effect on the sensitivity, the maximum sensitivity being achieved at lowest substoichiometry. However, in this reaction where 100% extraction is barely possible, this condition also introduces maximum error. E_x is, therefore, important and must be kept as low as possible.

E_x has been defined by Equation 9 as the ratio E_2/K_3', but it is also equal to E/K_3 where K_3 is the familiar conditional constant

$$K_3 = \frac{[MY]}{[M][Y']} \qquad (15)$$

used in Chapter 3.

From a knowledge of this constant can be calculated

$$E = \frac{[MSal_3]_o}{[M][Sal]^3}$$

the true extraction constant under these conditions.

The conditional constants K_3 for Ce-EDTA are shown in Table 5.3.

Table 5.3

Conditional Constants for Ce-EDTA

Calculated from data in Ref. 9

pH	log K_3	pH	log K_3	pH	log K_3
0	-5.4	4	7.4	8	13.7
1	-1.4	5	9.4	9	14.6
2	2.3	6	11.1	10	15.5
3	5.2	7	12.6	11	15.9

These figures can be regarded as average working values insofar as they are determined (or corrected) to correspond to ionic strength $\mu = 0.1$. Between $\mu = 0.1$ and $\mu = 0.5$ variations of these constants will not be great. It is felt that this generalisation, which Ringbom continually emphasises throughout his work, is acceptable in this type of problem.

The results of calculating E from the previous experiment are shown in Table 5.4.

Table 5.4

Calculation of E, the Extraction Constant of Cerium Salicylate into Hexone. From Experiment 5(ii)

	Conc. Sal^-	pH	E_x	K_3	E	log E
1	0.14	5.5	7.6×10^{-5}	$10^{15.9}$	1.20×10^{6}	6.08
2	0.23	5.6	4.13×10^{-5}	$10^{15.9}$	6.55×10^{5}	5.82
3	0.50	6.0	7.3×10^{-6}	$10^{15.9}$	9.20×10^{5}	5.96

The value of $\alpha_{Y(H)}$ changes rapidly with pH even at pH 5 to 6 and small changes can bring about large differences in the value of E_x.

Comparison of the conditional stability constants for the rare earth aminocarboxylic acids, Chapter 2, shows that they are all very similar except at high pH. The experiment described above was repeated for cerium and DTPA using both hexone and amyl alcohol solvents, 5(iii). The hexone results are shown in Fig. 5.5. Two pH values were used, 5.6 and 6.6, i.e. the highest range permissible. The results were similar to those obtained with EDTA at the lower pH. Again the reasons for poorer results of extraction at high pH are debatable. As mentioned previously, cerium probably does not behave as a typical rare earth in these more alkaline solutions. At pH 11.5, the organic phase has a yellow colour even though little metal is extracted. There is also some indication that the reaction approaches equilibrium more slowly at the higher pH values. At

Fig.5.5

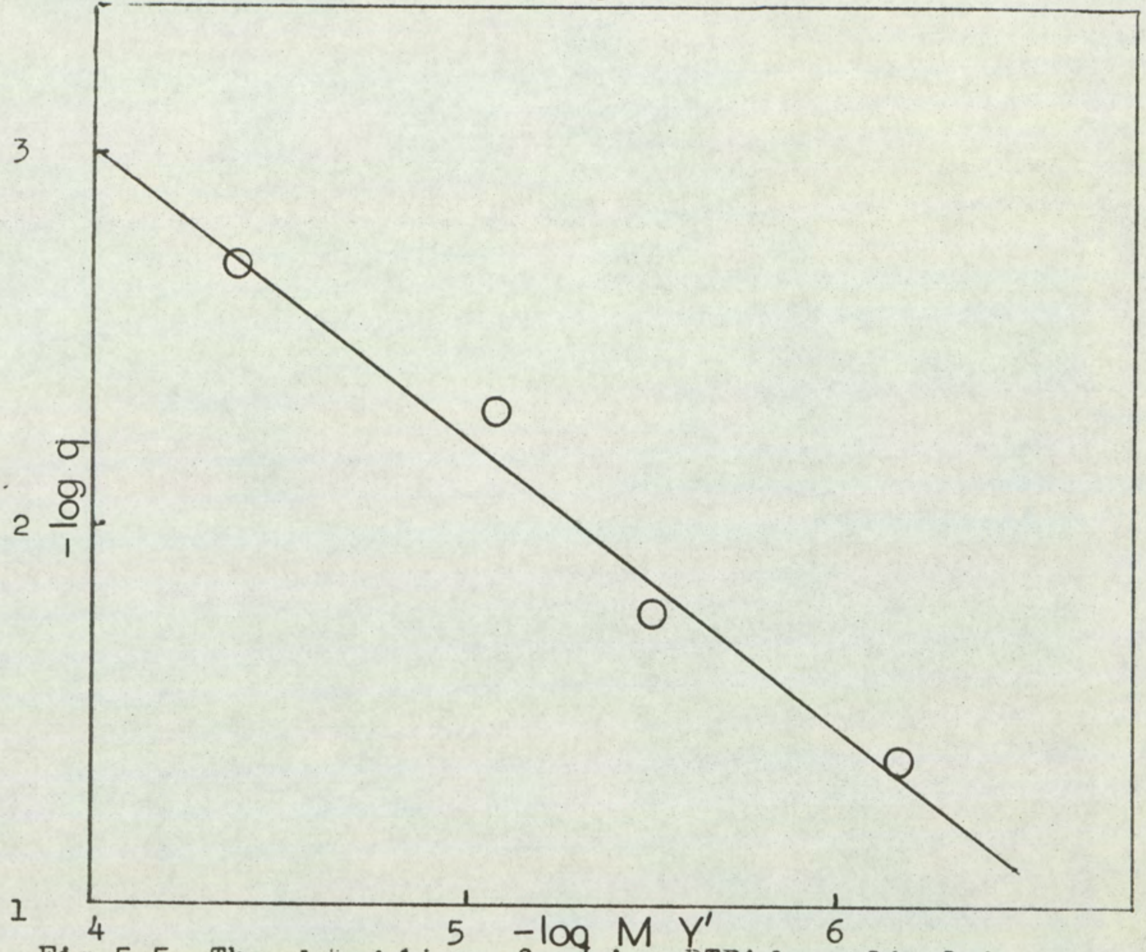


Fig.5.5. The breakdown of cerium-DTPA by salicylate.
Extraction into hexone.

Fig.5.6.

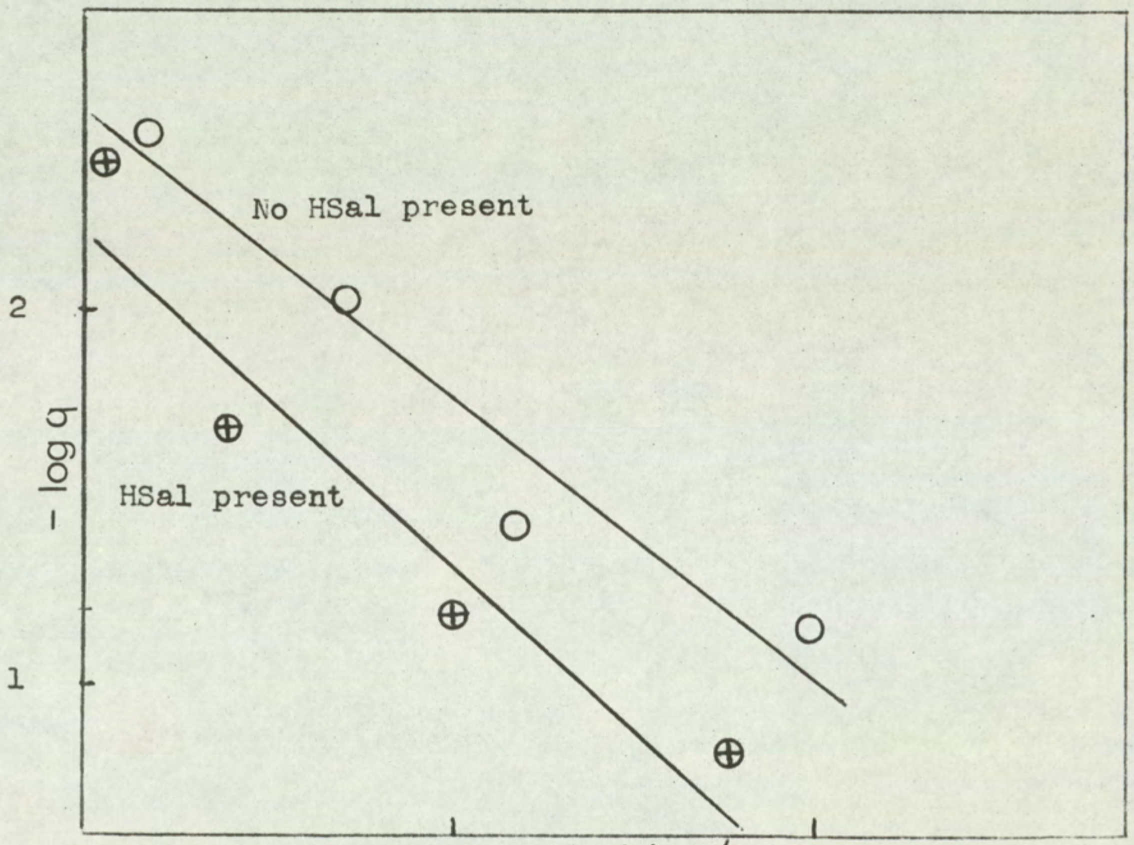


Fig.5.6. The breakdown of cerium-DTPA by salicylate.
Extraction intoamyl alcohol.

pH 5.6 the data fit to a straight line of slope -0.77. This is not significantly different from slope equal to -1.0 on the basis that -1.0 is the expected result. E_x in this case equals 8.92×10^{-6}.

The value of E can be calculated from K_3 for Ce-DTPA, for comparison with the EDTA result.

There are several conflicting values for log K_2 for Ce-DTPA. Moeller and Thomson[27] quote a value of approximately 20.5 whereas Powell and Spedding[28] in reviewing the stabilities of all the light rare earths, show that the values of log K_2 for rare earth DTPA complexes lie on a continuous curve from 18.6 to 21.0 so that K_2 for cerium should be 19.2, and 20.5 would correspond to promethium or samarium. This lower value, when used in the present results, gives a value of $E = 7.05 \times 10^5$, in good agreement with the EDTA experiment.

The results of using amyl alcohol solvent are shown in Fig. 5.6. They indicate clearly that the breakdown reaction is more extensive than with hexone. The figures at high pH are somewhat better than those obtained for hexone at the same pH, although still not very good.

At pH 5.6 the best straight line fitted by the least squares method has a slope of -0.87, again not significantly different from -1.0. At pH 6.6, the slope is -0.76. The values of E_x obtained from these figures are 6.97×10^{-5} and 2.58×10^{-5}, respectively. Earlier work had suggested that the opposite was true, namely that hexone was the better extractant. Obviously no such generalisation can be made as the behaviour of the metals toward this extraction depends upon which metal is chosen, Table 5.5.

Table 5.5

A Comparison of the Extraction of Cerium and Ytterbium into Amyl Alcohol and Hexone. From Experiment 5(v)

	Metal	Conc. salicylate M	q	$\frac{q_{Yb}}{q_{Ce}}$
Hexone	Ce	0.17	27.2	6.30
	Yb	0.17	172	
Amyl alcohol	Ce	0.19	77.3	1.32
	Yb	0.19	102	

Ratio q am.alc./q hex.

Ce	2.84
Yb	0.59

A summary of extraction results with cerium and DTPA is given in Table 5.6. Values of E are subject to uncertainty arising from the known values of the equilibrium constants for DTPA. This becomes more noticeable as pH increases.

Table 5.6

Values of E_x from the Extraction of Ce-DTPA

Mean q	Conc. salicylate	pH	$[Y']$	E_x	log K_3	E
Hexone						
9.30×10^{-3}	1.67×10^{-1}	5.6	5.30×10^{-6}	8.92×10^{-6}	10.9	7.08×10^{5}
3.24×10^{-3}	1.44×10^{-1}	6.6	5.32×10^{-6}	5.73×10^{-6}	13.0	5.72×10^{7}
Amyl alcohol						
3.07×10^{-2}	1.91×10^{-1}	5.6	1.58×10^{-5}	6.97×10^{-5}	10.9	5.53×10^{6}
1.70×10^{-2}	1.87×10^{-1}	6.6	9.88×10^{-6}	2.58×10^{-5}	13.0	2.58×10^{8}
6.16×10^{-3}	1.65×10^{-1}	6.70	1.01×10^{-5}	1.37×10^{-5}	13.0	1.37×10^{8}

So far as substoichiometry is concerned, this system is obviously very complicated. The analyst is restricted to working with extraction systems which are barely good enough, and also to relatively concentrated metal solutions. Whilst one could envisage such a system as being useful in non-instrumental (non-automatic) activation analysis or separations with similar amounts of metal, it is clearly not a powerful tool in trace metal analysis.

5.3 Reproducibility Curves

It is interesting now to re-examine the idea of reproducibility curves which has hitherto been accepted in this and other work as a test of 'satisfactory substoichiometry'. Such graphs have already been presented in this thesis, and can be obtained in the salicylate case subject to the concentration limits already described. It is worthwhile pointing out that the salicylate results represent an extension of the ideas expressed in the TTA work. That is, it is possible with this reagent to have conditions where the MY complex is partly destroyed, even though the concentration of salicylate is insufficient to bring about quantitative extraction when Y is absent. This is a consequence of the lower degree of flexibility in the range of salicylate concentrations and is reflected by reproducibility curves which resemble those described as unacceptable in the TTA work, Fig. 3.7, and have sloping plateau rising above the theoretical horizontal line.

In making practical use of this reaction, say in a separation following the addition of carrier, the metal concentration could be controlled and it is instructive in this instance to confirm that one can carry out the substoichiometric step at differing degrees of substoichiometry from a single metal concentration with equal reliability.

Using the Ce, DTPA, salicylate, amyl alcohol system, conditions were chosen such that successful substoichiometry should just be possible, i.e. the limiting conditions for both quantitative extraction and the permissible MY plus salicylate reaction, 5(iv).

A solution of 2×10^{-3} M cerium was reacted with a number of DTPA solutions ranging from $1.5-7.5 \times 10^{-4}$ M in the presence of 0.18 M salicylate. The metal not complexed as DTPA was extracted with pure amyl alcohol and the amount not extracted compared to the theoretical amount, assuming DTPA to be quantitatively consumed. The percentage recovery of the substoichiometric step was, therefore, determined at five differing degrees of substoichiometry. The reader will realise that this condition pH 6.6 is equivalent to that already described as unpredictable so far as the exchange (breakdown) reaction is concerned. However, no exchange is anticipated here and advantage is taken of the knowledge that such conditions give 99.7-99.8% extraction of cerium with only a five-fold excess of organic phase. Moreover, it should represent the most favourable conditions for the stability of the DTPA complex. Not all rare earths could be analysed in this way.

The results are given in Table 5.7.

Table 5.7

Extraction of Cerium at Differing Degrees of Substoichiometry

% Substoichiometry	% Ce in aqueous phase Theory*	% Found	% Difference
6.58	6.87	6.67	-2.90
13.16	13.42	12.60	-6.10
19.72	19.96	19.95	-0.05
26.30	26.52	25.90	-2.34
32.95	33.15	33.00	-0.45

* allowing for 99.7% extraction.

The variation in the differences obtained was within the known confidence limits for the precision of this kind of substoichiometric separation. It is some cause for concern that all the recoveries were slightly low, although again the variation from 100% recovery is within the limits of reproducibility of q, and, therefore, within the increased limitations as posed by the substoichiometry. Adsorption losses during transfer processes at this pH are another possible cause of low results.

In conclusion, it is possible to say that the reaction of complexones with rare earth metals in the presence of salicylate is suitable as a substoichiometric step. However, the system is of little use in isotope dilution analysis because the most satisfactory conditions for extraction interfere seriously with the stability of the complex to be measured. In more concentrated solutions where, unfortunately, applications are fewer, substoichiometry can be performed with a workable precision, provided interferences due to hydrolysis and adsorption are avoided.

5.4 Experimental

Calculation of % Extraction from q at Various Values of V_a/V_o From Equation 10 for Fig. 5.1

$$\%\ \text{Extraction} = \frac{100\,q}{\left(q + \frac{V_a}{V_o}\right)} \qquad (10)$$

q	$\frac{V_o}{V_a} = 1$	$\frac{V_o}{V_a} = 5$	$\frac{V_o}{V_a} = 10$
30	96.77	99.33	99.67
50	98.04	99.60	99.82
70	98.63	99.72	99.86
100	99.02	99.79	99.91

In all extractions using hexone or amyl alcohol, each phase was equilibrated with the other before use.

5(i) The Extraction of Cerium from Strong Solutions of Salicylate with Hexone and Amyl Alcohol (From Section 5.2 and Fig. 5.2)

Hexone

Solutions: 10^{-3} M cerium

10^{-1} M sodium salicylate

5×10^{-1} M sodium salicylate

10^{-1} M salicylic acid in hexone.

Method. A 1 ml aliquot of cerium solution was added to 10 ml of salicylate solution of differing concentrations. The mixture was extracted for 5 minutes with 100 ml of organic phase. An aliquot of each phase was counted to determine q, pH, and total salicylate, as in 4(iv), 4(v).

Results

Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q	pH	Conc. salicylate M
64.20	1.30	49.40	5.95	0.50
64.20	1.50	42.80	5.62	0.253
63.50	3.04	20.80	5.40	0.103
737.30	37.40	19.70	5.33	0.087

These are shown in Fig. 5.2

Amyl Alcohol

(a) At constant salicylate concentration.

Solutions: 5×10^{-1} M sodium salicylate

10^{-1} M salicylic acid in amyl alcohol

5×10^{-2} M salicylic acid in amyl alcohol

5×10^{-4} M cerium.

Method. A mixture of 5 ml metal solution and 5 ml salicylate was extracted for 5 minutes with an equal volume of amyl alcohol or salicylic acid solution. The phases were separated and parted, and 5 ml aliquots were taken to determine q, as in 4(iv), 4(v).

Results

Salicylic acid conc. M	Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q
0	3052	56.53	53.8
5×10^{-2}	3110	40.28	77.4
10^{-1}	3017	71.83	42.0

(b) At varying salicylate.

Solutions: Sodium salicylate, various concentrations
1 to 5×10^{-1} M
5×10^{-5} M cerium solution
Salicylic acid in amyl alcohol, various concentrations 1 to 4×10^{-1} M.

Method. Distribution ratios were determined as in 4(iv) and 4(v), using an aqueous phase of 1 ml cerium and 9 ml salicylate, and 10 ml of salicylic acid of the appropriate concentration.

Results

Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q	pH	Conc. salicylate
537.0	16.34	32.84	5.22	9.55×10^{-2}
556.1	9.76	57.10	5.10	1.86×10^{-1}
556.3	9.28	60.70	5.02	2.72×10^{-1}
557.7	8.18	68.10	4.95	3.70×10^{-1}

Conclusion. These results are shown in Fig. 5.2 and discussed fully in Section 5.2.

5(ii) The Extraction of Mixtures of Ce-EDTA and Salicylate

Solutions: A range of labelled Ce-EDTA solutions, made by adding an exactly equivalent amount of EDTA to the metal, followed by the necessary dilution.

10^{-1} M salicylic acid in hexone

5×10^{-1} M sodium salicylate.

Method. Reaction mixtures of 10 ml salicylate and 2 ml of each metal-EDTA solution were prepared. Each was extracted for 5 minutes with 100 ml of 10^{-1} M salicylic acid in hexone. Distribution ratios were measured by the methods previously described, 4(iv). As in previous experiments, both ^{141}cerium and ^{144}cerium were used. The ^{141}cerium was of low specific activity and, therefore, only the single photopeak was counted, allowing a background of only 2.0 counts per second.

Results

Conc. of Ce-EDTA used M	Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q
4.75×10^{-3}	0.17	16.79	0.0103
2.06×10^{-3}	0.80	52.38	0.015
4.80×10^{-4}	13.49	599.0	0.0225
2.40×10^{-4}	12.30	248.6	0.0485
4.80×10^{-5}	4.17	36.0	0.116

pH of solutions = 6.0. Salicylate concentration 4.55×10^{-1} M

Measured equilibrium volumes: Aqueous 10.4 ml
Organic 102 ml

% Extraction	Conc. EDTA = Y'	E_x
9.10	7.18×10^{-5}	8.30×10^{-6}
13.10	5.10×10^{-5}	4.14×10^{-6}
18.80	1.73×10^{-5}	6.07×10^{-6}
32.40	1.49×10^{-5}	7.16×10^{-6}
53.20	4.91×10^{-6}	7.60×10^{-6}
		7.27×10^{-6} Mean

The values of q versus $[Y']$ are shown in Fig. 5.3.

<u>Calculation of E</u> from Equation 9, 15, and Table 5.4.

$\log {}_{Y(H)} = 4.8$ at pH 6.0

$\log K_2$ for Ce $= 15.9$

$$\therefore \ E = \frac{7.27}{10^{11.10}} \times 10^{-6} = 9.2 \times 10^{5}$$

Determination at other salicylate concentrations.

The 4.80×10^{-4} M reagent was diluted to make two further solutions:

(a) 5 ml 5×10^{-1} M salicylate, 5 ml water, 2 ml reagent

(b) 3 ml 5×10^{-1} M salicylate, 7 ml water, 2 ml reagent.

Each mixture was extracted and analysed as above.

<u>Results</u>

Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q
14.37	586.1	0.0244
13.07	609.9	0.0214

% Extraction	$[Y']$	Conc. salicylate M x 10	E_x x 10^5
23.35	2.165×10^{-5}	2.34	4.13
21.00	9.76×10^{-6}	1.40	7.60

Calculation of E

$\log K_2$	pH	$\log \alpha_{Y(H)}$	E
15.9	5.50	5.7	6.55×10^5
15.9	5.50	5.7	1.20×10^6

Conclusion. These results are discussed in Section 5.2 and summarised in Table 5.4. There is measurable breakdown of the EDTA complex, and the reaction behaves in the way predicted by the equilibrium equations.

5(iii) The Extraction of Ce-DTPA Complex with Salicylate (From Section 5.2)

Solutions: Equilibrated solutions of Ce-DTPA were prepared by diluting stock concentrated solution which had been standardised by titration using xylenol orange indicator. Concentrations thus obtained were 8.2×10^{-3} M, 8.2×10^{-4} M, 8.2×10^{-5} M, 8.2×10^{-6} M.

5×10^{-1} M sodium salicylate

1×10^{-1} M salicylic acid in hexone

5×10^{-2} M salicylic acid in amyl alcohol.

Considerable care was taken to ensure complete equilibration of each solution with the appropriate solvent under the conditions of the proposed test.

Method. The reaction mixture was 5 ml of salicylate, 5 ml of each complex solution, extracted for 5 minutes at 25°C with 50 ml of either

(a) Hexone

(b) Amyl alcohol

(c) Salicylic acid in hexone

(d) Salicylic acid in amyl alcohol.

Distribution ratios, pH and salicylate concentration were all determined as described in 4(iv). It was observed that all the salicylate concentrations in each set were equal, as intended, and in some of the later sets not all were measured.

Results

(a) Hexone solvent - no salicylic acid.

	Activity counts s^{1}	q	% Ext.	pH	Conc. DTPA = [Y']	Conc. sal. M x 10
1	1245	0.00163	0.81	6.50	3.32×10^{-5}	-
1 org.	2.03					
2	1203	0.00214	1.07	6.85	4.4×10^{-6}	1.64
2 org.	2.57					
3	859	0.0131	5.30	6.60	2.17×10^{-6}	1.63
3 org.	11.30					
4	82.95	0.0169	7.68	6.60	3.14×10^{-7}	1.64
4 org.	1.40					

(b) Hexone solvent - salicylic acid present.

	Activity counts s^{-1}	q	% Ext.	pH	Conc. DTPA = [Y']	Conc. sal. M x 10
1	1290	0.0021	1.00	5.55	4.10×10^{-5}	1.66
1 org.	2.67					
2	1231	0.0052	2.08	5.50	8.52×10^{-6}	-
2 org.	6.35					
3	960.4	0.0170	7.84	5.50	3.22×10^{-6}	1.68
3 org.	16.32					
4	75.5	0.0411	17.00	5.50	6.98×10^{-7}	-
4 org.	3.10					

(c) Amyl alcohol solvent - no salicylic acid.

	Activity counts s^{-1}	q	% Ext.	pH	Conc. DTPA = [Y']	Conc. sal. M x 10
1	1558	0.0033	1.65	6.60	6.76×10^{-5}	1.87
1 org.	5.14					
2	1173	0.0094	4.75	6.70	1.95×10^{-5}	1.92
2 org.	11.09					
3	948	0.0397	16.50	6.60	6.75×10^{-6}	1.89
3 org.	37.63					
4	85.37	0.0707	26.2	6.60	1.07×10^{-6}	1.89
4 org.	6.03					

(d) Amyl alcohol solvent - salicylic acid present.

	Activity counts s^{-1}	q	% Ext.	pH	Conc. DTPA = [Y']	Conc. sal. M x 10
1	1521	0.0041	2.06	5.60	8.45×10^{-5}	-
1 org.	6.27					
2	1140	0.0214	9.72	5.62	3.98×10^{-5}	1.93
2 org.	24.40					
3	849	0.0666	25.0	5.65	1.02×10^{-5}	1.90
3 org.	56.61					
4	65.6	0.154	43.6	5.60	1.79×10^{-6}	-
4 org.	10.13					

Further results at high pH were obtained by substituting 1 ml of 10^{-1} or 10^{-2} M NaOH for 1 ml of metal solution in test 2 above. Extraction was carried out as described above.

Results

Hexone

	Activity counts s^{-1}	q	% Ext.	pH	Conc. DTPA = [Y']	Conc. sal. M x 10
aq.	861.0	yellow in org.	-	11.5	-	-
org.	0.35					
aq.	928.9	0.00324	1.62	6.6	5.32×10^{-6}	1.44
org.	3.00					

Amyl Alcohol

	Activity counts s^{-1}	q	% Ext.	pH	Conc. DTPA = [Y']	Conc. sal. M x 10
aq.	960.8	yellow in org.	-	11.5	-	-
org.	0.20					
aq.	934.8	0.00616	3.08	6.70	1.01×10^{-5}	1.65
org.	5.72					

Discussion of Results and Conclusion

The results of extractions at constant salicylate were plotted as log q versus log [Y'] . They are shown in Fig. 5.5 and 5.6 as straight lines fitted by the method of least squares. The theoretical graphs should have slope of -1.0. This clearly becomes more difficult to achieve in 5 minutes as the pH increases, and is better for amyl alcohol than hexone. The results are summarised in Table 5.6, and in the Table below.

	Slope of Graph	E_x
Hexone pH 5.6	-0.77	8.92×10^{-6}
Amyl alcohol pH 5.6	-0.82	6.97×10^{-5}
Amyl alcohol pH 6.6	-0.76*	2.58×10^{-5}

* Analysis of variance of this line shows slope not significantly different from -1.0.

5(iv) The Extraction of Cerium at Differing Degrees of Substoichiometry

Solutions: 10^{-2} M cerium

10^{-3} M DTPA solution (1.32×10^{-3} M)

7.5×10^{-1} M sodium salicylate

10^{-1} M salicylic acid in amyl alcohol.

Method. The cerium was titrated with the DTPA so that exact equilibrium could be known in the substoichiometry.

The following mixtures were extracted for 5 minutes with 50 ml 10^{-1} M salicylic acid solution.

10^{-3} M DTPA ml	H_2O ml	10^{-2} M Ce ml	Salicylate ml
1	4	2	2
2	3	2	2
3	2	2	2
4	1	2	2
5	0	2	2

The activity of each phase was determined after separation.

Results

Activity aq. phase counts s^{-1}	Activity org. phase counts s^{-1}	% in aq. phase	% Subst.	% metal aqueous allowing 99.7% Ext.	% Diff.
4.94	12.43	6.67	6.58	6.87	-2.90
8.95	11.24	12.60	13.16	13.42	-6.10
14.10	10.20	19.95	19.72	19.96	-0.05
18.50	9.59	25.90	26.30	26.52	-2.34
23.80	8.81	33.00	32.95	33.15	-0.45

These results are also presented in Table 5.7.

Conclusion. At this concentration, the substoichiometric reaction takes place exactly as predicted, and separation of the substoichiometric complex is achieved within the predetermined limits of accuracy, at each degree of substoichiometry.

5(v) A Comparison of the Extraction of Cerium and Ytterbium into Amyl Alcohol and Hexone (From Table 5.5)

Solutions: 10^{-3} M cerium

10^{-3} M ytterbium

5×10^{-1} M sodium salicylate.

Method. A 5 ml aliquot of metal solution was added to 5 ml of salicylate and extracted for 5 minutes with 10 ml of the appropriate solvent. After separation, 5 ml aliquots were used to measure the distribution ratio q.

Results

		Activity org. phase counts s^{-1}	Activity aq. phase counts s^{-1}	q	Conc. sal. M
Yb	Hexone	4697	27.34	172	0.168
	Amyl alcohol	6044	59.35	102	
Ce	Hexone	599.2	22.10	27.2	0.190
	Amyl alcohol	618.8	8.00	77.3	

Conclusion. There are two obvious points of importance in these results. Firstly, they indicate that amyl alcohol is the preferred solvent for cerium extraction, and apparently hexone for ytterbium. However, there is loss of total metal in this last case and adsorption on glassware is a possibility. Much of the early exploratory work on this extraction system was conducted with heavy or middle rare earths and in all cases hexone was the more efficient extractant. The figures emphasise greater reliability of the amyl alcohol results.

CHAPTER 6

Ion Exchange and Substoichiometry

A part of this work was presented at an Ordinary Meeting of The Society for Analytical Chemistry, and is reported in summary in The Proceedings of the Society, Oct. 1968.

6.1 Introduction

The original authors of substoichiometry envisaged a number of ways of carrying out the separation step. Among these was the use of ion exchange resins for separating charged complexes. Solvent extraction has far outweighed any other substoichiometry technique and little attention has been given to these other possibilities. For this project, the use of ion exchange resins deserves consideration for two main reasons. Firstly, the charged complexes such as those formed with EDTA are strong and well characterised for the rare earth metals, a point already made. Secondly, the concept of using such an arrangement has not received such a thorough treatment from theoretical principles as solvent extraction, and some contribution is required to make the basic ideas of Ruzicka and Stary more complete.

In the first instance, emphasis was on the development of a usable analytical separation. Very similar work was being conducted at the same time in Prague by Prasilova, a colleague of Ruzicka and Stary. Nothing was known of this until a paper was published[29] in late 1966. This paper presents such a method based on filtration on small columns as in previous publications for the determination of iron[30] and indium[31]. The results of model analyses are excellent.

Similar results had been obtained in this present work, but in addition many unsatisfactory results were available and difficulty had been experienced in choosing the optimum size of column and ensuring adequate and reproducible washing techniques. These points are not discussed in any of the cited references. For this reason it was felt that further study was advisable and that the results obtained at Aston should be extended and presented as part of this thesis.

6.2 Choice of Ion Exchange Resin and Complexing Agents

All previous work in this field has been carried out using EDTA and sodium form sulphonated polystyrene resin. EDTA is by far the most studied and best understood complexone of the type required and was also used in this work. Strong cationic resin was also used, and those chosen were Dowex 50 X8 (Dow Chemicals), Amberlite IR 120 (Rohm and Haas) and Zeocarb 225 (Permutit). These are essentially identical resins. Dowex 50 was used in most of the work, but the others were used from time to time, especially when a form was required (say, small mesh size) for which the Dowex was not available. Any conclusions drawn with each can be extrapolated to the others with a fair margin of safety.

6.3 Theory of Ion Exchange Substoichiometry

(a) As presented by Ruzicka and Stary[30].

Using terms previously encountered:

For substoichiometry $[MY] \gg 0.999\ C_{HY}$

and, therefore, $[M] = C_M - [MY] = C_M - C_{HY}$.

The equilibrium concentration of

$$Y = \sum_{n=0}^{n} [H_nY] = [Y]\sum_{n=0}^{n} \frac{[H]^n}{k_o \ldots k_n} \ll 0.001\ C_{HY}$$

where $k_o = 1$

$$k_n = \frac{[Y][H_{n-1}]}{[H_nY]}$$

$$k_{MY} = \frac{[MY]}{[M][Y]} = \frac{C_{H_nY}}{C_M - C_{HY}} = \frac{\sum_{n=0} \frac{H^n}{k_o \ldots k_n}}{0.001\ C_{HY}}$$

If $C_M = 2\ C_{HY}$ $\qquad \frac{C_{HY}}{C_M - C_{HY}} = 1$

$$n = \sum_{n=0} \frac{[H]^n}{k_o \ldots k_n} = 1 \quad \text{at high pH.}$$

Thus substoichiometry requires a minimum value of the stability constant of the metal complex.

It is immediately noticeable that this treatment does not take into account the possible interference with this equilibrium which results from the resin being present.

(b) By using the now familiar ideas of conditional stability constants, the dependency denoted by the equations above can be expressed alternatively.

The conditional stability constant $K_3 = \frac{[MY]}{[M][Y']}$ which under the conditions required for ideal 50% substoichiometry becomes

$$K_3 = \frac{0.999\ C_{HY}}{\frac{C_M}{2} - 0.001\ C_{HY}} \qquad (1)$$

where C_{HY} = total EDTA concentration

and C_M = total metal concentration

$$K_3 = \frac{2000}{C_M} \qquad (2)$$

That is, 50% substoichiometry is possible if the apparent stability constant of the metal complex is greater than $\frac{2000}{C_M}$. This means only that the substoichiometric reaction is possible; nothing can be said at this stage about the separation.

Table 6.1

The Value of Log K_3 for Two Rare Earths Lanthanum and Lutetium

(No account is taken of hydrolysis)

pH	Log K_3 La	Log K_3 Lu
0	-5.9	-1.6
1	-1.9	2.4
2	1.8	6.1
3	4.7	9.0
4	6.9	11.2
5	8.9	13.2
6	10.7	15.0
7	12.1	16.4
8	13.2	17.5

Thus at $C_M = 10^{-5}$ M, 50% substoichiometry is possible at pH = 4.7 (La) or 2.8 (Lu).

The actual removal of unreacted metal by resin can act as a competitive reaction to the EDTA complexation as in the solvent extraction of earlier Chapters, and optimum conditions must be decided so that the separation does not affect the substoichiometry.

Such equilibria are much more difficult to ascertain than the corresponding case for solvent extraction. Nevertheless, it is instructive to treat the system in a very similar way which at least points the way to the most useful experimental course.

The condition for 99.9% removal of unreacted metal must be found remembering that the conditions $[MY] = 0.999\ C_{HY}$ and $[Y'] = 0.001\ C_{HY}$ must still apply at equilibrium.

Let the ratio

$$\frac{\text{Metal in system not present as EDTA complex}}{\text{Final free metal concentration after ion exchange}} = \alpha_R = \frac{[M']}{[M_f]} \qquad (3)$$

so that

$$K_3' = \frac{[MY]}{[M'][Y']} = \frac{K_3}{\alpha_R} = \frac{K_2}{\alpha_R \alpha_{Y(H)}} \qquad (4)$$

K_2 = true stability constant of MY.

Now consider what information is needed to calculate $_R$. The exchange reaction is assumed to be a stoichiometric chemical reaction so that an equation can be written analogous to solvent extraction.

$$M + 3H_R \rightarrow M_R + 3H$$

H_R represents resin in the hydrogen form.

One way of writing an equilibrium constant for the exchange is

$$K_{3H}^{M} = \frac{[M_R][H]^3}{[M]\ [H_R]^3} \qquad (5)$$

$[M_R]$ and $[H_R]$ need to be expressed in some suitable units, e.g. milli mole/g.

This type of expression will be used here, and the constant called the apparent equilibrium constant. In the case of this reaction being part of the substoichiometry indicated previously

$$K_{3H}^{M} = \frac{\frac{[M'] V}{R}\ [H]^3}{[M_f][H_R]^3} \qquad (6)$$

where V = volume of solution

and R = weight of resin

Assuming $[M'] \quad [M_f]$

Writing $\sqrt[3]{K_{3H}^{M}} = K_H^{M/3}$ and taking logs

$$3 \log K_H^{M/3} = \log \alpha_R + \log \left(\frac{V}{R}\right) - 3\ \mathrm{pH} - 3 \log [H_R] \qquad (7)$$

If metal concentration is very low, i.e. $[H_R] = C$ capacity of resin

$$\log \alpha_R = 3 \log K_H^{M/3} - \log \frac{V}{RC^3} + 3\ \mathrm{pH} \qquad (8)$$

Data available for such a calculation are few but some values can be substituted to give an estimate of α_R. (Values are calculated later in the Chapter)

Suppose $R = 1$ g

$V = 10$ ml

$C = 5$ milli eq/g

$K_H^{La/3} = 2.8$ According to Ringbom[9] for Dowex 50 resin

$$\log \alpha_R = 2.45 + 3\ \mathrm{pH} \qquad (9)$$

Thus α_R is never less than $10^{2.45}$ even at pH = 0. Now recalculating a new conditional stability constant for La-EDTA as in Table 6.1 gives Table 6.2.

Table 6.2

pH	$\log K_3(La)$	$\log \alpha_R$	$\log K'_3(La)$
1	-1.9	5.45	-7.35
2	-1.8	8.45	-6.65
3	-4.7	11.45	-6.75
4	6.9	14.45	-7.55
5	8.9	17.45	-8.55
6	10.7	20.45	-9.75
7	12.1	23.45	-11.35
8	13.2	26.45	-13.25

This is, of course, a purely hypothetical calculation, since it implies hydrogen form resin existing at high pH, but it does show quite clearly that α_R values are so high that one could never achieve substoichiometry with the resin in hydrogen form because, in its presence, the EDTA complex is unstable. For substoichiometry to be successful, α_R needs to be much smaller. The implication is that (a) the resin needs to be present in some exhausted form, say, sodium, (b) this metal ion (Na) also needs to be present in solution, to maintain the resin composition constant.

One way of continuing this so far completely theoretical treatment is to assume a suitable value of α_R and show that this corresponds to a real concentration of sodium ions present in solution when the resin is in the sodium form.

Let us assume that log $\alpha_R = 3$, i.e. 99.9% of the metal is exchanged

$$\text{La} + 3\text{Na}_R \rightarrow \text{H}_R + 3\text{Na}$$

$$K_{3\text{Na}}^{\text{La}} = \frac{[\text{La}_R]\,[\text{Na}]^3}{[\text{La}]\,[\text{Na}_R]^3} \qquad (10)$$

Call $\frac{[\text{La}_R]}{[\text{La}]} = D_{\text{La}}$

$$D_{\text{La}} = \frac{K_{3\text{Na}}^{\text{La}}\;[\text{Na}_R]^3}{[\text{Na}]^3} \qquad (11)$$

If log $\alpha_R = 3$, i.e. log $D_{\text{La}} \sim 3$

$$[\text{La}_R]\, R = 99.9\, [\text{La}]\, V \qquad (12)$$

$$D_{La} \gg \frac{99.9\ V}{R}$$

$$K_{3Na}^{La} \cdot \frac{[Na_R]^3}{[Na]^3} = \frac{99.9\ V}{R} \qquad (13)$$

In this equation, $[Na]$ represents the maximum concentration of sodium ions present in solution that will allow 99.9% exchange of lanthanum when the resin is present in the sodium form.

Substituting the values used earlier, this equals 0.898 M, say, 0.90 M Na^+, and the value is independent of pH.

The minimum value of sodium ions required to stabilise the complex in the presence of the resin is not independent of pH because it requires the conditional constant K_3 in its calculation.

Thus when $LaY + 3Na_R \longrightarrow 3Na + Y + La_R$ is the reaction we wish to avoid

$$\frac{K_3}{K_{3Na}^{La}} = \frac{[LaY]\,[Na_R]^3}{[La_R]\,[Na]^3[Y']} \qquad (14)$$

Let $\frac{[La_R]}{[LaY]} = D_{LaY}$

Taking logs

$$3 \log \frac{[Na_R]}{[Na]} - \log D_{LaY} - \log\,[Y'] = \log K_3 - \log K_{3Na}^{La} \qquad (15)$$

If $[LaY] = 0.999\ C_{HY}$

and $[Y'] = 0.001\ C_{HY}$

$$\text{then} \quad [La_R] = \frac{V}{R}\left(\tfrac{1}{2}\ C_{La} + 0.001\ C_{HY}\right) \qquad (16)$$

at 50% substoichiometry.

But $\frac{1}{2}\, C_{La} = C_{HY}$

i.e. $\left[La_R \right] = \frac{V}{R}\, 1.001\, C_{HY}$.

Take again the case where $V = 10$ ml

$R = 1$ g.

The minimum concentration of sodium required in solution to limit the extent of the breakdown of LaY as represented by D_{LaY} can be calculated.

Say $\left[Na_R \right] = 5$ meg g   At 50% substoichiometry

$C_{HY} = 10^{-5}$ M $D_{LaY} = 1$

$\therefore \left[Y' \right] = 10^{-8}$ M   Take $K^{La}_{3Na} = 5.8$ as suggested by Ringbom[9].

$$3 \log \left[Na \right] = 3 \log \left[Na_R \right] - \log D_{LaY} - \log \left[Y' \right] - \log K_3 + \log K^{La}_{3Na}$$

pH	$\log K_3$	$3 \log [Na_R]$	log D	$\log [Y']$	$3 \log [Na]$	$\log [Na]$	$[Na]$
3	4.7	2.1	0	-8	6.16	2.05	112) ?
4	6.9	2.1	0	-8	3.96	1.32	52)
5	8.9	2.1	0	-8	1.96	0.65	4.26
6	10.7	2.1	0	-8	0.16	0.05	3.15
7	12.1	2.1	0	-8	-1.24	-0.41	0.39

Obviously there is difficulty in reconciling this condition with the maximum sodium concentration just calculated.

The absence of hydrogen form resin can be easily confirmed.

$$Na + H_R \longrightarrow Na_R + H$$

$$K_H^{Na} = \frac{[Na_R][H]}{[H_R][Na]}$$

$$\log \frac{[Na_R]}{[H_R]} = \log K_H^{Na} + pH + \log [Na] \qquad (17)$$

$$K_H^{Na} = 1.56 \quad (\text{Ringbom}^9)$$

$$\therefore \log \frac{[Na_R]}{[H_R]} = 0.19 + pH + \log [Na] \qquad (18)$$

It can be assumed that the resin is wholly in sodium form if

$$\frac{[Na_R]}{[H_R]} \gg 1000.$$

For any particular concentration this could be achieved by varying the pH. For example

Conc. sodium (M)	pH
1.0	2.8
10^{-1}	3.8
10^{-2}	4.8
10^{-3}	5.8
10^{-4}	6.8

This treatment divides the work into several questions which need to be answered.

(a) Does the exchange reaction at trace concentration of metal behave in the proposed way so that the mass action law is obeyed? That is, is there any experimental justification for the above equations?

(b) Are the literature values true enough for the calculations to be valid?

(c) Does any treatment of this sort uphold the success of more empirical studies in substoichiometry both at Aston and Prague?

(d) Would other ion exchangers be more satisfactory?

In this last context, it is worth pointing out that the dividing line between liquid cation exchange with, for example, di-2-ethylhexylphosphate and solvent extraction systems such as tributylphosphate or even ion association extraction into oxygen containing solvents, is very diffuse, if it exists at all. Liquid cation exchangers have not been considered at this stage but rather avoided as a consequence of the ion-association extraction work of Chapters 4 and 5.

6.4 Choice of Buffer

Again in this work, unlike other aspects of substoichiometry, there is need for a buffer in the solution. It has already been explained that there is no buffer which does not complex rare earth to some extent. Hexamine and acetate were both used in this work. Acetate complexes of rare earth are quite strong but very much weaker than those for EDTA. Furthermore, the affinity of these metals for strong acid resins is so high that although acetate formation lowers the distribution ratio considerably, the percentage exchange is hardly affected at all.

Hexamine buffers gave rise to unexpected difficulties. Closer investigation, Experiment 6(i), disclosed that the resin was reacting with the HexH$^+$ cation most probably according to the exchange processes

$$\mathrm{HexH^+ + Na_R \longrightarrow HexH^+_R + Na} \qquad (19)$$

and/or

$$\mathrm{HexH^+ + Na_R \longrightarrow Hex + H_R + Na} \qquad (20)$$

HexH$^+$ is the cation of the partly neutralised hexamine. The effect is that neither the pH nor resin composition remain constant. Despite this, substoichiometry can be successful as will be shown below.

6.5 Choice of Exchange Conditions

Previous authors[29,30,31] have used ion exchange resins in columns of unspecified but inferably small size. The same technique was used in this work. For equilibrium measurements, however, batch exchange was used. Such extractions take many hours to reach equilibrium but with rare earth metals are essentially complete in less than 1 h, and practicable measurements can be made without resort to impossibly long experiments. The amount of resin affects this slightly, 6(ii). Substoichiometry can also be achieved by batch exchange, but when considering exchange of this type one must bear in mind that any separation which is barely possible in this way will be achieved much better with a very simple column arrangement. Reservations are explained below, which restrict the limits of column sizes.

6.6 Equilibrium Measurements Made in Batch Extraction

The measurements made and techniques used in these experiments roughly divide into two parts corresponding to the two sets of detection apparatus available. Some were done on a relatively macroscopic scale using greater than 10 ml of solution and in this case activities in the resin phase were calculated by difference from the total, known to be present at the start of the exchange, and that found in solution by taking aliquots. In the other case when small quantities of both resin and solution were used, it was convenient to measure the activity of an aliquot and compare this with the activity of the residual solution and resin measured at the same time. With such small quantities of resin, there is no question of shielding of high energy gamma rays and this method proved to be both rapid and accurate.

The experiments are divided roughly into three for discussion:

(a) The exchange of traces of rare earth with the strong cation resins, 6.7.

(b) The effects of changes in solution and metal present in the resin, 6.8.

(c) Reproducibility curves prepared using this type of separation, 6.9.

6.7 The Exchange of Rare Earths with Strong Cationic Resins

The exchange process has been accepted as being a stoichiometric reaction obeying the law of mass action in dilute solutions. Before presenting results of the present work, let us consider what this statement implies.

The true thermodynamic equilibrium constant, e.g.

$$K = \frac{a_{M_R^{n+}} \; a_{Na}^{n}}{a_{M^{n+}} \; a_{Na_R}^{n}}$$

is easily accepted. The concentration or apparent constant previously defined would be expected to also be analogous to its counterpart in electrolyte solution equilibria, that is a constant over a wide range of dilute solutions.

$$K^{M}_{nNa} = \frac{[M_R][Na]^n}{[M][Na_R]^n} \qquad \text{as in 5, 10.}$$

In ion exchange, however, not all of these terms can describe a 'dilute' solution. The resin must be saturated with ions of one sort or another. Thus if we consider it as a solid solution of ions then when M_R is low, Na_R must be high, of the order of 5 molar. Indeed at the very low loadings expected in trace analysis Na_R would be affected to so slight an extent as to be constant, if M^{n+} ions are the only metal in solution.

$$K^{M'}_{nNa} = \frac{[M_R]}{[M]} . [Na]^n \tag{21}$$

There have been many derivations of similar equations. Since K^{M}_{nNa} is an apparent constant, it will vary with ionic strength, but in addition, the distribution of rare earth between solution and resin has been shown by Tomkins and Mayer to depend on the metal concentration, all other parameters being constant[32]. They conclude that the distribution is constant over a wide range of low concentrations but falls off sharply above a critical concentration.

Furthermore, it is not possible to conveniently study the variation in exchange of a constant amount of one ion, say Ce^{3+} with a resin exhausted with, say Na^+, as the concentration of sodium changes, at constant ionic strength. A third cation would need to be introduced which would itself be exchanged to some degree.

The distribution of cerium between Dowex 50 X8 and strong sodium perchlorate was studied, 6(iv). Distribution fell as the sodium increased, but the slight change in ionic strength (μ) is barely reflected in the value of K^{Ce}_{3Na}, Table 6.3.

Table 6.3

Values of Exchange Constants for Cerium-Sodium

Conc. sodium M	K^{Ce}_{3Na}
0.248	4.00
0.496	5.15
0.744	5.142
0.992	6.92

The mean value of $K^{Ce/3}_{Na}$ is 1.75, in good agreement with 1.8 quoted by Ringbom[9]. Some variation arises from taking resin concentrations in milli eq/g of sodium form rather than hydrogen form.

Values were also obtained for the exchange of sodium with barium form Dowex 50 X8, 6(v), in the presence and absence of barium.

The mean value of $K^{Ba/2}_{Na}$ is 4.22. These results are also in agreement with those of Connick and Mayer[33] which in turn show similar variations between determinations.

Table 6.4

Values of Exchange Constants for Barium-Sodium

Conc. sodium M	K_{2Na}^{Ba}
0.008	14.8
0.008	18.0
0.015	14.25
0.022	11.5
0.029	11.5
0.045	23.7
0.092	29.1
0.478	18.6

These exchanges, trace cerium for sodium and higher concentrations of barium for sodium, obey the mass action law. By exchanging trace cerium for barium, 6(vi), it was possible to gain insight into the possibilities of substoichiometry with this system and also make further estimates of K_{3Na}^{Ce}.

Thus

$$K_{3Na}^{Ce} = \frac{[Ce_R]\,[Na]^3}{[Ce]\,[Na_R]^3}$$

and
$$K_{3Ba}^{2Ce} = \frac{[Ce_R]^2\,[Ba]^3}{[Ce]^2\,[Ba_R]^3}$$

and
$$K_{2Na}^{Ba} = \frac{[Ba_R]\,[Na]^2}{[Ba]\,[Na_R]^2}$$

therefore
$$K_{3Na}^{Ce} = \sqrt{(K_{2Na}^{Ba})^3 \cdot K_{3Ba}^{2Ce}} \qquad (22)$$

The mean value of K^{2Ce}_{3Ba} was 0.127, resulting in K^{Ce}_{3Na} of 26.5 or $K^{Ce/_3}_{Na}$ of 2.98.

This seems reasonable agreement with the previous value, allowing for magnification of errors by the third power relationships.

It can be concluded from these observations that changes in μ have much less effect than might be supposed, as recently proposed for monovalent ions[34]. Further, the apparent constants are of the order anticipated in the earlier calculations. These experiments do not in any way demonstrate behaviour in very dilute solutions in which the exchange is markedly affected by concentration[35]. Similar effects have been observed in these experiments, for example in 6(vii).

6.8 Exchange Reactions Involving a Substoichiometric Amount of EDTA

Substoichiometry with these resins was studied on the basis that the exchange took place in the anticipated manner. Thus the equilibrium established between the resin, metal (say cerium), and a substoichiometric amount of EDTA can be written in a fashion analogous to that already presented for solvent extraction.

It is not possible, however, to study the equilibrium of the complexation and exchange reactions as in solvent exchange work since (a) one cannot alter the effective concentration of ions present on the resin (as done with TTA), nor (b) can one use a fixed amount of resin over a wide range of complex concentration (as with salicylate) without poorly understood concentration effects masking the true meaning of the results.

The stability constant defines

$$\frac{[CeY]}{[Y]} = K_2 [Ce]$$

or
$$\frac{[CeY]}{[Y']} = \frac{K_2 [Ce]}{\alpha_{Y(H)}}$$

If
$$Ce_T = Ce + Ce_R$$

Then
$$\alpha_{Ce_R} = 1 + \frac{Ce_R}{Ce} \sim \frac{Ce_R}{Ce} \qquad (23)$$

$$\alpha_{Ce_R} = 1 + K_{2Na}^{Ce} \frac{Na_R^{\;3}}{Na^3}$$

The amount of CeY at equilibrium will depend not only on pH, but also on the amount of residual metal present on the resin and in solution.

Substoichiometry will only be successful if the product $\alpha_{Y(H)} \cdot \alpha_{Ce_R}$ allows $[CeY]/[Y']$ to be sufficiently large for a given Ce_T value. The exchange of trace cerium in strong sodium perchlorate was also studied for a substoichiometric reaction mixture. The result is shown in Fig. 6.1 from Experiment 6(viii). The curve passes through a minimum and rises to activities in excess of that required by the EDTA. There is no immediate explanation of these facts, although it will be shown that the time of contact between resin and solution, 1½ h in this case, is critical.

Parallel experiments conducted with terbium and Amberlite IR 120 gave the same pattern of results, 6(ix). The overall

Fig.6.1

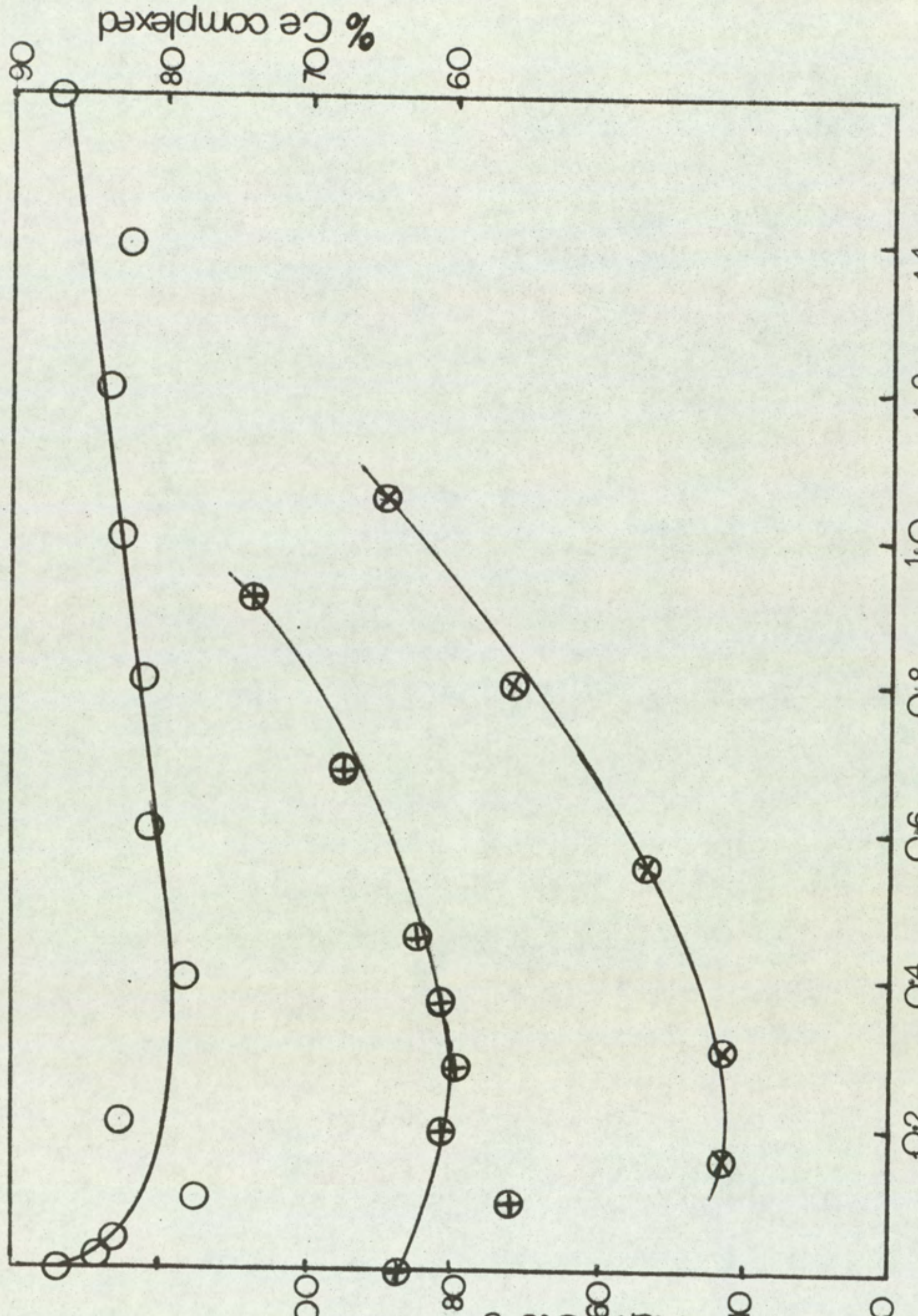


Fig.6.1. Variation of Ce-EDTA decomposition by Dowex 50X8(Na)
Effect of sodium concentration.

effect is constant below sodium concentrations of about 1 molar as seen in Fig. 6.2.

The conclusions made earlier, therefore, need modification. Substoichiometry, notwithstanding the approximation of simpler exchange to the mass action law, is obviously more complicated than proposed in the theoretical treatment. The closeness of the prediction that 1 molar sodium would interfere also relies upon ideal behaviour, and it can scarcely be regarded as a dilute solution.

A study of reproducibility curves is helpful to see the direct consequences of these results for substoichiometric analysis.

6.9 Reproducibility Curves (Collected in Experimental Section 6(x))

A good deal of difficulty was experienced in using the small column filtration technique of Ruzicka and Prasilova. Quantitative washing of even small columns caused unwanted dilution of the test solution. Experiments were tedious and often failed to be reproducible even on the same day. As the affinity of rare earths for Dowex 50 and Amberlite IR 120 is high, batch exchange was preferred.

Early experiments with terbium-EDTA at 10^{-5} M and acetate buffer gave unacceptable sloping curves, Fig. 6.3. Better results were obtained in very strong hexamine, which effectively used up all the resin sites and resulted in a solution pH of 7, Fig. 6.4. Reproducibility of any one point is poorer due to hydrolysis and loss of metal. With cerium, on shaking for a period of 70 h chosen to test for slow equilibration, almost all the metal was lost with both Dowex 50 and Amberlite IR 120. The same reaction shaken for only 30 minutes gave an excellent reproducibility curve with

Fig.6.2

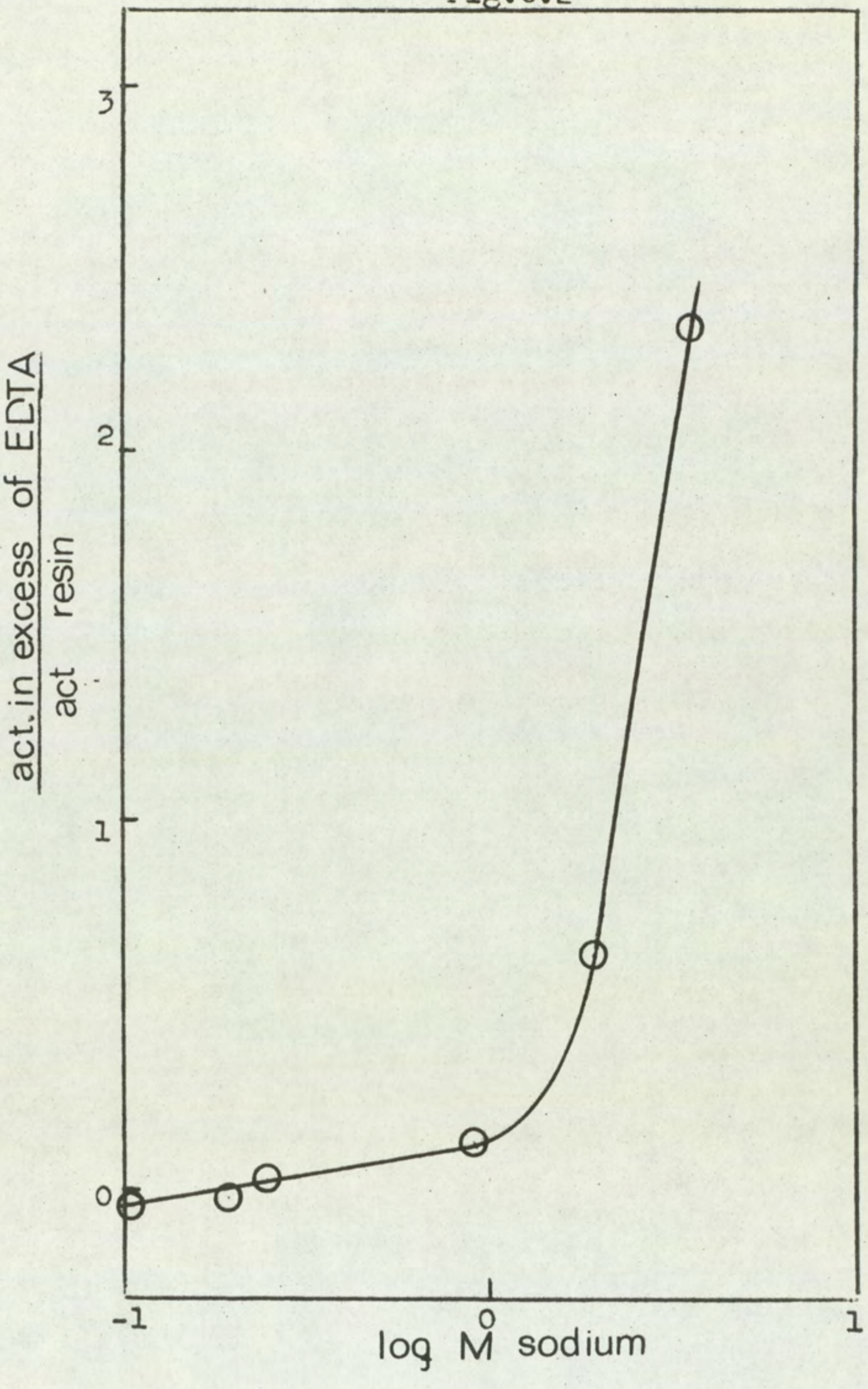


Fig.6.2. Variation of terbium-EDTA decomposition by Amberlite IR 120.Effects of sodium concentration.

the equivalence point slightly lower than theoretical. The implication is that the EDTA complex is destroyed but only very slowly.

The plateau of the reproducibility curve was observed at intervals over a wide period of time. The activities fell steadily as expected, but the predicted slope of the line at equilibrium was not discernible. This was, however, thought to be due to a lowering of the precision with which each point could be measured as the time increased. On a small sample of 5 tests, standard deviation was 2.2% of the mean after 15 minutes and 9.9% after 60 minutes.

The slope of the reproducibility curve plateau was measured in another experiment. EDTA solution 10^{-5} M, and pH of 5 in acetate buffer were chosen. A high sodium concentration 0.5 M ensured that a measurable amount of metal remained after shaking. A contact time of 75 h was used.

A plot of $\frac{[CeY]}{[Ce]}$ versus $[Ce_R]$ was drawn. This graph, Fig. 6.5, tends toward a straight line passing the origin and having a slope of 4.35×10^2. Thus it appears that substoichiometry is obeying a law

$$\frac{[CeY]}{[Ce]} = \text{const.}\ [Ce_R]$$

The conditional constant so determined is not in agreement with that expected on the basis of previous experiments, but is several orders of magnitude less.

These batch exchanges were all conducted with 0.2 to 1.0 g of resin. Adsorption possibilities were more fully investigated as a possible source of this further complication.

Fig.6.3

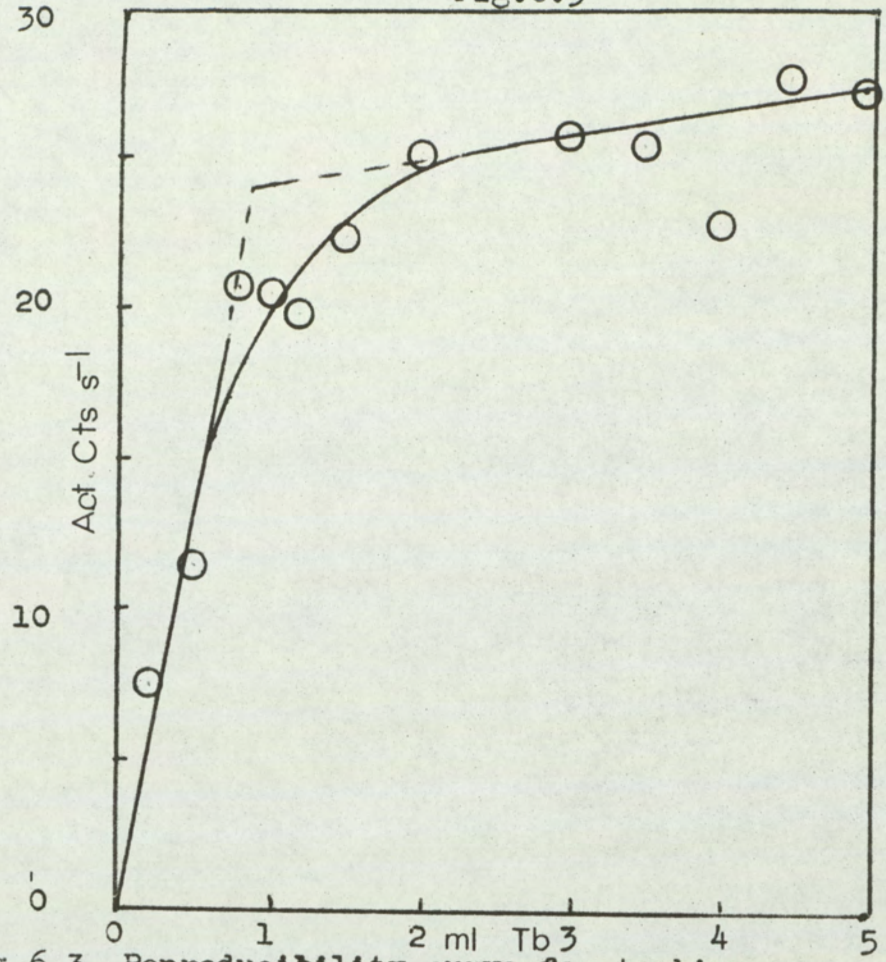


Fig.6.3. Reproducibility curve for terbium.

Fig.6.4

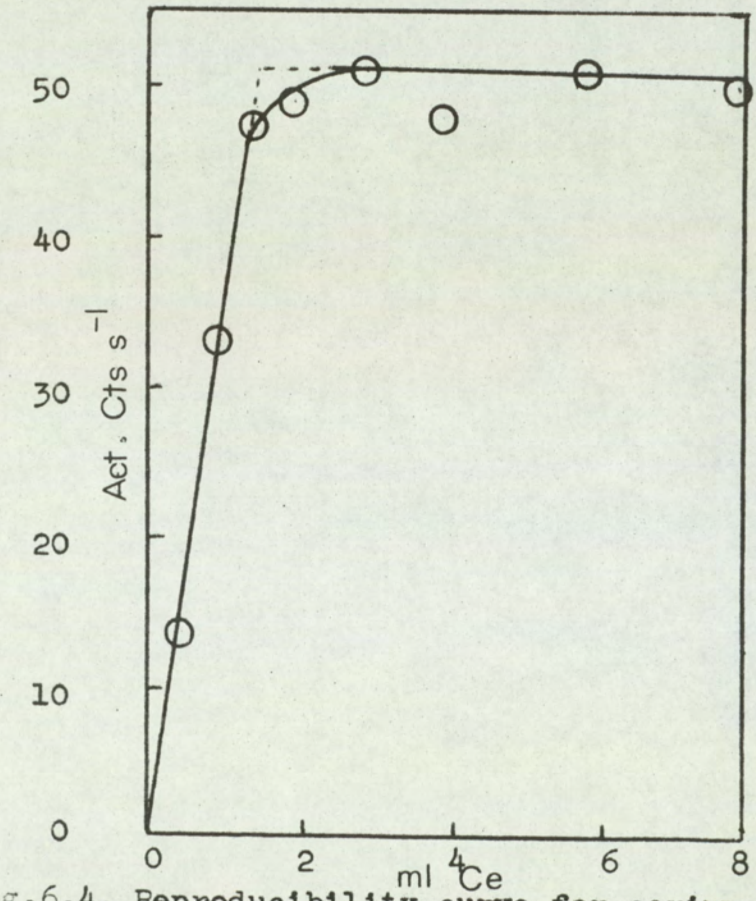


Fig.6.4. Reproducibility curve for cerium.

A substoichiometric reaction mixture was separated using varying amounts of resin. The result shown in Fig. 6.6 indicated this factor to be very important. Table 6.5 is a summary.

Table 6.5

Variation of Cerium Retained in Solution by a Substoichiometric Amount of EDTA with Total Resin Content

Wt. resin g. (dry)	Activity aq. phase counts s^{-1}
0.2	87.4
0.5	75.1
1.0	48.8
1.5	24.6
2.0	11.5

This result cannot be explained by penetration or water absorption, as it is the reverse of behaviour explicable on these grounds. It was assumed for this experiment that interstitial solution was the same concentration as the supernatant.

The possibility of adsorption without any exchange was tested in several ways, collected in 6(xi). A substoichiometric separation was attempted using varying amounts of resin and times of contact. Sodium concentration of 0.2 M was chosen as being neither too concentrated or too dilute for 'ideal' behaviour, and which should from past experiments allow quantitative exchange of free metal. The result is shown in Fig. 6.7.

Several points are obvious. The reaction took several hours to reach equilibrium and resulted in loss of EDTA complex in most cases. The very small resin weights did not remove all free metal, perhaps

Fig.6.5

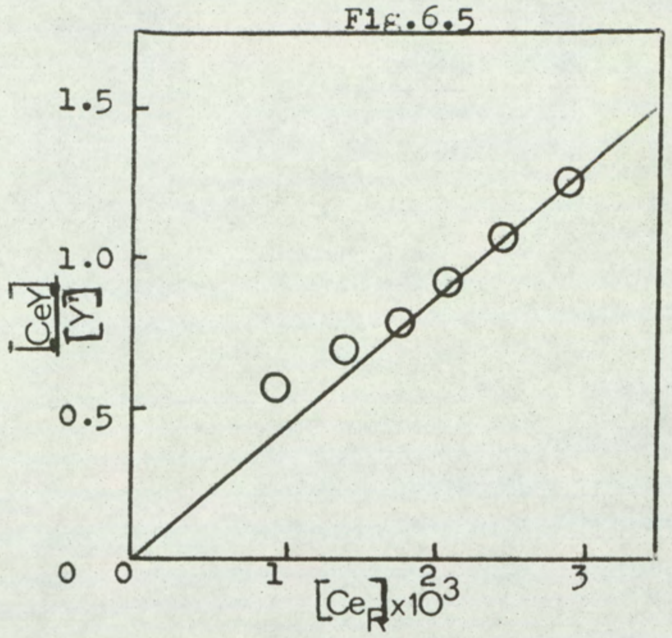


Fig.6.5. Slope of reproducibility curve plateau for cerium, caused by Dowex 50X8.

Fig.6.6

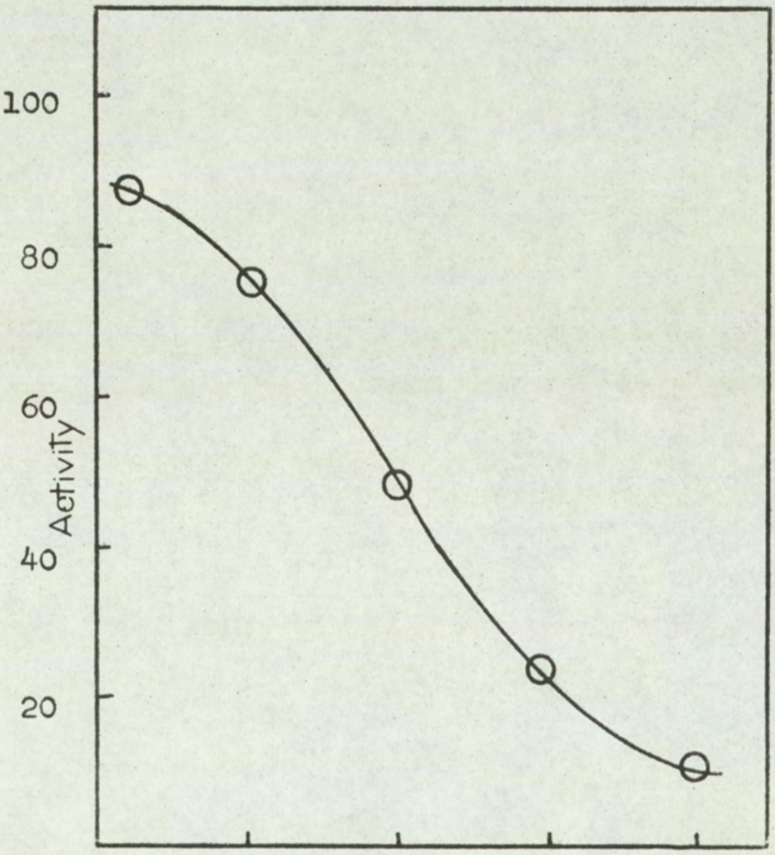


Fig.6.6. Effect on reproducibility of varying the amount of resin.

due to the impossibility of adequate contact. The 10 mg and 50 mg curves, therefore, are probably fortuitously close to optimum conditions.

The activities present on each resin sample do not represent a common concentration.

Adsorption is unlikely to be severe when the amount of resin is small. Reproducibility curves made at 10^{-5} M EDTA and 10 mg resin at pH 5.0 (acetate) are shown in Fig. 6.8. Parallel curves were obtained in 4 or 15 h. The equivalence point was less than the theoretical, and the part which should have been horizontal in fact had a slope of 1.2% of the mean activity for every 1 ml of approximately 10^{-5} M metal present.

Adsorption was finally disproved by conducting substoichiometric separations using ^{14}C labelled EDTA. Neither the sodium content of the solution, nor the amount of resin from 10 to 200 mg caused any difference in the amount of labelled compound in the final solution.

6.10 Use of Resins in Other Than Sodium Form (Experimental Section 6(xii))

The remaining point for discussion is the possibility of inhibiting the decomposition of the metal EDTA and subsequent exchange, by having a more strongly bound metal on the resin. Barium has been considered, as figures were already available from other experiments.

The question of buffer is again important and the situation complicated by the formation of barium complexes on reacting resin with buffer.

The direct exchange of cerium for barium was measured in the presence and absence of sodium perchlorate, the effect of which upon the barium resin was already known. There was little difference in the two cases, and Ce_R / Ce was equal in the

Fig.6.7

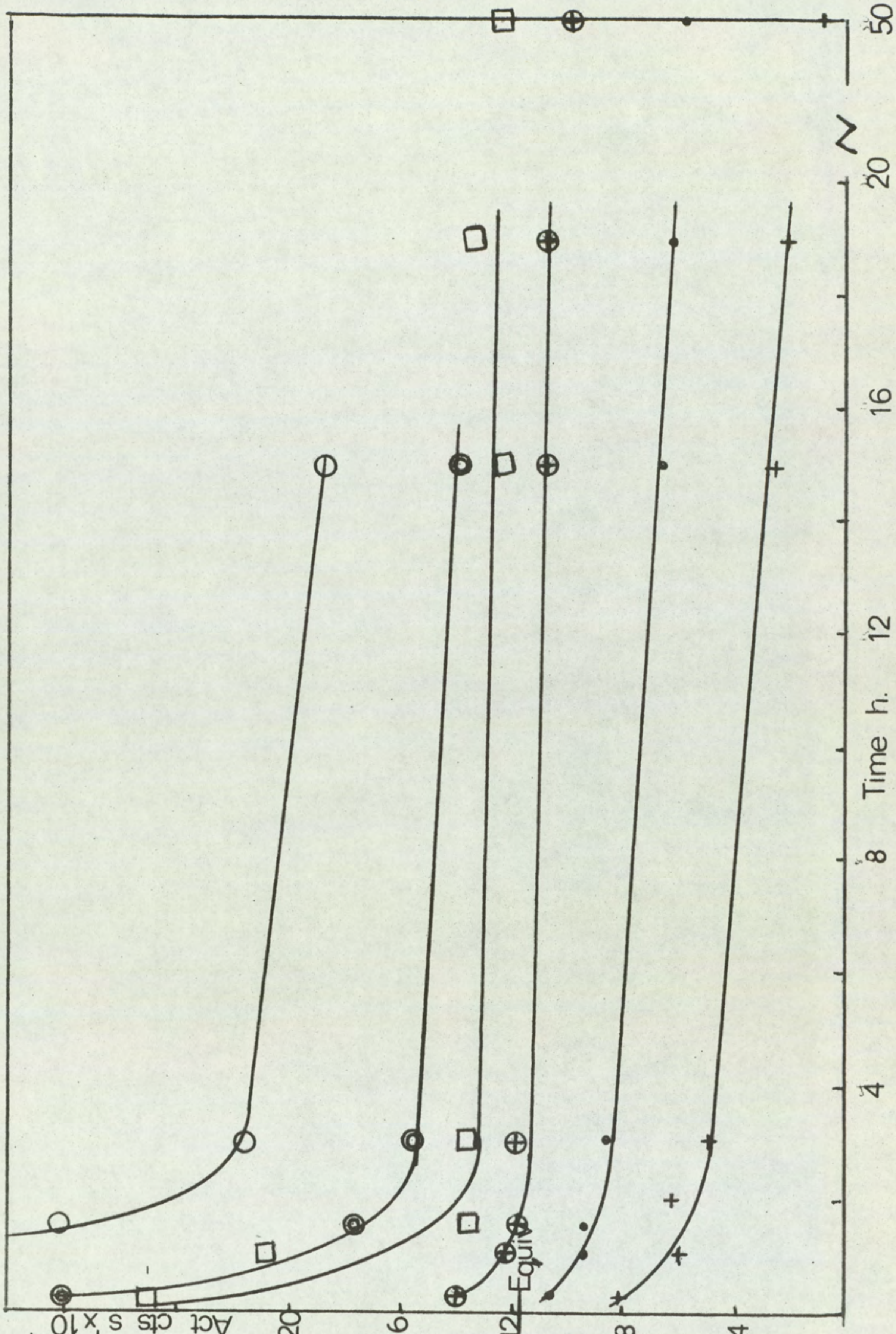


Fig.6.7. To test the possibility of adsorption, by varying the time of contact and resin weight.

two experiments until sodium concentration was as high as 0.04 M. There was appreciable decomposition of Ce-EDTA by barium resin in 20 h, and the amount decreased as the sodium ion concentration increased at constant μ.

Reproducibility curves made at 10^{-5} M EDTA were unsuitable for substoichiometry and the success obtained with sodium resins with short shaking times could not be repeated.

6.11 Conclusions

Substoichiometric analysis can be achieved using ion exchange resins. Published work[29,30,31] is available to prove its success. Equal success has been achieved using the much less tedious technique of batch exchange with a short time of shaking. This method takes advantage of the fact that the equilibrium in the reaction between complex and resin is approached very slowly indeed unless the resin is present in large amounts. With contact times of the order of 15 minutes, almost perfect reproducibility curves are obtained and it is thought that these conditions approximate to rapid filtration through very small columns. With longer times of shaking, errors become much larger and it would be impossible to analyse completely unknown solutions.

6.12 Experimental

General

Exchange Techniques for Equilibrium Measurements

All exchanges were conducted at room temperature. Batch exchanges were achieved by shaking together dry resin, and solution in stoppered vessels. For the purpose of these experiments it was assumed that all ions not bound to the resin were present in

Fig.6.8

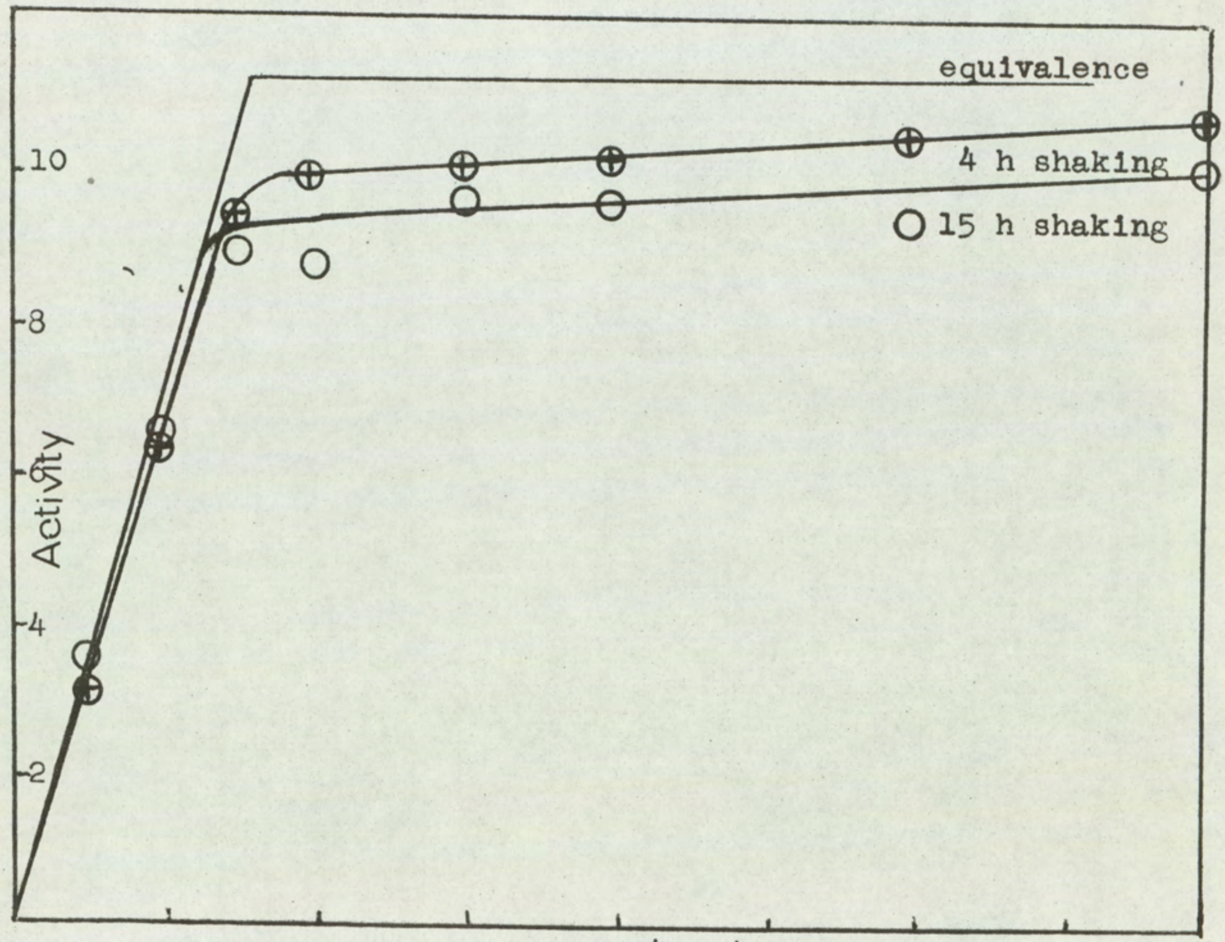


Fig.6.8. Reproducibility curve with 10 mg resin.

solution in uniform concentration, and that penetration and swelling of the relatively small amounts of resin had negligible effect on these concentrations. Thus metal concentration was determined by measuring activity of an aliquot of supernatant solution for the aqueous phase, and for the resin phase by subtracting solution activity from the total. This was done in two ways.

1. <u>For the Smaller Na I Well</u>

   Resin and solution of known volume and known total activity and concentration, etc., were shaken together in glass stoppered tubes for the required time. Any visible cloud was filtered off and the activity of an aliquot determined. Activity on the resin was found by difference.

2. <u>For the Larger Na I Well</u>

   Counting vials for this well were glass with plastic stoppers and had a volume of about 12 ml. Batch exchange was conducted with 10 ml of solution and from 10 mg to 1 g of resin (usually 200 mg) in these vials. At equilibrium, a 5 ml aliquot of supernatant solution was removed and added to 2 ml of water in a second vial. The pipette was rinsed into the first vial with 2 ml water. Both vials were counted, the first giving solution activity and the difference giving the resin activity.

For following experiments using these methods, only the starting solution conditions, and results, are given.

Calculation of Constants for Tables 6.1 and 6.2

$\log K_2$ (La) = 15.5; $K_H^{La/3} = 2.8$[9]

$\log K_2$ (Lu) = 19.8; $V = 10$; $R = 1$; $C = 5$ meg g

pH	$\log \alpha_{Y(H)}$[9]	$\log K_3$ (La)	$\log K_3$ (Lu)	$\log \alpha_R$	$\log K'_3$ (La)
1	17.4	-1.9	2.4	5.45	-7.35
2	13.7	1.8	6.1	8.45	-6.65
3	10.8	4.7	9.0	11.45	-6.75
4	8.6	6.9	11.2	14.45	-7.75
5	6.6	8.9	13.2	17.45	-8.55
6	4.8	10.7	15.0	20.45	-9.75
7	3.4	12.1	16.4	23.45	-11.35
8	2.3	13.2	17.5	26.45	-13.25
9	1.4	14.1	16.4	29.45	-15.35
10	0.5	15.0	19.3	32.45	-17.45

No account taken of hydrolysis.

6(i) Hexamine Buffer Reactions

Hexamine buffer was observed to change pH on shaking with Dowex 50 X8 (Na).

The dissociation constant pKa for hexamine was determined by pH titration with standard acid. The result obtained was pKa = 4.82.

Calculating from this figure, one can determine hexamine rapidly by titrating with acid or base to find the amount consumed in changing pH from 3.05 to 8.75. This first approximation was found to be as reliable as acid hydrolysis methods.

The exchange reaction was investigated as follows:-

Solutions: 8.2×10^{-2} M NaOH

8.8×10^{-2} M $HClO_4$

10^{-1} M hexamine.

Method. Hexamine buffer was made by mixing 50 ml of acid with 100 ml of buffer. The solution was shaken with 20 g of dry sodium form Dowex 50 X8 for 20 hours. A 15 ml aliquot was analysed for hexamine content. Sodium concentration was determined by evaporating a further aliquot to small volume and precipitating with zinc uranyl acetate. An equal aliquot of unreacted buffer was also analysed for hexamine content.

Results

	Total hexamine content (mg)	Hex H^+ (mg)	Free hexamine (mg)	Sodium content (mg)
Standard	142.0	62.0	80.0	-
Sample	89.2	2.2	87.5	9.66

9.66 mg Na = 58.9 mg hexamine.

Conclusion. The hexamine buffer reacts with the resin probably according to the reactions

$$\text{Hex } H^+ + Na_R \rightarrow \text{Hex } H_R^+ + Na$$

and/or

$$\text{Hex } H^+ + Na_R \rightarrow \text{Hex} + H_R + Na.$$

6(ii) Time to Reach Equilibrium in Batch Exchange between Trace Rare Earth (Terbium) and Dowex 50 X8 (Na)

Solutions: Buffered metal solution, 5 ml 10^{-5} M terbium plus 10 ml 10^{-1} M acetate buffer pH 4.0.

Method. The solution was shaken for varying times with 1 g of dry resin.

Results

Time of shaking (min)	Activity of 5 ml aliquot counts s^{-1}	Time of shaking (min)	Activity of 5 ml aliquot counts s^{-1}
0		45	6.6
10	26.6	50	9.3
20	15.3	55	6.4
30	7.8	60	7.4
40	7.0	120	7.0

Conclusion. Approximately 99.9% of metal is removed in 30 minutes. For future equilibrium measurements, especially with small amounts of resin, shaking times of several hours were often convenient.

6(iii) Determination of Resin Capacity

Solutions: Amberlite IR 120 (Na)
Dowex 50 X8 (Na)
10^{-1} M sodium perchlorate labelled ^{22}Na.

Method. Each resin was shaken for 50 hours with 0.099 M $^{22}NaClO_4$. Capacity was determined by measuring activity in both phases after isotopic exchange was complete.

Results Weight of resin 0.20 g
Volume of solution 10.00 ml

	Activity 5 ml counts s^{-1}	Activity resin	Capacity m eq g^{-1}
Amberlite IR 120	241.6	414.1	4.24
	247.1	400.3	4.01
Dowex 50 X8	242.0	420.2	4.29
	242.0	420.5	4.29

Conclusion. The resin capacity in m eq per gram was 4.12 (Amberlite) and 4.29 (Dowex).

6(iv) Exchange of Trace Cerium with Dowex 50 X8 (Na)

Solutions: 10^{-4} M cerium

5 M sodium perchlorate.

Method. The following reaction mixtures were exchanged with 0.2 g resin. Time of shaking was 6 hours.

ml Ce	ml $NaClO_4$	H_2O
5	0.5	4.5
5	1.0	4.0
5	1.5	3.5
5	2.0	3.0

Results

Activity 5 ml solution counts s^{-1}	Resin activity 0.2 g counts s^{-1}	Sodium concentration M	K^{Ce}_{3Na}
0.96	796.9	0.248	4.00
5.78	789.8	0.496	5.15
17.85	744.0	0.744	5.42
32.27	731.2	0.992	6.92
			5.35 Mean

$K^{Ce/3}_{Na} = 1.75$

Conclusion. This exchange obeys a simple mass action law. The result is in agreement with Ringbom[9], and is little affected by changes in   at this concentration.

6(v) Exchange Reaction of Sodium with Dowex 50 X8 (Ba)

This experiment was performed in two parts, (a) having no barium initially in solution, (b) having varying barium concentration initially.

Solutions: Sodium perchlorate solution labelled ^{22}sodium

10^{-1}M barium perchlorate.

Method. The following reaction mixtures were exchanged with (a) 0.2 g resin, (b) 1.0 g resin, for 6 hours.

(a) 10 ml sodium perchlorate 0.496 M, 0.099 M, 0.050 M, 0.010 M.

(b)

ml 10^{-1} M Ba	ml ^{22}Na	H_2O
0.33	4.0	5.67
0.67	3.0	6.33
0.99	2.0	7.01
1.34	1.0	7.67

Results

Activity 5 ml soln counts s^{-1}	Activity resin counts s^{-1}	Conc. sodium (M)	Conc. barium (M)	K^{Ba}_{2Na} (as Ba resin)	K^{Ba}_{2Na} (as Na resin)
310.57	110.6	.008	0.0145(b)	17.8	14.8
410.2	73.9	.008	0.0008	21.6	18.0
644.3	239.7	.015	0.0023(b)	17.1	14.25
963.1	390.8	.022	0.0034(b)	13.8	11.5
1301.6	561.1	.029	0.0109(b)	13.8	11.5
439.0	152.9	.045	0.0122	28.5	23.7
1031.7	88.4	.092	0.0105	35.0	29.1
804.1	160.4	.478	0.0088	22.4	18.6

Conclusion. These results, mean 17.7, agree with those of Connick and Mayer[33]. The amount of resin consumed by sodium and, therefore, likely to affect the exchange of rare earth can be seen from, for example, experiment (b).

Original sodium concentration. M	% Resin in sodium form
0.04	3.03
0.03	2.11
0.02	1.26
0.01	0.82

6(vi) The Exchange of Trace Cerium onto Dowex 50 X8 (Ba)

This experiment, like 6(v), was also conducted in two parts with (a) 0.2 g, (b) 1.0 g resin.

Solutions: (a) 8.25×10^{-4} M cerium solution

(b) 5.9×10^{-5} M cerium solution

10^{-1} M barium solution.

Method. In each case, 5 ml of labelled cerium was made to 10 ml with barium solution and water, to give a range of barium concentrations. Exchange time was 3 hours.

Results

(a)

Activity 5 ml soln counts s^{-1}	Activity resin counts s^{-1}	$\frac{Ce_R}{Ce}$	Initial conc. of Ba (M)	K^{2Ce}_{3Ba} (as Ba resin)	K^{2Ce}_{3Ba} (as Na resin)
19.11	252.4	305	0.02	0.195	0.162
32.67	240.5	158	0.03	0.180	0.150
45.49	251.9	98	0.04	0.165	0.137
59.91	302.9	60	0.05	0.120	0.100

(b)

Activity 5 ml soln counts s^{-1}	Activity resin counts s^{-1}	$\frac{Ce_R}{Ce}$	Initial conc. of Ba (M)	K_{3Ba}^{2Ce} (as Ba resin)	K_{3Ba}^{2Ce} (as Na resin)
4.72	2925	3100	0.0033	0.059	0.050
18.12	2944	813	0.0067	0.034	0.029
15.03	2906	970	0.0099	0.162	0.135
18.98	2906	769	0.0134	0.248	0.206
45.53	2906	320	0.0167	0.082	0.067

Mean $K_{3Ba}^{2Ce} = 0.127$

Conclusion. From this result and 6(v), $K_{3Na}^{Ce} = 26.5$, $K_{Na}^{Ce/3} = 2.98$.

6(vii) Exchange in Very Dilute Solution

These results above do not represent exchange from very dilute solutions as described by Levin et al.[35]. The effect on distribution ratio brought about by progressively diluting the metal solution before exchange was studied by exchange method 1, described earlier, in both buffered and unbuffered solution with Dowex 50 X8. The results are summarised below.

(a) Solutions: 10^{-5} M terbium in 1.64 x 10^{-1} sodium perchlorate.

Method. A series of solutions, made by diluting the solution above, were exchanged with Dowex 50 X8 resin for 6 h, using 10 ml to 1 g resin.

Results

Activity 5 ml of solution counts s^{-1}	Activity of resin 1 g counts s^{-1}	Ionic strength	Dist. ratio
27.5	6568.0	0.164	1190
17.7	1140.0	0.033	334
6.0	183.2	0.0066	156
3.5	22.4	0.0013	32

(b) Solutions: Sodium acetate buffer, acetate concentration 1.8 M to 10^{-3} M

10^{-5} M terbium.

Method. Equal volumes of each solution were mixed and exchanged for 6 h, using 1 g resin to 10 ml.

Results

Activity 5 ml of solution counts s^{-1}	Activity of resin 1 g counts s^{-1}	Acetate concentration pH 4.6	Dist. ratio
1003.0	6414.0	0.001	32.0
336.5	7747.0	0.01	115.0
74.5	8271.0	0.10	555.0
152.4	1184.2	0.45	36.0
989.0	248.0	0.90	1.25
3320.0	1780.0	1.00	2.68
1241.0	16.0	1.80	0.0645

Conclusion. Distribution between resin and solution increases as solution concentration increases as long as there is no complexation in solution.

6(viii) Substoichiometric Extraction onto Dowex 50 X8 (Na) in the Presence of Varying Concentration of Sodium Perchlorate

Solutions: 10^{-4} M cerium

10^{-4} M EDTA

5 M sodium perchlorate

Method. Both exchange methods 1 and 2 were used

1. 10 ml of solution, 1 g of resin
2. 10 ml of solution, 0.2 g of resin.

In method 1, exactly equivalent Ce-EDTA solution 2.0×10^{-4} M was shaken with Dowex 50 (Na) at various sodium concentrations. Shaking time was 90 minutes. In method 2, excess metal was present. The shaking time was 30 minutes. Only the activity of the aqueous phase and pH were measured.

Results

1. Activity 2 ml Ce-EDTA complex 1297.9 counts s^{-1}

1301.8 counts s^{-1}

Activity 5 ml sol. counts s^{-1}	Conc. sodium M	% cerium EDTA at equilibrium
553.2	0.00	87.0
537.9	0.02	84.5
531.5	0.04	83.6
492.4	0.10	77.5
526.6	0.20	82.7
497.0	0.40	78.3
514.6	0.60	80.9
515.2	0.80	81.1
525.6	1.00	82.7
531.6	1.20	83.7
522.6	1.40	82.1
553.9	1.60	87.0

pH of solutions 6.00 (hexamine buffer)

2(a) 3 ml 8.2×10^{-5} M cerium plus 1 ml 1.24×10^{-4} M EDTA.

Activity 5 ml of solution counts s^{-1}	Conc. sodium M	Activity 5 ml of solution counts s^{-1}	Conc. sodium M
87.40	0.0	82.01	0.364
72.01	0.091	84.81	0.455
81.03	0.182	95.51	0.682
79.40	0.273	108.81	0.910

pH of solutions 5.00 (acetate buffer)

2(b) 2 ml cerium 8.2×10^{-5} M plus 1 ml EDTA 1.24×10^{-4} M.

Activity of Ce equivalent to EDTA 63.50 counts s^{-1}.

Activity 5 ml of solution counts s^{-1}	Conc. sodium M	Activity 5 ml counts s^{-1} 16 h shaking
42.95	0.15	24.11
43.20	0.30	28.19
53.62	0.55	42.89
71.80	0.80	57.27
88.80	1.05	77.02

pH of solutions 4.95

Conclusion. These results are shown in Fig. 6.1 and discussed in Section 6.8. The time factor is obviously important, but the minimum which occurs in the activity curves at pre-equilibrium condition, and the failure to obtain complete exchange at high concentrations, offers added difficulties for substoichiometry.

6(ix) Exchange of Substoichiometric Terbium-EDTA by Amberlite IR 120 in Varying Concentrations of Sodium Chloride

Solutions: 3 ml 4×10^{-2} M terbium plus 2 ml 4×10^{-2} M EDTA made to 10 ml in 10^{-1} M acetate buffer with varying conditions of sodium chloride.

Method. A 5 ml aliquot was exchanged with 1 g resin. Tests with no EDTA and large excess EDTA were also carried out. Shaking time was 90 minutes.

Results

Activity 2 ml of solution counts s^{-1}	EDTA present	Activity in excess of EDTA (10 ml)	$\frac{\text{Excess activity}}{\text{Resin activity}}$
8.7	0.0		
8.5	0.0		
912.0	Excess		
914.0	Excess		
686.0	Subst.	1020	0.91
688.0		1030	0.927
703.0		1105	1.07
725.0		1215	1.31
829.0		1735	4.28
910.0		2140	210.00
Standard 912.0			

This result is shown in Fig. 6.2.

Conclusion. The effect of the sodium ions becomes appreciable at concentrations of about 1 M.

6(x) Reproducibility Curves with Sodium Form Resin

Solutions: Hexamine buffer pH 6.0

Acetate buffer pH 5.0

10^{-4} M terbium

10^{-4} M cerium

10^{-4} M EDTA.

Reproducibility curves were normally made using a total of about 10 ml of solution containing substoichiometric reagents at about 10^{-5} M. Buffer was included, and from 0.1 to 1.0 g of resin. A 5 ml aliquot was counted to plot the graph.

Results

(a) Terbium, 10^{-1} M acetate buffer

Volume of EDTA 1 ml: Total volume 10 ml: 1 g resin: Shaking 1 h.

ml terbium	Activity counts s^{-1}	ml terbium	Activity counts s^{-1}
0.2	740	2.0	2522
0.5	1289	3.0	2572
0.8	2069	3.5	2555
1.0	2045	4.0	2285
1.2	1970	4.5	2775
1.5	2235	5.0	2730

Shown as Fig. 6.3.

(b) Cerium, 2 x 10^{-1} M hexamine buffer

Volume EDTA 2 ml: Total volume 17 ml: 1 g resin: Shaking 1 h.

ml cerium	Activity counts s^{-1}	ml cerium	Activity counts s^{-1}
0.5	13.70	3.0	51.00
1.0	33.10	4.0	47.70
1.5	47.30	6.0	51.00
2.0	48.90	8.0	49.70

Shown as Fig. 6.4.

(c) Cerium, 5×10^{-2} M acetate buffer

Volume of EDTA 1 ml: Total volume 11 ml: 0.2 g resin:

(i) Shaking 40 h.

Theoretical value of equivalence activity 57.2 counts s^{-1}.

Amberlite IR 120		Dowex 50 X8	
ml cerium	Activity counts s^{-1}	ml cerium	Activity counts s^{-1}
2.0	10.40	2.0	2.50
3.0	14.60	3.0	7.30
4.0	19.70	4.0	5.40
5.0	6.70	5.0	4.60

(ii) Shaking 30 min. Dowex 50 X8

ml cerium	Activity counts s^{-1}
0.2	17.9
0.5	37.5
1.0	43.0
1.5	44.2
2.0	45.2
3.0	45.1
4.0	44.6
5.0	45.7

Conclusion. An excellent reproducibility graph, but having plateau lower than expected.

(d) Cerium, 5×10^{-2} M acetate buffer

Volume of EDTA 1 ml: Total volume 10 ml: 0.2 g resin:

Shaking for varying times.

Theoretical value of equivalence activity 104.5 counts s^{-1}.

Time (min)	ml cerium	Activity counts s^{-1}	Time (hrs)	ml cerium	Activity counts s^{-1}
15	3*	98.6	3	3	66.9
	4	101.8		4	69.5
	5	98.5		5	72.5
30	3	92.8	4.5	3	62.0
	4	89.4		4	62.0
	5	90.8		5	64.0
90	3	80.5	7	3	45.2
	4	78.5		4	52.8
	5	77.3		5	53.5
			20	3	23.3
				4	35.4
				5	24.9

Conclusion. The complex is decomposed by the resin, but only very slowly.

* The reproducibility of this one point was tested with 5 replicates after (i) 15 min, (ii) 1 h.

Activity counts s^{-1}	
15 min	1 h
110.40	82.91
110.97	101.35
107.32	97.46
112.81	88.89
113.91	94.82

Theoretical equivalence activity 120.00 counts s^{-1}

At 15 min, standard deviation is 2.2% of the mean, which is in turn 92% of the theoretical value. At 1 h, standard deviation is 9.9%.

(e) Cerium, 5×10^{-2} M acetate buffer

Volume of EDTA 1 ml: Total volume 12 ml: 0.2 g resin: Shaking 75 h.

ml cerium	Activity counts s^{-1} replicate extractions		
3.0	49.44	54.07	51.68
4.0	55.36	58.10	57.98
5.0	57.97	66.70	53.92
6.0	59.05	61.68	61.25
7.0	70.08	62.74	67.42
8.0	68.35	73.89	67.31

Theoretical equivalence activity 104 counts s^{-1}

Added conc. metal $\times 10^5$	Equil. conc. CeY $\times 10^6$	$\frac{[CeY]}{[Y']}$	$[Ce_R] \times 10^4$
2.05	4.10	0.575	9.8
2.73	4.37	0.68	14.3
3.42	4.87	0.794	17.8
4.10	5.40	0.930	21.4
4.78	5.70	1.08	25.3
5.47	5.94	1.25	29.4

$[Ce_R]$ was plotted against $\frac{[CeY]}{[Y']}$, Fig. 6.5.

Conclusion. The graph has the form expected from previous reproducibility curves. The slope, 4.35×10^2 is lower than previous equilibrium results indicated.

(f) Variation of amount of resin present

(i) Reaction mixture 1 ml 10^{-4} M EDTA: 3 ml 10^{-4} M cerium: 6 ml 10^{-1} M acetate buffer.

Method. On small columns, separation was achieved on columns of resin 1 cm diameter, at a flow rate of 0.5 ml per minute. Each was washed with 2 x 10 ml water and the eluent made to 50 ml. A 5 ml aliquot was counted.

Results

Size of column g dry resin	Activity counts s^{-1}
1	19.50
2	6.70
3	6.90
4	1.40

(ii) By batch exchange

Shaking time 30 min.

Wt resin (g)	Activity counts s^{-1}
0.2	87.4
0.5	75.1
1.0	48.8
1.5	24.6
2.0	11.5

The cerium solutions used here (i) and (ii) are of different specific activities.

Conclusion. These results are shown in Fig. 6.6, Table 6.5 and are fully discussed in Section 6.9.

6(xi) Experiments to Test for Adsorption Without Exchange

(a) Solutions: 10^{-1} M acetate buffer

10^{-4} M cerium

10^{-4} M EDTA

1 M $NaClO_4$.

Method. The reaction mixture chosen for minimum complex breakdown was buffer 2 ml, EDTA 1 ml, cerium 5 ml, M perchlorate 2 ml.

Shaking time was varied from 15 min to 50 h.

Resin weights of 2, 5, 10, 50, 200, 500 mg were used.

Results. Activities of 5 ml in counts s^{-1}.

mg resin	Time of shaking (h)						
	0.25	1.0	1.5	3	15	19	50
2	336.50	-	282.40	215.93	187.15	-	-
5	284.55	-	175.77	154.95	138.46	-	-
10	250.95	208.04	134.85	136.45	120.42	134.17	123.18
50	138.58	122.47	117.50	118.87	106.92	108.24	98.50
200	105.32	93.70	93.63	85.05	65.01	63.18	58.69
500	80.51	58.68	61.33	49.29	26.21	21.41	7.36

These results are shown in Fig. 6.7.

Equivalence activity 112 counts s^{-1} is also shown.

Conclusion. There is inadequate contact with the very small weights of resin. The larger weights bring about serious loss of metal from the complex, but equilibrium is reached only very slowly.

(b) A reproducibility curve was made for 10^{-5} M cerium using only 10 mg resin at two sodium concentrations. There should be possible breakdown of complex, but little adsorption.

Volume 10^{-4} M EDTA 1 ml, total volume 11 ml, acetate buffer.

Results

ml cerium	Activity counts s^{-1} 15 h shaking sodium 0.06 M	Activity counts s^{-1} 4 h shaking sodium 0.017 M
0.5	34.90	30.90
1.0	64.79	63.48
1.5	88.90	94.80
2.0	87.19	99.77
3.0	96.25	102.70
4.0	95.64	103.27
6.0	93.64	106.86
8.0	99.93	113.71
Equivalence	112.00	
2 ml. Excess EDTA	141.50	

Conclusion. Results show clearly that substoichiometry is poor, but do not indicate adsorption. They are illustrated in Fig. 6.8.

(c) Test of adsorption with ^{14}Carbon labelled EDTA

Solutions: 8×10^{-5} M inactive cerium

10^{-4} M labelled EDTA

10^{-1} M acetate buffer

1 M sodium perchlorate

Method. Substoichiometric mixtures were exchanged for 5 h as before. Volume of EDTA 1 ml, cerium 5 ml, total 10 ml.

A 1 ml aliquot was taken for counting by liquid scintillation. NE 220 scintillator was used, which required 1 ml of alcohol for each 10 ml of scintillator, in order to obtain an homogeneous solution.

Background counts were determined by preparing a blank exactly as the sample, omitting ^{14}Carbon EDTA and substituting water. In this way quenching effect was eliminated.

Results

	Activity counts s^{-1}		
Weight of resin (mg)	10	50	200
Conc. of sodium (M)			
0.05	98.77	95.93	105.84
0.10	100.93	102.74	107.99
0.15	104.18	99.93	101.42
0.20	101.19	100.29	108.69
0.25	108.00	100.64	109.23

Conclusion. Neither change in sodium concentration nor resin weight has any major effect on total concentration of EDTA present. Therefore no complex or complexone is adsorbed.

6(xii) Reproducibility Curves with Dowex 50 X8 (Ba)

Method. Reproducibility curves were prepared using 0.2 g barium resin and (a) acetate buffer pH 5.0 for 30 min shaking, (b) acetate buffer pH 5.0 for 3 h shaking, (c) 10^{-1} M hexamine buffer pH 5.5.

Results

ml cerium	Activity counts s^{-1} (a)	(b)	(c)
0.5	38.59	36.29	35.60
1	70.18	69.16	69.39
2	98.95	90.88	103.19
3	102.63	90.33	114.02
5	117.22	109.33	134.80

Equivalence activity 116.00 counts s^{-1}.

Conclusion. The resin does not successfully remove the rare earth metal from solution.

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RADIOACTIVE SUBSTOICHIOMETRIC ISOTOPE-DILUTION PROCEDURE FOR THE DETERMINATION OF RARE EARTH METALS

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Summary—A theory is developed which describes the equilibrium conditions when solutions containing trace metals and substoichiometric amounts of EDTA are extracted with thenoyltrifluoroacetone. Experimental evidence is given to support the theory. A method for the determination of microgram quantities of rare earth metal is outlined as an application.

Analysis for trace quantities of metals, by activation analysis or radioactive isotope-dilution analysis, can be simplified by using the technique of substoichiometry. Equal quantities of metal are removed from the active standard and treated sample solutions by a known amount of complexing agent which is insufficient to react with all the metal present. The separated fractions are then compared. In this way, the need for chemical yield determination is avoided, and selectivity improved.[1]

Most substoichiometry has been performed by solvent extraction with strong chelating agents. Extraction of ion-association complexes has been used[2,3] and also the reaction with EDTA, followed by removal of excess of metal by ion-exchange.[4,5,6]

Of these methods, the first is the most straightforward. The last, EDTA reaction, can become very involved when applied to the general case. Unlike the solvent extraction method, optimum conditions have to be calculated for two reactions, the complexation and the exchange of excess of metal with the resin. In the first case, all the EDTA present must react, and in the second, no EDTA complex must be involved in the exchange. The choice of pH, and the nature and strength of the buffer for the first reaction, all have a marked effect on the ion-exchange. For example, acetate buffers, commonly used for EDTA reactions, themselves complex many metals sufficiently to prevent efficient exchange, unless they are very dilute. At large dilutions the ionic strength of the solution is a critical factor.

In this paper, the simpler case is dealt with, in which the excess of metal is removed by solvent extraction, using a weaker complexing agent than EDTA.

The system containing rare earth, EDTA, and thenoyltrifluoroacetone was studied. A possible method for the determination of microgram quantities of rare earth after separation by ion-exchange was developed.

THEORY

There are two reactions to consider.

1. Rare earth (M) plus thenoyltrifluoroacetone (HA).
2. Rare earth (M) plus EDTA (Y).

$$M + 3HA_{org} \rightarrow (MA_3)_{org} + 3H \qquad (1)$$

$$M + Y \rightarrow MY \qquad (2)$$

The subscript "org" indicates solution in an organic solvent immiscible with water. Electrical charges are omitted for simplicity.

The following theory makes use of the idea of conditional equilibrium constants, in a similar way to the work of Schwarzenbach and Ringbom.[7] This means that the equilibrium concentration [X] of any species, is replaced by the total amount present in any form [X′]. The equation must be modified by a so-called α coefficient given by

$$\alpha = \frac{[X']}{[X]}\,. \tag{3}$$

Equilibrium constants calculated in this way are not really constant, but depend on the conditions used: hence the name conditional constant.

The extraction constant from equation (1) is

$$K_1 = \frac{[MA_3]_{org}[H]^3}{[M][HA]^3_{org}}\,. \tag{4}$$

The stability constant from equation (2) is

$$K_2 = \frac{[MY]}{[M][Y]}\,. \tag{5}$$

Instead of K_2 we use K_3, the conditional constant:

$$K_3 = \frac{[MY]}{[M][Y']} \tag{6}$$

where [Y′] is the total equilibrium concentration of EDTA in all its forms, *i.e.*, $[Y'] = [H_4Y] + [H_3Y] + [H_2Y] + [HY] + [Y]$ (again with charges omitted).

Then

$$\frac{[Y']}{[Y]} = \alpha_Y$$

and

$$K_2 = \frac{[MY]\alpha_Y}{[M][Y']}\,. \tag{7}$$

By combining equations (4) and (7):

$$K_4 = \frac{K_1}{K_2} = \frac{[MA_3]_{org}[H]^3[Y']}{[MY][HA]^3_{org}\alpha_Y}\,. \tag{8}$$

Assuming that a reaction equilibrium is reached, let us take the case where half of the metal present is complexed to form MY, *i.e.*, 50% stoichiometry; HA removes the remainder, which becomes transferred to the organic phase. It must be remembered that this paper follows the terminology of previous authors, *i.e.*, *x*% stoichiometry or substoichiometry refers to the relative amounts of the reacting species, that is the degree to which one is equivalent to the other. The actual reaction is assumed to be stoichiometric.

Under these conditions, and when the volumes of both phases are equal,

$$[MY] = [MA_3]_{org}$$

and equation (8) simplifies to:

$$K_4 = \frac{[\mathrm{H}]^3[\mathrm{Y}']}{[\mathrm{HA}]_{\mathrm{org}}^3 \alpha_{\mathrm{Y}}}. \tag{9}$$

$[\mathrm{HA}]_{\mathrm{org}}$ is not a simple term, for two reasons. First HA dissociates, $\mathrm{HA} \rightleftharpoons \mathrm{H} + \mathrm{A}$, the constant for the reaction being

$$K_{\mathrm{diss}} = \frac{[\mathrm{H}][\mathrm{A}]}{[\mathrm{HA}]}, \tag{10}$$

and secondly, HA is not entirely in the organic phase. The partition is described by:

$$P_{\mathrm{HA}} = \frac{[\mathrm{HA}]_{\mathrm{org}}}{[\mathrm{HA}]}. \tag{11}$$

Dividing equation (10) by equation (11):

$$\frac{K_{\mathrm{diss}}}{P_{\mathrm{HA}}} = \frac{[\mathrm{H}][\mathrm{A}]}{[\mathrm{HA}]_{\mathrm{org}}}. \tag{12}$$

Let us call the sum of the concentrations of all the forms of HA present, [HA′]. In the case already mentioned, where the phases have equal volumes, [HA′] is in fact the concentration added in the organic phase at the start of the reaction, providing there is no association or polymerization in either phase.

Then

$$[\mathrm{HA}'] = [\mathrm{HA}]_{\mathrm{org}} + [\mathrm{HA}] + [\mathrm{A}]$$

or

$$\frac{[\mathrm{HA}']}{[\mathrm{HA}]_{\mathrm{org}}} = 1 + \frac{[\mathrm{HA}]}{[\mathrm{HA}]_{\mathrm{org}}} + \frac{[\mathrm{A}]}{[\mathrm{HA}]_{\mathrm{org}}} \tag{13}$$

and we can call this α_{A}:

$$\alpha_{\mathrm{A}} = 1 + \frac{1}{P_{\mathrm{HA}}} + \frac{K_{\mathrm{diss}}}{P_{\mathrm{HA}}[\mathrm{H}]}. \tag{14}$$

From a knowledge of the partition coefficient and the dissociation constants, α_{A} can be calculated. The result is conveniently shown in graphical form in Fig. 1.

Equation 9 becomes

$$K_4 = \frac{[\mathrm{H}]^3[\mathrm{Y}']\alpha_{\mathrm{A}}{}^3}{[\mathrm{HA}']^3\alpha_{\mathrm{Y}}}. \tag{15}$$

An essential condition of substoichiometry is that all the reagent must be consumed by the metal. As a practical condition, this is taken to be true if $[\mathrm{Y}'] < 0{\cdot}001\ C_{\mathrm{HY}}$, where C_{HY} is the concentration of EDTA that would be present if no reaction had taken place.

Thus

$$K_4 = \frac{[\mathrm{H}]^3 \,.\, 10^{-3} C_{\mathrm{HY}} \alpha_{\mathrm{A}}{}^3}{[\mathrm{HA}']^3 \alpha_{\mathrm{Y}}}. \tag{16}$$

From this equation can be calculated a value of [HA′] for a particular EDTA reaction. It represents the maximum concentration of HA which may be used to remove free metal from a solution in which a substoichiometric reaction with EDTA

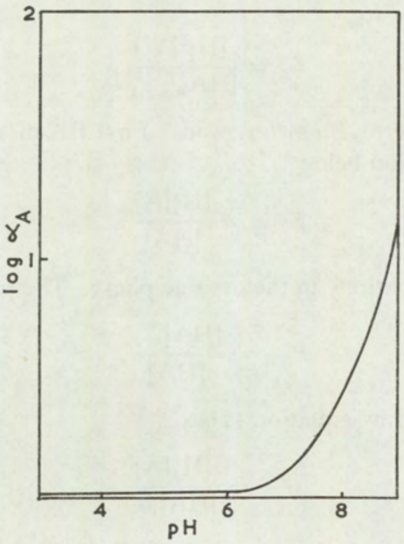

Fig. 1.—Variation of the conditional constant for thenoyltrifluoroacetone with pH.

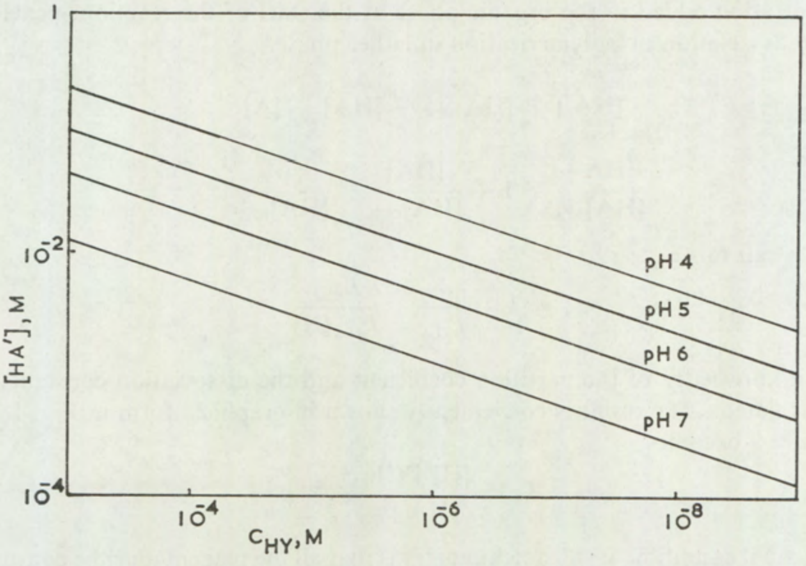

Fig. 2.—Influence of hydrogen-ion concentration on the maximum concentration of thenoyltrifluoroacetone which may be used to remove free metal from a metal–EDTA complex. Calculated for terbium.

is taking place, without breaking down more than 0·1% of the EDTA complex. A further condition is that $[HA'] \gg [MA_3]$ so that the change of concentration on reaction is negligible. This will be true for a weak complexing agent. Figure 2 shows how this value of [HA'] varies with pH for fixed concentrations of C_{HY}. The values given are calculated for terbium. Figure 3 shows how this graph is affected, at any one EDTA concentration, by the choice of metal. Like many other rare earth properties, the equilibrium constants for both these reactions, *i.e.*, K_1 and K_2, vary as the atomic

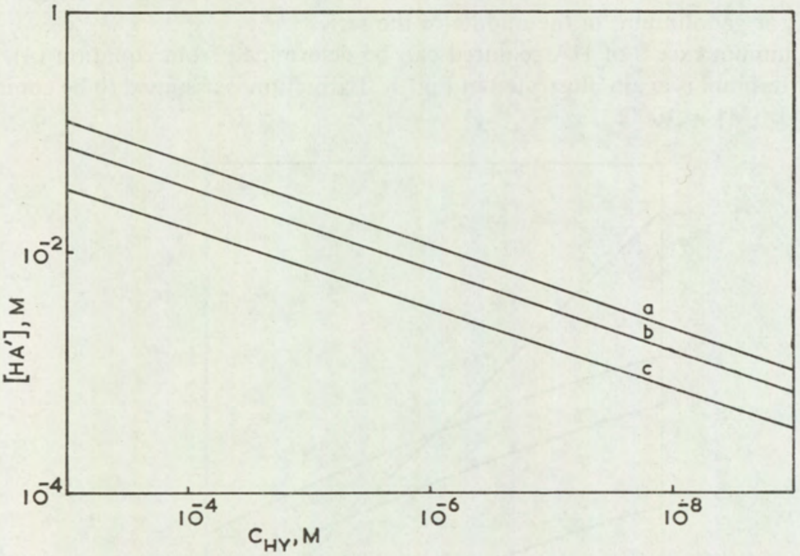

FIG. 3.—Influence of rare earth metal at a fixed pH on the maximum concentration of thenoyltrifluoroacetone which may be used to remove free metal from a metal-EDTA complex. *a*. Calculated for lutetium at pH 6. *b*. Calculated for lanthanum at pH 6. *c*. Calculated for gadolinium at pH 6.

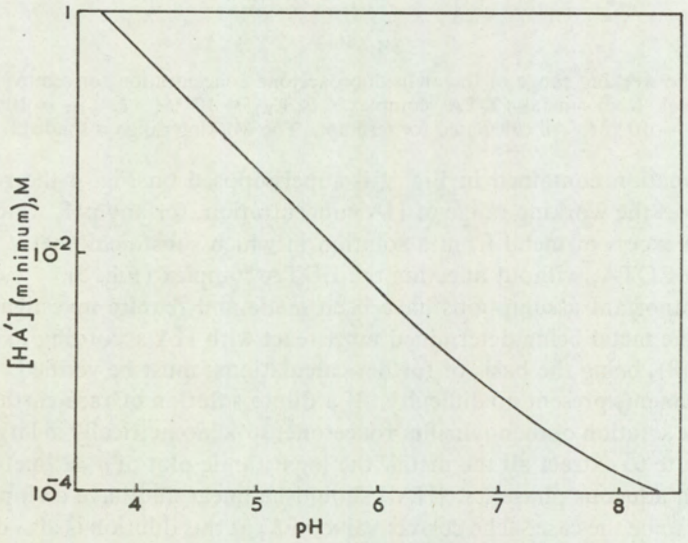

FIG. 4.—The minimum excess of thenoyltrifluoroacetone required for the extraction of rare earth metal at various pH values. Calculated for terbium.

number increases. The trends are different in each case, resulting in a maximum value of K_4 at gadolinium, in the middle of the series.

The minimum excess of HA required can be determined from equation (4), and the case of terbium is again illustrated in Fig. 4. Extraction is assumed to be complete when $[\mathrm{MA}]_3/[\mathrm{M}] = 1000$.

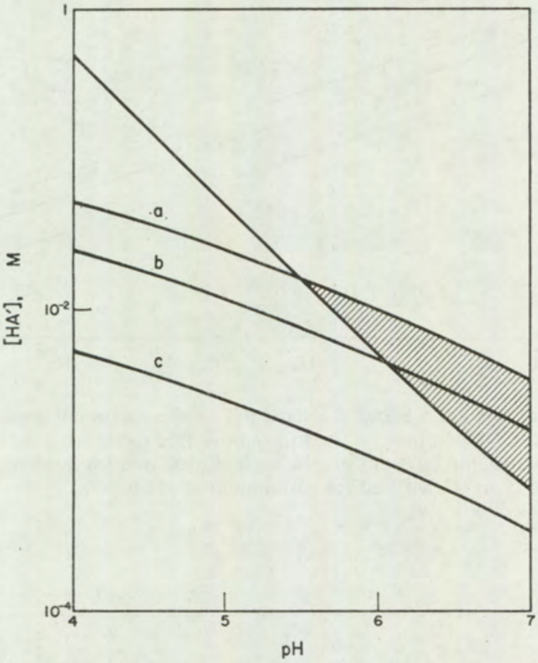

Fig. 5.—The working range of thenoyltrifluoroacetone concentration for removal of excess metal from metal–EDTA complex. *a.* $C_{\mathrm{HY}} = 10^{-5}M$ *b.* $C_{\mathrm{HY}} = 10^{-6}M$ *c.* $C_{\mathrm{HY}} = 10^{-8}M$. All calculated for terbium. The working range is shaded.

If the information contained in Fig. 2 is superimposed on Fig. 4 the result is a graph which gives the working range of HA concentration, for any pH, which can be used to remove excess of metal from a solution in which substoichiometry has been performed with EDTA, without affecting the EDTA complex (Fig. 5).

Two very important assumptions have been made and require investigation. At high dilutions the metal being determined must react with HA according to equation (4). Equation (8), being the basis of further calculations, must be verified.

These experiments present no difficulty. If a dilute solution of rare earth metal is extracted with a solution of thenoyltrifluoroacetone, stoichiometrically in large excess, but still too dilute to extract all the metal, the logarithmic plot of q = [metal in org. phase]/[metal in aqueous phase] *vs.* [HA′] should be linear and have a slope of $+3$. This was found to be the case. The correct value of K_1 at this dilution is also determinable from the intercept.

Verification of equation (8) can be achieved in a similar way. Consider the case where all the EDTA present is just sufficient to complex all the metal, but the HA present in the organic phase is strong enough to partly decompose the EDTA complex.

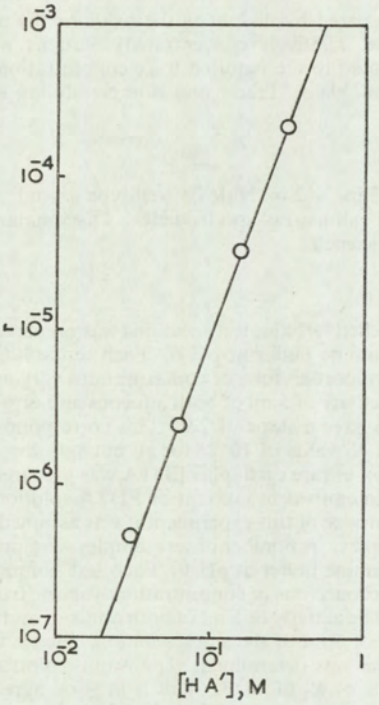

FIG. 6.—Experimental verification of equation (8).

$$r = \frac{[\text{metal in organic phase}]^2}{[\text{metal in aqueous phase}]}.$$

Any MA_3 (or free EDTA) present can be assumed to come from the decomposition of MY. Hence $[MA_3] = [Y']$.

Thus, introducing the α_A term into equation (8) and rearranging

$$\frac{K_4\alpha_Y}{[H]^3\alpha_A{}^3} = \frac{[MA_3]^2_{org}}{[MY][HA']^3}. \tag{17}$$

That is, a logarithmic plot of $r =$ [metal in org. phase]^2/[metal in aqueous phase] *vs.* [HA′] should be linear and of slope +3, having an intercept of $K_4\alpha_Y/[H]^3\alpha_A$. This was also found to be true (Fig. 6).

It was also observed that the reaction between HA and free metal came to equilibrium many times faster than the decomposition of metal–EDTA complex by HA. This is itself an important factor when considering the development of an analytical method.

EXPERIMENTAL

Reagents

Buffer solution. The choice of buffer, which must be suitable for both the EDTA reaction and the extraction, was a little difficult. The one finally used was $1M$ hexamine, adjusted to the required pH with nitric acid. Only laboratory-reagent grade hexamine was available and it was thought that further trouble might arise from metallic impurities in it. In the simplest case these would give rise to a large reagent blank, although much more complicated interferences can be envisaged. These interferences did not occur, at least not at the concentrations used in the experiments. At very large dilutions there are several other factors which may cause difficulty. These are outlined below.

All other reagents were of analytical-reagent grade purity.

Rare earth solutions were prepared by dissolving the oxide or the nitrate in nitric acid or water respectively. Whenever possible, relatively concentrated solutions were made and standardized against EDTA, before being diluted to the required trace concentration.

Water was twice distilled from glass. Tracer and isotope-dilution experiments were carried out with ^{141}Ce, ^{160}Tb and ^{170}Tm.

Apparatus

The detector used was a 1·75 in. × 2 in. NaI(Tl) well-type crystal: well-volume 5 ml. This was associated with a single channel gamma-ray spectrometer. Discriminator settings were used to give the highest possible counting efficiencies.

Verification of equations (4) *and* (8)

Equation (4). A series of labelled terbium test solutions was prepared by diluting 1 ml of a $10^{-5}M$ stock solution with 9 ml of hexamine buffer at pH 6. Each test solution was extracted with 10 ml of a xylene solution of thenoyltrifluoroacetone of concentrations varying from $10^{-4}M$ to $10^{-3}M$, until equilibrium was reached. The activity of 5 ml of both aqueous and organic phases was measured and the final pH noted. The results gave a slope of 2·9. This corresponds to a value of K_1 of $10^{-8{\cdot}25}$. An assumed slope of 3·0 gives a K_1 value of $10^{-8{\cdot}1}$ for all but very low q values.

Equation (8). A stock solution of rare earth plus EDTA was prepared by mixing 25 ml of a $10^{-3}M$ labelled terbium solution with an equivalent amount of EDTA solution, neutralizing to pH 4·5 and making up to 50 ml. For the purpose of this experiment it was assumed that this solution was a pure solution of terbium–EDTA complex. A number of test samples were prepared by diluting 5 ml of this stock solution with 5 ml of hexamine buffer at pH 6. Each test sample was extracted with 10 ml of a xylene solution of thenoyltrifluoroacetone of concentrations varying from $3 \times 10^{-2}M$ to $3 \times 10^{-1}M$, until equilibrium was reached. The activity of 5 ml of both aqueous and organic phases was measured and compared with the activity of 5 ml of the stock solution. Hence the exact amount of metal in both aqueous and organic phases was determined. The results, plotted in Fig. 6, show a slope of 2·8. This corresponds to a value of K_4 of 10^{-25}. This is in good agreement with a value of $10^{-24{\cdot}8}$ calculated from available literature values of $K_1 = 10^{-6{\cdot}9}$ at $2 \times 10^{-1}M$ thenyoltrifluoroacetone concentration,[8] and $K_2 = 10^{17{\cdot}9}$ for the terbium–EDTA complex.[7]

Time to reach extraction equilibrium

As has been reported,[8] the rare earth metal was found to be extracted by the thenoyltrifluoroacetone very quickly. It was completely removed from the hexamine buffer at pH 6 in less than 30 sec. Similarly, after addition of a substoichiometric amount of EDTA to a rare earth metal solution the excess of metal was removed in just over 60 sec. The destruction of the metal-EDTA complex by the thenoyltrifluoroacetone took much longer to complete although equilibrium was virtually reached in a little over 60 min. For the verification experiments an extraction time of 2 hr was used.

Reproducibility

A series of test solutions was prepared by diluting 0·5–5 ml portions of a $10^{-4}M$ labelled terbium solution to 10 ml with hexamine buffer at pH 6. To each was added 1 ml of $10^{-4}M$ EDTA, this being insufficient to react with all of the metal in the more concentrated solutions. The excess of metal was extracted by adding 10 ml of $10^{-2}M$ thenyoltrifluoroacetone in xylene and shaking for 5 min. The resulting aqueous phase was filtered and a 5 ml aliquot counted. A typical plot of activity against concentration of terbium solution is shown in Fig. 7.

The sloping section of this curve indicates that the EDTA is successfully retaining the metal. Further, no metal–EDTA complex is being broken down, for if this were the case the extrapolation of this part of the curve would not rise to the equivalence point X. The flat plateau shows that when the metal is in excess a constant amount is retained in the aqueous phase. A good reproducibility curve, determined at similar concentrations to a solution to be analysed by a method based upon it, means that the analysis must be successful and give an answer correct within experimental error.

Non-reproducible conditions (*Fig.* 7). Some attempts to produce reproducibility curves show divergences from the type of curve illustrated and can be the result of one or all of three conditions:

(*i*) As the concentration of metal in the test solution decreases to the order of $10^{-6}M$ the working range of extractant concentrations becomes very small at practical pH values. The required equilibrium condition becomes increasingly difficult and finally impossible to achieve. For work at this level the K_4 values should be accurately determined under the test conditions before the range of extractant concentrations is calculated. In the rare earth series, the end members have the lowest K_4 values, and therefore the central members, are most affected.

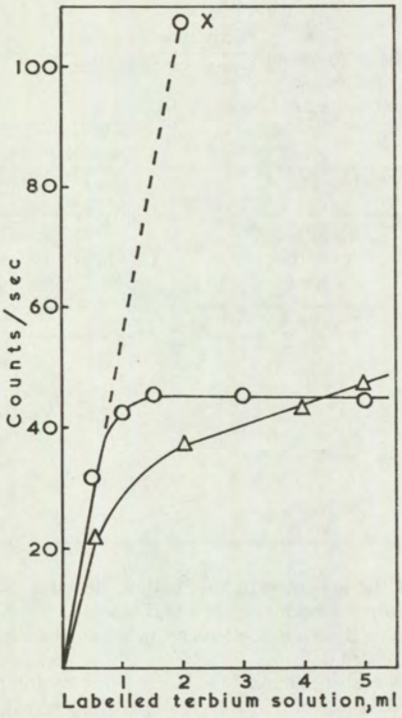

FIG. 7.—Reproducibility of extraction.

○—Reproducibility of the substoichiometric extraction of terbium in presence of EDTA.
△—Non-reproducible substoichiometric extraction of terbium in presence of EDTA.

(*ii*) The EDTA is not at all selective and foreign metal ions present in concentrations of say $10^{-7}M$ might interfere by upsetting the equilibrium. To overcome this a preliminary extraction could be used.[6]

(*iii*) The EDTA reaction may fail to reach equilibrium. We feel, however, that it is inadvisable to heat the reagents to bring the reaction to equilibrium as loss by adsorption and/or hydrolysis would give rise to even further complications. The difficulties can be partly resolved by careful choice of the degree of substoichiometry, since the value of C_{HY} [concentration of EDTA, equation (16)] rather than metal ion concentration affects the working range.

Analysis of test samples

As examples of how the technique can be used as an analytical method, a number of rare earth solutions of known concentration were analyzed by isotope dilution.

The solutions used were terbium solution labelled with ^{160}Tb, and ytterbium solution labelled with ^{170}Tm. The latter solution was readily available in our laboratory whereas radioactive isotopes of ytterbium or pure inactive thulium was not. For thulium and ytterbium the ratio of K_1/K_2 is very similar ($10^{25\cdot6}$).

To each of a number of separating funnels were added 5 ml portions of $1M$ hexamine/hexamine nitrate buffer (pH 6·0). To each were added 2 ml of a standard labelled solution, comparable in concentration to the sample. Then 2 ml of sample were transferred by pipette into some of the funnels (samples), and 2 ml of water into the rest (standards). A substoichiometric amount of EDTA (2 ml of $10^{-4}M$ EDTA for ytterbium and 1 ml of $10^{-4}M$ EDTA for terbium) was added to all the funnels, and unreacted metal was removed by shaking for 5 min with a suitable concentration of thenoyltrifluoroacetone in xylene. (The concentration is indicated by the theory and in these experiments was $10^{-2}M$.) The aqueous phases were separated and filtered, and the activity of an aliquot was measured. The amount of metal in the samples was calculated by using the substoichiometric formula applied to isotope dilution:[1]

$$x_{\text{sample}} = x_{\text{standard}} \left(\frac{\text{activity of standard}}{\text{activity of sample}} - 1\right)$$

where x = weight of metal. The results are shown in Table I.

TABLE I

Ytterbium			Terbium		
Taken, *μg/ml*	Found, *μg/ml*	Standard deviation, *μg/ml*	Taken, *μg/ml*	Found, *μg/ml*	Standard deviation, *μg/ml*
38·14	37·85	0·51	17·10	16·82	0·55
	38·77			17·75	
	38·46			17·42	
	38·81			17·52	
	37·85			16·87	
	38·46			16·26	
	37·33				
	37·96				
	38·66				

It must be remembered that the accuracy of the method depends on the precision of the substoichiometric extraction procedure for both standard and sample. Thus the standard activity must be accurately known and should be determined as many times as possible in each set of analyses.

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Zusammenfassung—Es wird eine Theorie entwickelt, die die Gleichgewichtsbedingungen beschreibt, wenn Lösungen, die Spurenmetalle und unterstöchiometrische Mengen EDTA enthalten, mit Thenoyltrifluoraceton extrahiert werden. Zur Stützung der Theorie werden experimentelle Ergebnisse mitgeteilt. Als Anwendung wird eine Methode zur Bestimmung von Mikrogrammengen seltener Erdmetalle skizziert.

Résumé—On développe une théorie qui décrit les conditions d'équilibre lorsqu'on extrait des solutions contenant des traces de métaux et des quantités substoechiométriques d'EDTA au moyen de thénoyltrifluoracétone. On donne des preuves expérimentales à l'appui de la théorie. A titre d'application, on donne un aperçu d'une méthode pour le dosage de métaux des terres rares en quantités de l'ordre du microgramme.

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