A radiochemical study of chemical equilibria by partition methods

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"A Radiochemical Study of Chemical Equilibria by Partition Methods"

THESIS

Presented in candidature for the degree of

DOCTOR OF PHILOSOPHY

in the

UNIVERSITY OF DURHAM

by

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MEMORANDUM

The work described in this thesis was partly carried out in the Londonderry Laboratory for Radiochemistry, University of Durham, and partly in the Chemical Laboratory, University of Kent at Canterbury between October 1963 and October 1966 under the supervision of Dr. S.J. Lyle, Lecturer in Chemistry.

This thesis contains the results of some original research by the author; no part of the material offered has previously been submitted by the candidate for a degree in this, or any other University. When use has been made of the results and conclusions of other authors in relevant investigations, care has always been taken to ensure that the source of information is clearly indicated, unless it is of such a general nature that indication is impracticable.

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ABSTRACT

A radiochemical study has been made of complex formation in aqueous solutions containing trivalent lanthanide and actinide metal ions and selected ligands. Partition methods using a cation-exchanger and a liquid extractant (di(2-ethylhexyl)phosphoric acid $[HY]_2$, in toluene) as the second phase were developed and measurements carried out with La, Ce, Eu, Gd, Am and Cm with one or more of the ligands, α-hydroxy-isobutyrate, fluoride, sulphate and oxalate. The isotopes La^{140}, Ce^{144}/Pr^{144}, $Eu^{152,154}$, Gd^{153} and Am^{241} were used in conjunction with conventional methods of measurement of β- and γ-emitters. Liquid-scintillation counting procedures were developed for the measurement of the α-activity from Cm^{244}.

It was found that in the presence of a constant and representative concentration of each of the ligands used only $M(HY_2)_3$ extracts into the toluene phase and metal ion complexed by the ligands concerned does not partition. A cation-exchange resin on the other hand is known to take up partially complexed species in addition to 'free' metal ions. A method was evolved whereby data obtained separately by the ion-exchange and solvent-extraction methods could be used to calculate distribution coefficients of partially complexed species partitioning into the resin phase. The results showed that residual cation charge as well as the size of the exchanging species are important in determining the extent to which ion-exchange partition occurs. It was also found that the Fronaeus' method of treatment of ion-exchange data where more than two ligands are attached to a metal ion may be inadequate and that assumptions frequently necessary regarding the distribution coefficient of partially complexed species may be considerably in error depending on the ligand.

The investigations carried out in this work have indicated the application of HDEHP to the determination of equilibrium constants particularly of α-emitting higher actinides and in studies where more than two complexes are formed. Equilibrium constants for the complexes formed were computed and various tests applied to the method of computation from ion-exchange distribution data. Equilibrium constants obtained are generally in good agreement with relevant published data.

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CHAPTER I

INTRODUCTION

GENERAL: Few problems in the realm of physico-inorganic chemistry have attracted as much attention during the last hundred and thirty years or so, as those associated with the nature of chemical equilibria. In this field much work has been done on aqueous solutions and as a result of the persistent efforts of successive generations of chemists a considerable wealth of knowledge has been accumulated, contributing towards a better understanding of the subject.

The position of chemical equilibrium in a system can be related to concepts concerning the behaviour of ions and molecules in solutions. Also, like many branches of scientific knowledge there are several equally logical approaches to the interpretation of chemical equilibrium, namely through chemical thermodynamics, chemical kinetics and molecular statistics. It is, therefore, not surprising that what we now call 'Law of chemical equilibrium' was obtained as a result of the study of a series of chemical reaction rates, rather than of a chemical system in equilibrium. Almost a century ago the quantitative study of the chemical equilibrium attained by mixing ethyl alcohol and acetic acid led to the classical form of the law of chemical equilibrium, usually known as the law of mass action[1]. Soon after, however, a distinct change in emphasis occurred, for although in the relatively few cases where the rates of formation and dissociation of a product are sufficiently low, the kinetic approach has continued to be used, a large number of systems, where equilibrium is reached rapidly have been studied at equilibrium.

In the first volume of the '*Zeitschrift für physikalische Chemie*', Arrhenius[2] proposed that electrolytes are dissociated into ions to a degree which can be determined from the conductance or colligative properties of their solutions, and subsequently Ostwald[3] showed that in proton dissociation solutions of carboxylic acids conform to the law of mass action. If, following Arrhenius, the degree of dissociation, α, of an electrolyte at concentration, c, is given by the ratio of the molar conductance Λ to the conductance at infinite dilution, Λ_0, combination of α with the law of mass action gives $\left(\frac{\Lambda}{\Lambda_0}\right)^2 c/\left(1-\frac{\Lambda}{\Lambda_0}\right) = k$, which is known as the equilibrium constant. The work on the calculation of equilibrium constants for acetic acid and sodium acetate using this formula, however, showed that although values found for acetic acid were constant, the same was not true for sodium acetate. Discrepancies of the latter kind, and the disagreement between apparent degree of dissociation determined for the solution from the measurement of electrolytic conductance and certain colligative properties constituted one of the so-called 'anomalies of strong electrolytes' which was not quantitatively resolved until after about 1920 for dilute solutions, and has not yet been resolved for concentrated solutions. Nevertheless, they did not deter experimentalists from determining equilibrium constants for the dissociation of a wide range of weak electrolytes. Not only were protolytic equilibria studied by conductance and kinetic methods, but the introduction of the 'e.m.f.' method by Nernst[4] for determining metal ion concentrations was widely exploited at the beginning of the present century by Bodlander and others in the study of the complex ion equilibria of Ag(I), Cu(I) and Hg(I) with various ligands.

Little progress in the study of ionic equilibria involving other than weak electrolytes was made until the effects of long-range interionic forces on the properties of solutions had been appreciated[5] and quantitatively expressed[6]. However, the notion of maintaining constant effects other than those due to the equilibrium under study, by adding a 'swamping' excess of an inert salt seems to have been suggested by Bodlander to his student Grossmann. Grossmann[7], in 1905, published the result of a study of complex formation between Hg(I) and SCN in which potassium nitrate was added to maintain a one molar concentration of potassium ions. Later, Brönsted and Pederson[8] showed that the equilibrium constant for the reaction, $Fe^{3+} + I^{-} \rightleftharpoons Fe^{2+} + \frac{1}{2} I_2$, was constant in a swamping medium of 1.65 M KCl + 0.1 M HCl.

The extention of the concept of 'interionic forces' to the application of the law of chemical equilibrium led to the idea of 'ionic activities' which in the thermodynamic sense govern all the properties of a system in equilibrium. According to Jahn[9], the interionic forces by restricting the free and random movements of ions in solution must render some of them ineffective as 'active masses', so that in the end it is not the total stoichiometric concentration but only a fraction of it called the activity, which is available for taking part in the reaction. The activity of any ion in solution is, generally, represented by the expression:

$$a_i = \gamma_i c_i \qquad (1)$$

where a_i is the activity of the ion, γi the activity-coefficient, and c_i the stoichiometric concentration of the ion in terms of molality. Solutions of electrolytes, however, contain not only cations but also anions. The ionic activity is, therefore, an average term and is usually represented in terms of the so-called 'mean activity'. Thus, for, say a 1:2 electrolyte, the mean molal activity-coefficient $\gamma\pm$ is related to the individual ionic values, according to the relation:

$$\gamma\pm^3 = \gamma_i \gamma_j^2 \qquad (2)$$

At infinite dilution, the mean activity is unity regardless of the concentration scale.

The concepts of 'interionic forces' and 'activities' culminated in a yet more comprehensive approach to the problems associated with chemical equilibrium; this was through the concept of the 'ionic strength of solutions'. In 1921 Lewis and Randall[10] stated that in dilute solutions, the activity coefficients of a given strong electrolyte is the same in all solutions of the same ionic strength. The ionic strength μ is given by the relation:

$$\mu = \tfrac{1}{2}\Sigma\, c_i z_i^2 \qquad (3)$$

where c_i is a concentration term and z_i represents the charge of the ions concerned.

The activity factors governing the behaviour of ions in solution have been accounted for in the theory of electrolytic dissociation of weak electrolytes by Debye and Hückel[6] and in its refinement by Onsager and Fuoss[11-15]. According to the limiting law of Debye and Hückel

$$-\log f_{\pm} = A[z_i z_j]\{\sqrt{\mu}/(1+Ba\sqrt{\mu}) - Q(\mu)\} \qquad (4)$$

where A, B, Q and a are empirical parameters, a is the average cation-anion radius and z_i, z_j are the ionic charges of the ions i and j respectively, $f_{\pm}$ is the mean activity coefficient on the molarity scale and μ has its usual meaning. The equation under suitable conditions may be applied to a wide range of ionic strengths.

The idea of maintaining activity factors constant by using a high and constant ionic medium has led to a considerable body of quantitative information about ionic equilibria. Especially in the last two decades knowledge concerning ionic equilibria has increased rapidly as the result of measurements made by those primarily interested in the nature and relative stabilities of the complexes formed by transition metal cations with a variety of inorganic and organic anions and molecules. Three of the foremost workers in the field, J. Bjerrum, G. Schwarzenbach and L.G. Sillen, have compiled an invaluable source of information on ionic equilibria in the 'Table of Stability Constants'[16]. The constant ionic medium is, however, not free from limitations. Sillen[17] has recently pointed out that the method must be used with the utmost care and the interpretation of results should embrace all possible explanations. These limitations are listed below:

(1) Information obtained from the measurements using a constant ionic medium cannot account for complex formation between species present in the solution other than those on which the measurement is based.

(2) It is hard to distinguish between solvated species containing different numbers of solvent molecules in dilute solutions.

(3) Complications may arise if one of the ions of the medium can be converted to one of the reacting species by the addition or loss of a proton. For example, in the study of the Hg(I) - NH_3 system in NH_4NO_3 by pH measurement, it might not be possible to distinguish between amine (NH_3) and amide (NH_2^-) complexes on the one hand and amine and hydroxyl (OH^-) complexes on the other.

(4) The swamping effect of such media may undermine the effect of complex formation on certain physical properties. If so, the change in the measured property attributable to complex formation is very small and therefore interpretation of the measurement is rendered difficult or impossible[18].

(5) The method cannot be extended to studies of ionic equilibria based on measurements of conductivities of solutions.

Significance of equilibrium measurements: equilibrium constants

One of the most important objects of the study of ionic equilibria is to find out how complex molecules or ions are built up and what is their stability in terms of readiness to form from components in the chosen environment. The study of complex equilibria thus provides information on the nature and proportions of substances in a system and it may lead to the verification of postulates and theories connected for example with chemical bond formation and molecular structure. The results of such investigations are not only of interest to theoretical, physical and inorganic chemists, but their importance is being increasingly recognised in understanding biochemical processes. Information about complex equilibria is also of great value to the industrial chemists, especially those engaged in the atomic energy industry. This is particularly true in connection with ion-exchange and solvent extraction studies of equilibria, which have been the main target of investigation in the present work.

By far the most extensively studied ionic equilibria are those in which a cation combines with an anion or neutral molecule. Let us consider the general equilibrium between a metal atom, M and N donor molecules or ligands A

$$M + NA \rightleftharpoons MA_N \qquad (5)$$

(For simplicity charges are omitted.) The activity of the product $[MA_N]$ formed at a given temperature can be related to the activities of species M and A, through the law of mass action, so that the thermodynamic equilibrium constant or the so-called over-all stability constant ${}^{T}\beta_N$ can be defined as

$$^{T}\beta_N = \frac{[MA_N]}{[M][A]^N} \qquad (6)$$

where [ ] represents the activity of the species concerned. In general, according to Bjerrum, the formation of the species MA_N will involve a series of intermediate steps, so that step-wise equilibrium constants may thus be defined:

$$M + A \rightleftharpoons MA \qquad (7)$$

$$MA + A \rightleftharpoons MA_2 \qquad (8)$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$MA_{N-1} + A \rightleftharpoons MA_N \qquad (9)$$

and $$^{T}k_1 = \frac{[MA]}{[M][A]} \qquad (10) \qquad\qquad ^{T}k_2 = \frac{[MA_2]}{[MA][A]} \qquad (11)$$

$$^{T}k_N = \frac{[MA_N]}{[MA_{N-1}][A]} \qquad (12)$$

where ${}^{T}k_1$, ${}^{T}k_2$ ...., ${}^{T}k_N$ are the step-equilibrium constants for the respective reactions. The overall stability constant for the reaction (5) is related to step-equilibrium constants by the relation

$$ {}^{T}\beta_{N} = {}^{T}k_{1} \times {}^{T}k_{2} \times {}^{T}k_{3} \ldots\ldots\ldots {}^{T}k_{N} = \prod^{N} {}^{T}k_{N} \ldots\ldots \qquad (13) $$

As pointed out earlier, the activity of an ion is largely determined by the total ionic strength of a solution. It follows that at constant ionic strength the activity of any particular ion will be constant. In most equilibrium studies it may, therefore, be possible to keep the activity coefficient γ of each species constant by using a suitable ionic medium. In such cases the concentrations of the species up to and including MA_N, may be expressed in terms of corresponding stoichiometric molar concentrations. Then the constants ${}^{T}\beta_N$, and ${}^{T}k_N$ would become β_N and k_N respectively, and the corresponding expressions will be:

$$ \beta_{N} = \frac{\{MA_{N}\}}{\{M\}\{A\}^{N}} = {}^{T}\beta_{N} \frac{\gamma M \ \gamma A^{N}}{\gamma MA_{N}} \qquad (14) $$

$$ k_{N} = \frac{\{MA_{N}\}}{\{MA_{N-1}\}\{A\}} = {}^{T}k_{N} \frac{\gamma MA_{N-1} \ \gamma_{A}}{\gamma MA_{N}} \qquad (15) $$

where $\{ \ \}$ represents molar concentration.

From consideration of either step-equilibria or the general equation (5), it is evident that the corresponding equilibrium constants may be determined by using any combination of measurements which allows the calculation of the concentrations of three interacting species. A generalised treatment for calculations of the equilibrium constant is due to N. Bjerrum[19]. In general, a parameter $\bar{n}$ known as the average ligand number and defined as the average number of ligands bound to the central atom, is determined. It leads directly to the calculation of equilibrium constants.

$$\bar{n} = \frac{\{MA\} + 2\{MA_2\} + 3\{MA_3\} + \ldots\ldots + N\{MA_N\}}{\{M\} + \{MA\} + \{MA_2\} + \ldots\ldots\ldots + \{MA_N\}} \qquad (16)$$

By substituting for the values of $\{MA\}$, $\{MA_2\}$ .... $\{MA_N\}$, obtained from equations (10), (11) .... and (12), and eliminating $[M]$, $\bar{n}$ is obtained in terms of $\{A\}$, i.e. the concentration of free-ligand and the step equilibrium constants k_1, k_2, ... k_N. Thus,

$$\bar{n} = \frac{k_1\{A\} + 2k_1k_2\{A\}^2 + \ldots\ldots\ldots\ldots + Nk_1k_2\ldots k_N\{A\}^N}{1 + k_1\{A\} + k_1k_2\{A\}^2 + \ldots\ldots\ldots + k_1k_2k_3\ldots k_N[A]^N} \qquad (17)$$

Thus, any method that leads to the determination of the free-ligand concentration $\{A\}$ for a known total concentration of metal ion present, may be used to calculate $\bar{n}$ by the relation

$$\bar{n} = \frac{C_A - \{A\}}{C_M} \qquad (18)$$

where $C_M = \Sigma M = \{M\} + \{MA\} + \{MA_2\} + \;.....+\cancel{N}\{MA_N\}$ (19)

and represents total metal ion concentration present in all its forms, and

$$C_A = \Sigma\{A\} = \{A\} + \{MA\} + 2\{MA_2\} + \;....\; + N\{MA_N\}... \qquad (20)$$

represents total ligand concentration. $\{A\}$ is the free or unbound ligand concentration.

Since $\bar{n}$ may be readily evaluated once C_M, C_A and $\{A\}$ are known, the problem of determining equilibrium constants reduces to one of solving a series of N simultaneous equations.

The real significance of these equilibrium constants lies in the fact that they predict a measure of the stabilities of complexes in the system. A knowledge of such data is desirable from the stand point of predicting the optical and kinetic behaviour of a system. As well, stability constants can be used to predict the conditions for maximal formation of a given complex in a given chemical system.

The equilibrium constant ${}^{T}k$ for any reaction is directly related to the corresponding free energy change of the system it represents:

$$- RT \ln k = \Delta G = \Delta H - T\Delta S \qquad (21)$$

where ΔG, ΔH, ΔS represent the changes of free energy, enthalpy and entropy in that order, at equilibrium. R is the universal gas constant, and T is the absolute temperature. The corresponding changes in the entropy of complex formation may be obtained by determining the stability constant at a series of temperatures. The information obtained from stability constants in terms of enthalpy and entropy changes thereby leads to invaluable knowledge about the size, shape and electronic configuration of the central group and the influence of the ligand attached to it.

Methods of studying complex equilibria

In principle, any property which varies with the degree of complex formation may be used to determine the position of the equilibrium. Work on the determination of equilibrium constants of metal complexes and on the identification of different species present at successive stages of equilibria, has indicated that a number of methods may be used with success. Most of these methods of studying ionic equilibria were introduced before or around 1900. The history of methods of studying ionic equilibria has been reviewed in an article by Sillen[17] where full references to the early work can be found. An excellent book by Rossotti and Rossotti[20] on this subject is also available. In recent times the use of radioisotopes has made possible several extentions to the classical methods and some new methods have also been investigated. A brief survey of these methods is, therefore, pertinent.

Methods of studying ionic equilibria may be divided into groups:

(a) Methods that determine the concentration of an individual species, 'c_i', of a system, such as e.m.f., polarography, direct chemical analysis, and certain partition methods.

(b) Methods based on the study of colligative properties. Cryoscopy, ebullioscopy and other vapour pressure methods, constitute this group.

(c) Methods that involve the study of physical properties; they are optical absorption, Raman, and Nuclear Magnetic Resonance (n.m.r.) spectroscopy, magnetic susceptibility, conductance and enthalpy change of a chemical reaction.

(d) Miscellaneous methods. These include electrophoresis, dielectric polarization, ultra centrifugation, ultrasonic absorption, dialysis, filtration and light scattering[20]. Variations on existing methods include those based on the competition of two different metals for the same ligand.

Out of the methods of group (a), potentiometric methods are by far the most accurate and widely used. The basic principle of these methods is the measurement of the e.m.f. of chemical cells representing an equilibrium system. The potential originatesfrom two main types of phenomena, (i) oxidation-reduction, and (ii) the formation of ionic concentration gradients across membranes. The theory of the e.m.f. method is based on the equation of Nernst. Consider a general reversible electron transfer reaction

$$xX + yY + \ldots\ldots\ldots Ze \rightleftharpoons pP + qQ+ \qquad (22)$$

then the potential acquired by an electrode in contact with an equilibrium mixture such as that represented in (22) is given by

$$E = E^{o} + \frac{RT}{ZF} \ln \frac{\{X\}^{x}\{Y\}^{y}}{\{P\}^{p}\{Q\}^{q}} \quad .... \qquad (23)$$

where E^{o} is the standard electrode potential acquired when all the species are at unit activity. In practice the potential difference is measured between an electrode pair in reversible equilibrium with a known concentration of complexing agent and then without complexing agent.

Polarographic measurements involve the rise of the potential at a dropping mercury electrode as a measure of free metal ion concentration. Lingane[21] has discussed in detail the application of polarographic measurements to the investigation of equilibria involving metal ions.

Bonnar, Dimbat and Stross[22] have described the experimental techniques and the theory of methods based on a measurement of colligative properties of systems. With the exception of cryoscopy, these techniques appear to have been little used for determining equilibrium constants.

Spectrophotometric methods belong to group (c) and they have the decided advantage of providing a measurable property, the absorbancy, over a range of wavelengths which can add an additional dimension to the information obtained. Many species undergo electronic transitions in the near-ultraviolet and visual regions of the spectrum, and the intensities of the corresponding absorption bands of a solution have been widely used as a measure of the concentrations of the various species present. For example, the ionisation of a weak acid or base causes changes in the electronic absorption bands; the same is true of the attachment of a ligand to a transition metal cation having a suitable absorption band. The insensitivity of the absorption spectra of ions to the long-range coulombic interactions between ions which affect the thermodynamic and conductance properties, makes the spectrophotometric method useful for the study of both protolytic and complex ion equilibria. Although in the absence of a reliable model for the absorption process, interpretations of the results may be uncertain. These methods have developed rapidly since 1945 with the production of a range of commercial instruments capable of permitting measurements not only in the visible but also down to 1800 Å in the ultraviolet region. The spectrophotometric methods have, however, other inherent disadvantages. These methods are applicable only when one or two complexes are involved and when these are optically very different from the free components. This is a serious limitation not only with regard to ligand concentration range, but also to the choice of solvent.

Recently Raman spectroscopy and nuclear magnetic resonance frequency measurements have increased the scope of studies of chemical systems in equilibrium. The application of n.m.r. frequency measurements to the study of ionic equilibria is based on the determination of the so-called 'proton relaxation' time of a magnetically excited system or on the measurement of the 'chemical shift' of the system. The latter phenomenon is more widely used. When a nucleus with a characteristic spin is placed in an external magnetic field, its magnetic moment vector will precess about the field direction, and its component in the direction of the field will be restricted to certain values, that is it will be quantized. If, at the same time, a low-power radiofrequency transmitter is used, then the ensuing small oscillating electromagnetic field, will induce transitions between the energy levels, by a resonance effect when the frequency of the oscillating field corresponds in energy to that of a particular energy transition. Once the system is excited in such a fashion, it may return to its ground state either by emission of radiation or through a relaxation mechanism. This 'time elapse' can be determined by measuring the intensity of the resonance absorption and is the basis of the 'relaxation' technique. The proton relaxation time is affected by the presence of other paramagnetic species in the system. Naturally when an ion forms a complex the shortening of relaxation time will be less pronounced. Thus, this can be made a measure of the concentration of the ion, and can be used to calculate the equilibrium constant of the system.

In the measurement of the so-called 'chemical shift' the magnetic field at the nucleus is also considered. The resonance frequency depends on the magnetic field at the nucleus, which differs slightly from the applied field on account of magnetic influence of the environment. In liquid systems, the average magnetic interaction between nuclei is zero, and the small difference between the applied field and one at the nucleus is due to the partial screening of the nucleus by the electrons associated with it. Since the screening will vary with the type and number of groups bound to the nucleus different species will require slightly different fields. If applied fields of strength H_1 and H_2 are needed to produce resonance at a given frequency in the species S_1 and S_2, respectively, the quantity

$$\sigma = \pm \frac{H_1 - H_2}{H_1}$$

is known as the chemical shift of the species S_2 relative to S_1. The method has found wide application in the measurement of dissociation constants of a wide range of strong acids.

Conductivity methods are useful only in special cases, in particular if the complex is uncharged as with oxalates and malonates of bivalent metals.

According to Sillen[17], methods of group (a) and (c) are very convenient, specially when a third reagent is added to this system and which reacts with M or A, but which can be measured more easily compared to them. In optical and e.m.f. methods such provision may be of advantage. An example is the addition of Ag(I) to the

Cd^{2+} - SO_4^{2-} system when being studied by the e.m.f. method.

Methods of group (c) are often convenient when there is a single reaction to study, like the dissociation of an acid by the conductance method. The methods in group (b), in general, are not accurate over wide ranges of concentration, whereas the e.m.f. method in group (a) gives a logarithmic response and a good relative accuracy. Partition methods are of particular value in studying reactions at very low concentrations such as are obtainable using radioactive isotopes: they are used in the work described in this thesis.

Investigations of equilibria in solutions by partition methods

Partition methods, as pointed out earlier, belong to group (a), and embrace such widely used techniques as liquid-liquid extraction, ion-exchange and solubility measurements. Of these, measurements of the solubility of a sparingly soluble solid in an aqueous solution of a complexing agent is one of the oldest methods for studying ionic equilibria in solutions. The theory and the experimental techniques of this method have been reviewed by Zimmerman[23]. Solubility measurements are, however, limited by the fact that in saturated solutions there is only one degree of freedom in the concentration of the component, whereas in unsaturated solutions there are two. Solubility measurements cannot provide information on the state of aggregation in the solution phase. For instance, if the solubility of AgI in iodide solutions is expressed as a polynomial: $k_{-1}[I^-] + K_0 + k_1[I^-] + k_2[I^-]^2$ ...... , then the $[I^-]^2$ terms stand for the sum of the concentrations of all complexes of the form $Ag_nI^{2-}_{(n+2)}$, for example AgI_3^{2-}, $Ag_2I_3^{2-}$, $Ag_2I_4^{2-}$, $Ag_3I_5^{2-}$ ......

Liquid-liquid extraction and ion-exchange, on the other hand, are among the most widely used methods for the investigation of ionic equilibria in solutions. The use of solvent extraction in such studies was first suggested by Nernst[24] and it was applied to the study of a number of organic acids[25,26,27], metal-ion polyhalides[28], and polynuclear complexes around the turn of the century. In an excellent article, where references to earlier works can be found, Zozulya and Peshkova[29] have admirably reviewed the potentialities and limitations of this technique.

The ion-exchange technique is a comparatively recent one, in that work in the field was only taken up seriously after World War II, when modern synthetic resins became readily available. Hogfeldt, Ekedahl and Sillen[30] have reviewed work published before 1950 on the investigation of complex formation by ion-exchange methods. The recently revised compilation of stability constants tables[31] contains data published up to 1960. The extention of ion-exchange techniques to more complicated systems owes much to the work of Fronaeous and other pioneers such as Schubert and Connick.

In order to understand partition methods, let us consider a general two phase system, one phase being an aqueous solution which contains all species MA_n, and other phase which contains only a few of the MA_n species, where $0 \leqslant n \leqslant N$; thus showing selective properties. The partition ratio ϕ of the metal between this 'selective' phase and aqueous phase is given by the equation

$$\phi = \sum_{i}^{k} \beta_n \lambda_n [A]^n \Big/ \sum_{o}^{N} \beta_n [A]^n \qquad (24)$$

where λ_n is the partition constant of the n^{th} species between the two phases, and $[A]$ is the concentration of free ligand in the aqueous phase. This equation is applicable to most partition systems, provided the limits i and k are correctly chosen (see page 34), and that all activity factors are constant.

The discussion of partition methods, as applied in solvent extraction and ion-exchange procedures, may be further simplified if we assume that an uncharged complex MA_v is formed, that all complexes with $n<v$ are positively charged, and that all the complexes with $n>v$ are negatively charged. The solvent extraction system can be conveniently classified as set out below.

(a) Partitioning complexes:

When the assumption that only the uncharged complex Ma_v is extracted into the organic phase, is valid, $i = k = v$ in equation (24), which is then reduced to

$$\phi = \frac{\lambda_v \beta_v [A]^v}{\sum_{0}^{N} \beta_n [A]^n} \qquad (25)$$

(b) Non-partitioning complexes:

Sometimes it is of interest to study a complex between a central metal atom M and a ligand B, in which complexes which do not extract are formed. Let such a complex be MB_p, where B may be an inorganic ligand like HSO_4^-, or F^-. The ligand B is then called the secondary ligand. The primary ligand A may still be present in the system and may form an extractable complex MA_v. The partition equation for such a system may then be written as

$$\phi^{-1}_{[A]} = C\sum_{o}^{p}\beta p[B]^{p} \qquad (26)$$

Where $\phi_{[A]}$ is the measured distribution ratio at constant ligand concentration [A]. Since [B] is known, βp and C, the two unknown constants may be calculated by a suitable method. βp is the stability constant of the pth species, and C is a constant.

The theory of the distribution method has been more widely developed in recent years by a group of English investigators led by Irving. In a series of papers,[32,34,35,36,38,40,41] Irving et al have discussed the general form of the distribution law for a metal distributed between organic and aqueous phases, and have described the application of their results to the investigation of a number of systems[33-43]. Since the distribution method has been extensively used in the present work it is desirable that the theory is discussed in more detail, in order to appreciate the work.

Following Irving, the distribution method may be divided into (a) ideal and (b) non-ideal systems. An ideal system is defined as one in which wide variations in the experimental conditions do not produce any change in the properties of either solvent. This being so, the degree of solvation of any species remains unchanged in either phase, hence the average number of water and organic solvent molecules associated with each species remains constant, as remain the stability constant and the partition coefficient. In the non-ideal system this is not true.

Irving has also considered the types of extracted compounds. These are: (1) covalent compounds like SO_3 and Cl_2; (2) internal complexes of metals with organic reagents, e.g. diphenylthiocarbazone (dithizone), acetylacetone and Di-(ethylhexyl)orthophosphoric acid (HDEHP); (3) mineral acids, their salts and acid complexes of the type $HFeCl_4$; and (4) certain salts containing bulky anions and cations such as salts of Fe(II)-tris-(1,10,-phenanthroline) with, for example, alkyl sulphonates or alkyl sulphates.

The work to be described here involves compounds of the second and third types. In the case of internal complexes a quite stable unsolvated monomeric complex

MA_n is formed at such a low concentration of the ligand [A] that the properties of the aqueous phase as a solvent remain practically unchanged. Internal complexes which are very sparingly soluble in water are at the same time, as a rule, readily soluble in non-polar organic solvents (benzene, toluene, chloroform, etc.). The organic reagent HA whose anion A is the ligand in [MA_n] also dissolves in the same organic phase. Addition of foreign ions to the aqueous phase and the resulting change in composition do not usually affect the composition of neutral species which are extracted, and the absence of hydration in the extracted species eliminates the possibility of any change in the organic phase. This being true, the mutual immiscibility of the two phases remains unchanged, even when the concentration of HA and A is varied over a wide range, in order to obtain a partition coefficient more convenient to measure. If the ionic strength of the aqueous phase is kept constant, the stability constants of all the complexes in the aqueous phase and also the distribution constants of the extracted species will be constant and their value can be obtained by carrying out a sufficiently large number of measurements. In other words, the system is an ideal one.

The quantitative treatment given by Irving and his co-workers for complex formation using extraction techniques is actually based on a combination of Bjerrum's concept of the step-wise formation of complexes and the distribution law of Nernst. The treatment given by Irving is a general one and accounts for complex formation by metal ions and all other complex forming species present in the system containing two immiscible solvents. His equations governing extraction equilibria are based on certain assumptions set out below.

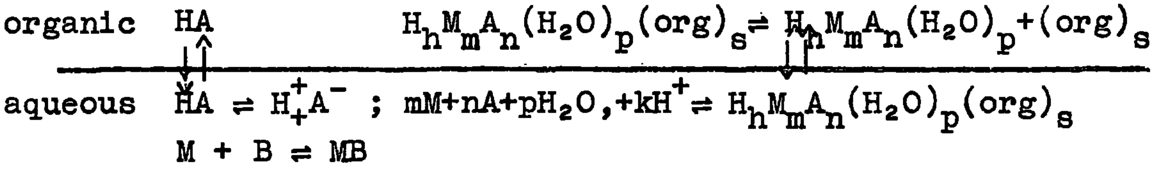
(a) In the aqueous phase, saturated with the organic solvent in question and containing metal ions, M, hydrogen ions, H^+, and ligand A^-, the concentrations of H^+ and A^- are such that hydrolysis of any cation can be neglected.

(b) All complexes of the type MA_n, acid complexes H_nMA_n and polynuclear complexes $[M_2A_6, H_2M_3A_{12}]$ are in equilibrium with each other and can be represented as a complex of the general type

$$H_hM_mA_n(H_2O)_p(Org)_s \text{ (I) } .... \quad (27)$$

where subscripts h, m, n, p, s in that order are the number of hydrogen, metal-cation, ligand, water and organic solvent molecules forming the complex I. If a secondary ligand B is also present, neutral species of the type MB_p are not formed.

Schematically 'I' may be represented as follows:



$$\text{organic} \quad HA \qquad H_hM_mA_n(H_2O)_p(org)_s \rightleftharpoons H_hM_mA_n(H_2O)_p + (org)_s$$

$$\text{aqueous} \quad HA \rightleftharpoons H^{+}_{+}A^{-}\ ;\ mM+nA+pH_2O,+kH^{+} \rightleftharpoons H_hM_mA_n(H_2O)_p(org)_s$$

$$M + B \rightleftharpoons MB$$

Now the concentration of type I complexes is determined by the stability constant β:

$$\beta_{h,m,n,p,s,} = \frac{H_hM_mA_n(H_2O)_p(org)_s}{[H]^h[M]^m[A]^n[H_2O]^p[org]^s} \tag{28}$$

and the distribution in two phases by the distribution constant Q:

$$Q_{h,m,n,p,s} = \frac{\{H_hM_mA_n(H_2O)_p(org)_s\}_{org}}{\{H_hM_mA_n(H_2O)_p(org)_s\}} \tag{29}$$

The partition ratio of the metal between the phases, numerically equal to the ratio of the total concentrations of all forms of metal containing species in the organic and the aqueous phases, can be represented as follows:

$$\phi = \frac{\Sigma Q_{h,m,n,p,s}\ \beta_{h,m,n,s,p,m}\{H\}^{h}\{M\}^{m}\{A\}^{n}\{H_2O\}^{p}\{org\}^{s}}{\Sigma\beta_{h,m,n,p,s,m}\{H\}^{h}\{M\}^{m}\{A\}^{n}\{H_2O\}^{p}\{org\}^{s}} \qquad (30)$$

Equation (30) reduces to equation (24) (page 24) when Q replaces λ and the experimental conditions are correctly chosen (see page 29).

Using the concept of mean number $\bar{E}$ of metal atoms per complex molecule in the organic phase and the corresponding mean $\bar{e}$ in the aqueous phase, and applying similar concepts to the mean number of hydrogen, ligand, water molecules and organic solvent molecule per atom of metal, Irving put forward an expression for ϕ in the form:

$$\phi = \frac{\bar{\theta}\ \bar{E}\ \bar{B}\ \{H\}^{\bar{E}\bar{H}}\{M\}^{\bar{E}}\{A\}^{\bar{E}\bar{N}}\{H_2O\}^{\bar{E}\bar{P}}\{org\}^{\bar{E}\bar{S}}}{\bar{E}\ \bar{\beta}\ \{H\}^{\bar{e}\bar{h}}\{M\}^{\bar{e}}\{A\}^{\bar{e}\bar{n}}\{H_2O\}^{\bar{e}\bar{p}}\{org\}^{\bar{e}\bar{s}}} \qquad (31)$$

where $\bar{H}$, $\bar{h}$ are the mean numbers of hydrogen ion in the organic and aqueous phases respectively; correspondingly $\bar{\theta}$ and $\bar{B}$ are the distribution and stability constants of the 'averaged' molecule in the organic phase, and $\bar{\beta}$ is the stability constant of the 'averaged molecule' in the aqueous phase. On taking logarithms (31) becomes:

$$\log\phi = \log\left(\frac{\bar{\theta}\bar{B}}{\bar{\beta}}\right) + \log\left(\frac{\bar{E}}{\bar{e}}\right) + (\bar{E}\bar{H}-\bar{e}\bar{h})\log[H^{+}]+(\bar{E}-\bar{e})\log[M]$$

$$+ (\bar{E}\bar{N}-\bar{e}\bar{n})\log[A] + (\bar{E}\bar{P}-\bar{e}\bar{p})\log(H_2O) + (\bar{E}\bar{S}-\bar{e}\bar{s})\log(org)$$

In the ideal systems, $\bar{B}$, $\bar{\beta}$, $\bar{\theta}$, $\bar{p}$, $\bar{P}$, $\bar{S}$, $\bar{s}$ are all constants. With constant ionic strength in the aqueous phase, the mutual solubility of the solvents is constant and, therefore, the expression (32) becomes:

$$\log \phi = \psi + \log(\frac{\bar{E}}{e}) + (\bar{E}\bar{H}-\bar{e}\bar{h})\log(H)+(\bar{E}-\bar{e})\log[M]+(\bar{E}\bar{N}-\bar{e}\bar{n})\log[A] \quad \text{....(33)}$$

where ψ is a constant independent of $\{M\}$, $\{H\}$, and $\{A\}$.

With the help of equation (33) it is possible to draw definite conclusions as to the composition of the various complexes existing in the organic and aqueous phases and it is also possible to calculate the constants it contains.

To find the mean number of metal atoms per averaged complex molecule, equation (33) is differentiated with respect to M at constant [H] and [A]. Then (33) becomes:

$$\left\{ \frac{\delta \log \phi}{\delta \log \{M\}} \right\}_{\{H\}\{A\}} = (\bar{E} - \bar{e}) \qquad (34)$$

Thus, if the value of the partial derivative (34) is found to be zero, the degree of polymerization of the metal containing species is the same in each phase. In the limiting case, when the concentration $\{M\}$ of metal tends to zero, the value of $\bar{E}$ and $\bar{e}$ tend to unity, i.e. at very low metal concentration only mono-nuclear complexes are formed in each of the phases.

This has been established for the majority of metals.

When $$\left[\frac{\delta \log \phi}{\delta \log\{M\}}\right]_{\{H\}\{A\}} \gg 0$$

then, the degree of polymerization in the organic phase is higher than in the aqueous phase, and conversely

when $$\left[\frac{\delta \log \phi}{\delta \log\{M\}}\right]_{\{H\}\{A\}} \ll 0$$

The difference in the mean number of ligands associated with each complex forming metal atom in the average complex in each phase is indicated by the value of the partial derivatives of the partition coefficient with respect to ligand for $\{M\}$ and $\{H\}$ constant.

$$\left\{\frac{\delta \log \phi}{\delta \log[A]}\right\}_{\{M\}\{H\}} = (\overline{\overline{EN}}-\overline{\overline{en}}) \qquad (35)$$

What has been said about equation (34) is true about (35). The value of the derivative obtained indicates either the same or different average ligand numbers in the organic and aqueous phases. If mononuclear complexes are formed $\bar{E} = \bar{e} = 1$ and (35) becomes

$$\left\{\frac{\delta \log \phi}{\delta \log\{A\}}\right\}_{\{M\}\{H\}} = \bar{N} - \bar{n} \qquad (36)$$

If it is established that a single neutral complex MA_n is transferred to the organic phase, equation (36) can be used to find all the stability constants of the complexes formed in the aqueous phase.

There are several methods of calculation which will be discussed later in the text.

Cation exchange: Consider the general equation (24). When only the adsorption of cations has to be considered, $i = o$ $k = (v-1)$, and (24) can then be written as

$$\Sigma(\phi-\lambda_n)\beta_n[A]^n = o \qquad \lambda_n = o \quad \text{for } n \geqslant v \qquad (37)$$

Here, λ_n and β_n are unknown, while $[A]$ and ϕ are known. In the equation (37) λ_o can be determined in the absence of complexing agent ($n = o$; $A = o$). If $n > 1$, β_n and λ_n cannot be determined independently of each other except when $\phi >>> \lambda_n$.

In the cation-exchange study of equilibria, a known volume of a solution containing M and also A which is varied and a background salt to maintain constant ionic strength is equilibrated with a known weight of the resin in a suitable form and the distribution ratio ϕ is found.

$$\phi = \frac{C_{MR}}{C_M} \qquad (38)$$

Where C_{MR} is the total concentration of the metal in all its forms in the resin phase, and C_M the corresponding concentration in the aqueous phase. If M is a trivalent cation, and A has a single negative charge, we can write

$$\phi = \frac{[M^{3+}]_R + [MA^{2+}]_R + [MA_2^+]_R}{[M^{3+}] + [MA^{2+}] + [MA_2^+]} \quad .... \qquad (39)$$

In the limiting case, the expression reduces to

$$\lim_{A \to o} \phi = \phi^o = \lambda^o = \frac{[M^{3+}]_R}{[M^3]} \qquad (40)$$

As pointed out earlier λ_0 can be found experimentally. Now consider the step equilibria, viz $M^{3+} + 3Na_R^+ \rightleftharpoons M_R^{3+} + 3Na^+$ which gives

$$K_1 = \frac{[M^{3+}]_R}{[M^{3+}]} = \lambda^o \qquad (41)$$

Similarly, $K_2 = \frac{\{MA^{2+}\}R}{\{MA^{2+}\}} = \lambda_1$ and $K_3 = \frac{\{MA_2^+\}R}{\{MA_2^+\}} = \lambda_2$, so that $\{M^{3+}\}R = \lambda^o \times [M^{3+}]$; $\{MA^{2+}\}R = \lambda_1[MA_2^+]$; $\{MA_2^+\}_R = \lambda_2\{MA_2^+\}$. Substituting these values in equation (37) we have

$$\phi = \frac{\lambda_0[M^{3+}] + \lambda_1[MA^{2+}] + \lambda_2[MA_2^+] +}{[M^{3+}] + [MA^{2+}] + [MA_2^+] + [MA_3]} \qquad (42)$$

Further by definition $[MA^{2+}] = \beta_1[M^{3+}][A^-]$ and so on.

Therefore (40) on substitution becomes

$$\phi = \frac{\lambda_0 \;+\; \beta_1\lambda_1[A] + \beta_2\;\lambda_2[A]^2 + \;......}{1 + \beta_1[A] + \beta_2[A]^2 + \beta_2[A]^3} \qquad (43)$$

$$\text{or,}\quad \phi = \lambda_0 \;\; \frac{1 + \frac{\beta_1\lambda_1}{\lambda_0}[A^-] + \frac{\beta_2\lambda_2}{\lambda_0}[A^-]^2}{1 + \beta_1[A^-] + \beta_2[A^-]^2 + \beta_3[A^-]} \qquad (44)$$

Let $\frac{\beta_1\lambda_1}{\lambda_0} = \lambda_1'$ and so on,

$$\text{so that}\quad \phi = \lambda_0 \;\left\{\frac{1 + \lambda_1'[A^-] + \lambda_2'[A^-]^2}{1 + \beta_1[A^-] + \beta_2[A^-]^2 + \beta_3[A^-]^3}\right\} \qquad (45)$$

Rearranging (43) we have

$$\frac{\lambda^0}{\phi} = \frac{1 + \beta_1[A^-] + \beta_2[A]^2 + \beta_3[A^-]^3}{1 + \lambda_1'[A^-] + \lambda_2'[A^-]^2 + \;.......} \qquad (46)$$

$$\text{or}\;\; \left(\frac{\lambda^0}{\phi} - 1\right)/[A^-] = \phi_1 = \frac{\beta_1 + \beta_2[A^-] + \beta_3[A^-]^2 - \lambda_1' - \lambda_2'[A^-]}{1 + \lambda_1'[A^-] + \lambda_2'[A^-]^2 + \;............}$$

$$= \frac{(\beta_1 - \lambda_1') + (\beta_2 - \lambda_2')[A^-] + \beta_3[A^-]^2 + \;.......}{1 + \lambda_1'[A^-] + \lambda_2'[A^-]^2 + \;.............} \qquad (47)$$

$$\text{and}\;\lim_{[A^-]\to o} \phi_1 = \phi_1{}^{\circ} = (\beta_1 - \lambda_1')\;............... \qquad (48)$$

at sufficiently low ligand concentrations, terms like $\beta_3[A^-]^2$, $\lambda_1'[A^-]$ and $\lambda_2'[A^-]^2$ should be negligible so that

$$\phi_1 = (\beta_1 - \lambda_1') + (\beta_2 - \lambda_2')[A^-]\;.................. \qquad (49)$$

On inspection of equation (49) it appears that a plot of ϕ_1 vs $[A^-]$ should be linear, giving the quantities $(\beta_1 - \lambda_1') = \phi_1^0$ as the intercept and $(\beta_2 - \lambda_2')$ as the slope of the line respectively.

From the knowledge of the quantities, viz. λ^0, ϕ, ϕ_1^0 and $[A^-]$, another function, F, defined as

$$f = \frac{\lambda_0\phi^{-1}[(\beta_1 - \lambda_1')[A^-] - 1] + 1}{[A^-]^2}$$

$$= \frac{\beta_1\phi_1^0 + \beta_2\phi_1^0[A^-] + \beta_3\phi_1^0[A^-]^2 - \beta_3[A^-] - (\beta_2 - \lambda_2)}{[A^-]^2} \quad \ldots\ldots \quad (50)$$

is calculated, where

$$\lim_{[A^-]\to 0} f = f^0 = \beta_1\phi_1^0 - (\beta_2 - \lambda_2') \quad \ldots\ldots\ldots \quad (51)$$

knowing f, f^0, ϕ_1 and ϕ_1^0, the following quantities are calculated

$$\Delta f = f - f^0$$

and $$\Delta\phi_1 = \phi_1 - \phi_1^0$$

Rearranging equations for ϕ_1 and f, we have,

$$\beta_1 = \frac{\Delta f}{\Delta\phi_1} + \beta_3\frac{[A^-]}{\Delta\phi_1} + \beta_4\frac{[A^-]^2}{\Delta\phi_1} - \lambda_2'\,\phi_1\frac{[A^-]}{\Delta\phi_1} \quad \ldots\ldots\ldots \quad (52)$$

On further rearrangement of equation (52)

$$\frac{\Delta f}{[A^-]} = \beta_1 \frac{\Delta\phi_1}{[A^-]} - \beta_3 - \beta_4 [A^-] + \lambda_2\phi_1 \;\ldots\ldots\ldots\ldots\ldots \quad (53)$$

Under favourable circumstances, the terms β_3, β_4 and $\lambda_2\phi_1$ are negligible and a plot of $\frac{\Delta f}{[A^-]}$ vs $\frac{\Delta\phi_1}{[A^-]}$ is linear, giving β_1 as the slope of the line. However, for those cases where quantities $\frac{\Delta\phi_1}{[A^-]}$ and $\frac{\Delta f}{[A^-]}$ are nearly constant, this method of evaluating β_1 can no longer be applicable. In such cases, following equation (52) a value of β_1 may be obtained by taking the arithmetic mean of the reliable $\frac{\Delta f}{\Delta\phi_1}$ values; this assumes that in equation (52) the terms $\beta_3 \frac{[A^-]}{\Delta\phi_1}$, $\beta_4 \frac{[A^-]^2}{\Delta\phi_1}$ etc. are negligible.

Knowing β_1, the quantity $(\beta_2 - \lambda_2')$ is calculated from

$$(\beta_2 - \lambda_2') = \beta_1\phi_1^o - f^o \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (54)$$

This enables the calculation of another function g, which is defined as

$$g = \frac{\lambda_0\phi^{-1}(\beta_2 - \lambda_2') + (f - \beta_1\phi_1)}{[A^-]} \quad (55)$$

$$= \beta_2\phi_1 - \beta_3 - X_4[A^-] \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (56)$$

In cases where the term $X_4[A^-]$ is negligible, a plot of g vs ϕ_1 will be linear with slope β_2 and intercept $-\beta_3$.

The use of radioisotopes in equilibrium studies

The property of radioisotopes of being easily detected in minute amounts makes them very useful in connection with two of the methods used for investigating ionic equilibria, namely solvent-extraction and ion-exchange. Advantages occurring from the use of very low metal-ion concentrations made possible by the use of radioisotopes of high specific activities are:
(a) easy determination of free ligand concentrations,
(b) avoidance of polynuclear complex formation,
(c) constant activity factors for the metal ion and its complexes, and (d) the extended concentration range of [M] which can be investigated. The last mentioned makes it feasible to study complicated systems more comprehensively than otherwise might be possible. Also, in many cases, particularly among the actinides, the radioisotope partition method is the only practical method available, largely because of complications arising from radiolysis if appreciable concentrations were used. The simplicity and economy of radio-tracer methods are also significant[43]. Even in 1938, Hevesy and Paneth could write recommending the use of radioisotopes, that "the acquisition of artificial radioelements as indicators does not necessarily involve large monetary expenditure".

On considering the equations governing the partition equilibria (see for example equation 24, page 24) it is evident that complexity constants can easily be determined provided that ϕ, $[A^-]$ and $[B^-]$ are known. As pointed out before the great advantage with radioisotopes is that the concentration of metal can be chosen so low that $M \lll [A]$ or $[B]$, which makes the determination of $[A]$ or $[B]$ very convenient. However, the use of radioisotopes is not quite free from limitations. In a recent article, J. Rydberg has discussed the subject in some detail. According to Rydberg[44] at very low concentrations of metal tracer M (say $M < 10^{-8}M$), a large fraction may be lost through adsorption on surfaces in contact with the solution. The adsorption increases with the decreasing concentration and increasing charge of the tracer, and varies with pH and nature of the surface[45,46]. Rydberg maintains that a suitable concentration may be that of $M > 10^{-5}M$. At such concentrations adsorption losses are in the region of only a few percent for transition metal ions and are still lower for less highly charged cations.

Outline of the present work

In the present work radioisotopes of selected lanthanide and actinide elements have been used to study complex formation in aqueous solution by means of solvent-extraction and ion-exchange methods. Both organic and inorganic ligands have been used.

Investigations with the radioisotope partition methods not only yield information about how complex compounds are built up, but also about how ion-exchange and solvent-extraction processes operate. Both these methods have been used for some time in the study of complexes of lanthanide, actinide and other highly charged transition metal-cations in solutions. Since both these methods can operate at tracer levels, much lower concentrations of metal can be studied than might be possible by potentiometry and other methods. The methods are, therefore, particularly suitable for investigations which can be carried out only in solutions very dilute in C_m. Data obtained by the solvent-extraction method alone, are of particular interest, for if the system is correctly chosen, they are considerably easier to interpret and more reliable than data obtained, for example, by conductivity, ion-exchange or spectrophotometry. The latter methods tend to be less reliable because in them a number - or even all - of the species present contribute to the property measured and many extra parameters may have to be introduced. Ion-exchange which has recently been extensively employed in such studies is, for example, a case in point. When an aquated metal cation M^{n+} is brought in contact with a cation-exchange resin, then all the positively charged species $MA^{(n-1)+}$, $MA_2{}^{(n-2)+}$ .... $MA_j{}^{(n-j)+}$ will exchange along with the unbound metal cation. The measurable property, the distribution ratio ϕ, therefore, will be described by an expression

$$\phi = \frac{\lambda^0 + \lambda_1\beta_1[A^-] + \lambda_2\beta_2[A^-]^2 + \ldots + \lambda_j\beta_j[A^-]^j}{1 + \beta_1[A^-] + \beta_2[A^-]^2 + \ldots\ldots \beta_j[A^-]^j}$$

that includes set of additional parameters λ_1 ...... λ_j which do not appear in a comparable relation for a suitably chosen solvent-extraction method where

$$\phi = \lambda^0/(1 + \beta_1[A^-] + \beta_2[A^-]^2 + \beta_3[A^-]^3 + \ldots\ldots \beta_j[A^-]^j).$$

The advantage of solvent extraction over the ion-exchange method has thus been a stimulus to undertake the present work. It is desirable that data from distribution methods may be compared with those obtained from other methods.

Also, as pointed out above, if a solvent-extraction system involves the partition of uncharged metal complex only, then a common aqueous phase may be equilibrated against such a solvent system and ion-exchange resin under identical conditions, a method may be developed to measure partition coefficients of partially charged species. This has been an important objective in the work to be described in this thesis. A quantitative treatment applicable to the method adopted will be given at a later stage in the text. So-called 'liquid cation-exchangers' like HDEHP and dinonyl naphthalene sulphonic acid (DNA) have been extensively used in works involving separation of rare-earth and actinide elements from fission-products and from indigenous ores. They are also reported to have the requisite property of extracting only uncharged complexes. The extractant HDEHP, in particular, has been extensively used for these purposes and it was therefore thought desirable to study complex-equilibria using a solution of HDEHP in an organic solvent as a second phase. The first objective was to test the relevant properties and potential application to the development of a direct method for obtaining partition coefficients of partially charged species in a convenient ion-exchange system.

Higher actinide isotopes are nearly all α-emitters, sometimes without significant γ-emission; they therefore pose problems in radioactive determination in the presence of appreciable concentrations of inert salts. Another objective of this work was the development of a liquid-scintillation method suitable for such equilibrium studies with such isotopes. Finally it was hoped to collect additional information on relative equilibrium constants of lanthanide and actinide elements.

The choice of ligands, α-hydroxy-iso-butyrate, fluoride, sulphate and oxalate has been made because they are not only used in much separation work by precipitation, solvent-extraction and ion-exchange procedures, but also because charges and sizes can provide additional information regarding the ion-exchange process. The separation factors for α-hydroxy-iso-butyrate acid are comparable to those of ethylenediamine-N,N,N',N'-tetra-acetate, and has been suggested[47] to be a superior eluting agent than the latter as a consequence of better flow rates and solubility characteristics.

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CHAPTER II

THE DEVELOPMENT AND GENERAL OUTLINE OF EXPERIMENTAL METHOD

Introduction

In the present work ion-exchange and solvent-extraction methods have been used to study equilibria involving complex formation between cations of certain lanthanide and actinide elements and some organic and inorganic ligands. In the ion-exchange studies modern synthetic ion-exchange resins have been used, whereas use has been made of dilute solutions of HDEHP in toluene in the solvent-extraction work. The partition constants of the systems studied by both methods have generally been measured radiometrically using conventional counting techniques (cf. Page 51)

The present chapter covers experimental aspects of the development and refinement of procedures in these studies and gives some results and data which were obtained during the course of preliminary measurements. Information on apparatus has also been given wherever relevant.

The determination of the partition-ratio

The partition ratio of a metal cation between a selective phase and an aqueous phase is defined as the ratio of the total concentration of the metal in all its possible forms in the selective phase to the corresponding concentration in the aqueous phase. For the solvent-extraction system the so-called selective phase is usually an organic solvent or a homogeneous solution of some organic reagent in an organic solvent. A solid cation-exchange resin replaces this phase in the ion-exchange method.

Let, $[M]_s$, represent the total molar concentration of all the metal-containing species in the selective phase, and, $[M]$, the corresponding concentration in the aqueous phase, then by definition,

$$\phi = \frac{[M]_s}{[M]} \tag{1}$$

where ϕ is the partition ratio.
The values of $[M]_s$ and $[M]$ are related to the total molar concentration, C_M, of the metal in the whole system by the expression

$$C_M = [M]_s v_s + [M]_v \tag{2}$$

where v_s and v are the volumes (in litres) of the phases in equilibrium. In the ion-exchange system v_s is replaced by mass, m, in gram of the resin. The above relation is, however, valid only when a 100% mass balance can be maintained. In most radiochemical work on partition studies by solvent-extraction method, such a mass-balance can easily be checked by measuring the radioactivity of the metal in both the phases.

Substituting from equations (1) and (2) we can arrive at the relation

$$\phi = \frac{C_M/[M] - v}{v_s} = \frac{v_s}{C_{M[M]_s} - v} \qquad (3)$$

If the initial total concentration, C_i, of the metal in the aqueous phase is known, then

$$C_i = [M]_s + [M] = \frac{C_m}{v} \qquad (4)$$

and equation (3) may be simplified to

$$\phi = \frac{C_i - [M]}{[M]} = \frac{[M]_s}{C_i - [M]_s} \qquad (5)$$

provided that the volumes of each of the two phases are equal. In solvent-extraction this condition can be easily fulfilled by equilibrating equal volumes of both phases. For the ion-exchange method, a modified expression

$$\phi = \frac{[C_i - [M]\delta]v}{[M]m} \qquad (6)$$

is appropriate where δ is the swelling factor of the resin (see page 62).

Consideration of equations (1 - 6) shows that the value of the partition ratio, ϕ, can easily be obtained from the measured values of either $[M]$ or $[M]_s$, provided that the appropriate quantities from among C_M, v, v_s, m and δ are known. It is conceivable, at least in principle, that any method leading to the measurement of $[M]$ or $[M]_s$ may be used for the determination of ϕ. Methods based on gravimetric, volumetric, spectrophotometric and fluorimetric analyses have been reported in the literature[1,2,3,4]. Although such methods are used in partition studies, they are frequently cumbersome and in some cases impracticable, for example in the study of higher actinide elements. Radiometric analysis on the other hand appears to be very convenient and well suited to such investigations.

Radiometric Determination of ϕ

The radioactivity, A, of a radioactive isotope is a quantity proportional to the number of atoms, N, of the isotope present in the sample at a given instant. The radioactivity of a particular element, an isotope of which is radioactive can, therefore, be taken as a measure of its concentration in the system. Determination of the partition ratio by radiometric analysis utilises this principle.

In actual practice, the initial activity, A_1 of an aliquot of the active-solution of the metal ion is measured before and after equilibration. Let the activity of the phase after equilibration be denoted by A_2. Then the difference, (A_1-A_2), gives the activity transferred to the other phase and, ϕ, is calculated using the following expressions:

$$\phi_L = \frac{(A_1 - A_2)v_S}{A_2\ v} \qquad (7)$$

$$\phi_R = \frac{(A_1 - A_2\delta)v}{A_2\ m} \qquad (8)$$

where the subscript L and R represent the partition ratios determined by solvent-extraction and ion-exchange methods respectively.

The advantages of radiometric analysis over other methods are many. The method is simple, rapid and can be carried out with good precision. The range of metal concentrations that can be studied by this method is probably greater than that possible by any other method.

Another advantage is that elements which themselves are not radioactive can be studied by reacting them with a suitable radioactive element. For example, silver ions may be determined by measuring the activity when radioactive iodide containing iodine-^{131} is used to precipitate AgI.

Radiometric determination of partition ratios has, however, its limitations. Care is necessary in order to avoid losses of radioactivity, for example, in preparing solid samples, by volatilisation or spurting during the process of evaporation. Also direct assay of solid residues is restricted to systems containing low concentrations of salts and other non-volatile solutes. Often cumbersome corrections for self-absorption must be applied if the samples are not, 'weightless'. Although the assay of liquid samples is quicker and more convenient, it is not always without drawbacks. For example, if for the measurement, the activity in both the phases is desired, problems of correction will arise because of the difference in absorption of radiation by the two solvents. A number of approaches have been applied to overcome such difficulties[5].

In the present work radioactive assay of liquid samples was done in identical solution medium. The effect on the response of the counting instrument at different activity levels was studied by measuring the radioactivity of identical liquid samples prepared by diluting a known activity. In general the observed and calculated counting rates were in good agreement.

Apparatus

The apparatus applied to the measurement of radioactivity of a sample make use of one of two main processes namely (a) excitation and (b) ionisation by which radiation transfers energy to a stopping material. In the present work both types of detector have been used.

Scintillation counter

One of the most convenient and versatile detectors in use to-day is the scintillation counter. The basic principles used in this device can be divided into three, namely (a) production of fluorescent light by the interaction of charged particles or electromagnetic radiation with the material of the scintillator,

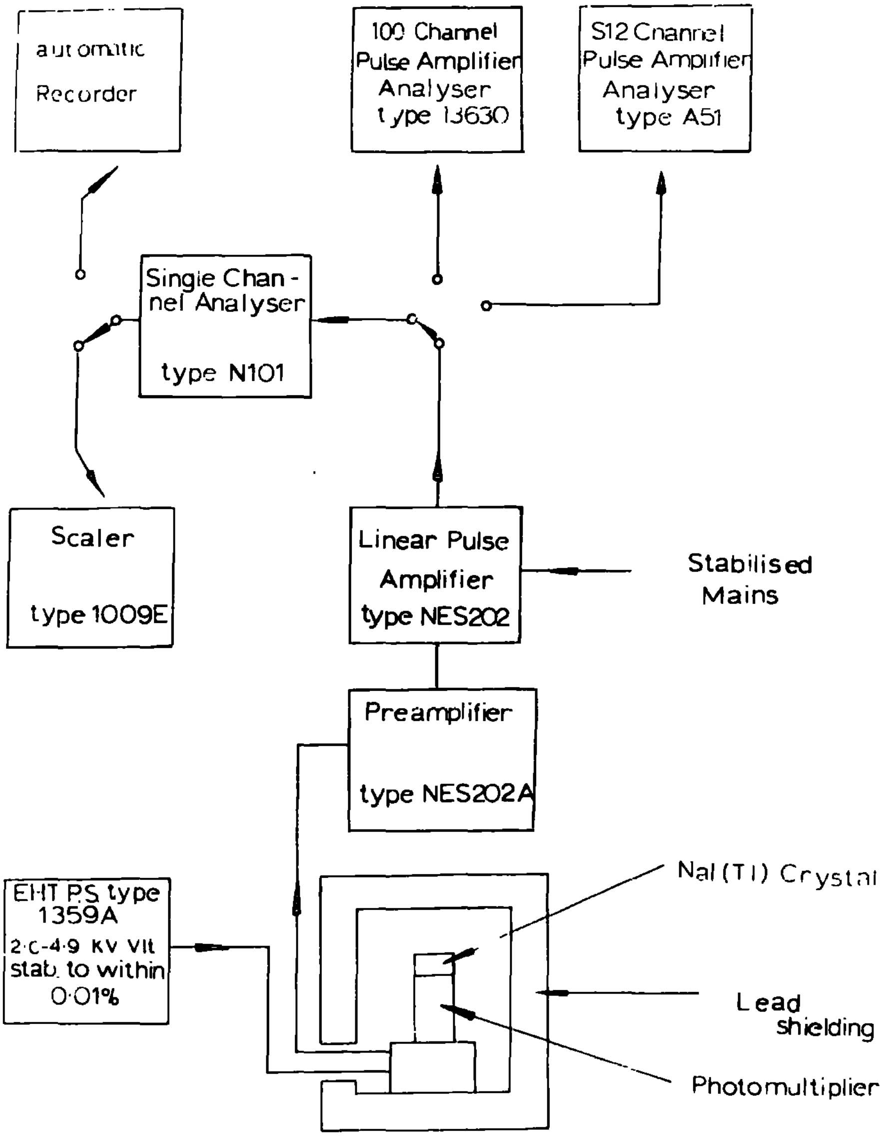

Fig. 1 Block diagram of the circuits used for scintillation counting.

(b) conversion of the light pulses into electronic pulses by their interaction with the photo-cathode of a photomultiplier tube and (c) amplification and registration of these pulses by means of an appropriate electronic circuit. The initial process here is essentially that of 'excitation', although in some cases the interaction of the incident particle and stopping medium may involve ionisation and molecular dissociation as well. A block diagram of a scintillation counter is given on the adjoining page.

In the present work a NaI(TlI) well-type scintillation counter was used for γ-ray measurements. Radioactivities of europium-152, 154, gadolinium-153, and americium-241 were assayed in snap-top polythene capsules using a Type-7F8, 1¾" diameter and 2" height crystal, connected with a single channel pulse-height analyser and accessory electronic scalater unit. Solid γ-ray scintillators have far greater stopping power for photons than gas-filled counters and therefore their detection efficiency for γ-rays is particularly high. Sodium iodide (NaI) activated with 0.1% thallium iodide (TlI) has the high density associated with alkali-halides and a moderately effective atomic number, both desirable properties for effective detection purposes.

The light output of solid NaI(TlI) per MeV of energy deposited is the largest of any known scintillator and is about twice that of anthracene.

As to the precision of scintillation counting, if tubes of reasonably uniform bore are selected and sample sizes do not differ, an overall precision of better than ± 1% may readily be obtained by taking adequate account of statistical fluctuations, at least with radioisotopes of γ-ray energies larger than 0.1 MeV. If care is taken in the canning of the crystal so as to provide a thin-walled well substantially less energetic γ-rays may be counted. However, there may be some sacrifice of precision unless careful attention is paid to uniformity of wall-thickness of the sample containers. Also at low energies the density of the solution will affect the efficiency and due consideration should be paid to this factor in devising the experimental procedure.

Liquid-scintillation counting in which the sample to be counted is dissolved in a liquid-scintillator solution has been used in some of the work: a separate account is given in chapter V.

Liquid Geiger-Müller Counting

The radioactivity of a sufficiently energetic β-emitter can readily be assayed by a Geiger-Müller tube. In the present work a '20th Century Electronics' annular tube Type-M6H was used for the measurement of cerium-144, praseodymium-144 and lanthanum-140 activities. The basic principles of this detector is 'ionisation' of a gas. When energetic charged particles interact with gas molecules, ionisation occurs. In a Geiger-Müller counting arrangement an applied electric field results in secondary ionisation, eventually building up a considerable electrical pulse which with little further amplification is capable of 'triggering' a scaling device. The mechanism by which a Geiger-tube operates has been reviewed in the literature[6].

Ion-exchange Resins

Organic ion-exchange resins consist of an elastic three dimentional net-work of hydrocarbon chains which carry fixed ionic groups such as $-SO_3^-$, $-COO^-$, $-PO_3^{2-}$ and $-AsO_3^{2-}$ in the case of cation-exchangers and $-NH_3^+$, $>NH_2^+$, $>N^+<$ and S^+ in anion-exchangers. The charge of the fixed ionic groups is balanced by mobile counter ions. The resin can, therefore, be regarded as a polyelectrolyte[7]. Resins are insoluble materials but they can swell to a limited degree. Ion-exchange behaviour depends chiefly on the nature of the fixed ionic groups. Important factors are the acid or the base strength of the fixed groups and their specific interactions with counter ions. In some cases the degree of cross-linking of a resin can also influence ion-exchange behaviour.

In the work to be described here, Zeo-Karb-225 (SRC-15), with 8% 'nominal' DVB cross-linking, and Zeo-Karb-225 (SRC-23), with 20% 'nominal' cross-linking both having a 100-200 mesh particle size were used. These are polystyrenes cross-linked by mixing the required quantity of divinyl-benzene with the monomer and after polymerisation sulphonating the benzene rings. The 'nominal' DVB content provides a measure of the degree of cross-linking which refers to the mole percent of pure divinylbenzene in the initial polymerisation mixture.

Preliminary treatment

Measurements with materials as supplied by the manufacturer tend to give irreproducible results[7]. The resins used in the present work were therefore 'conditioned' before use by the following procedure. An adequate amount of resin supplied in the sodium form was placed in a large beaker and washed free of 'fines' with

2M hydrochloric acid by decantation. The resin was then transferred to a large chromatographic column and washed with enough volumes of warm 2M hydrochloric acid to remove ferric ions; it is also thereby converted to the hydrogen form. The excess of acid was removed by washing with doubly distilled water until the effluent was neutral to litmus paper indicating complete neutralisation. The excess of chloride ion was removed by washing the resin with distilled water, the washings being checked with silver nitrate. The resin was finally dried in a hot air oven at 80°C, until the particles no longer adhered to each other, and finally stored in an air-tight screw-cap bottle.

The removal of ferric ions is an important step in resin conditioning. Helfferich[7] has recommended use of alcoholic-hydrochloric acid, thiocyanate solution or a solution of complexing agent like EDTA for the removal of iron. Leaching with hydrochloric acid was, however, found adequate for the present work. Washing with complexing agent solution like that of EDTA was considered to be undesirable in view of the strong complexing tendency of rare-earth ions with this substance.

Di-[2-ethyl-hexyl]orthophosphoric acid, (HDEHP)

The di-[2-ethyl-hexyl]orthophosphoric acid is a monobasic acid which dimerizes in benzene and in other inert solvents like toluene and naphthalene[8]. The molecular weight of the dimer $[\{(C_2H_5)(C_6H_{12})\}_2 PO(OH)]_2$, is shown to be 645 and has an eight-membered ring structure which results through hydrogen-binding.

(HDEHP) has been widely studied in solvent-extraction. Its use is cited 127 times in the review article by Coleman, Blake and Brown[9]. The first recorded use was that made by Peppard and co-workers[10, 11] during the course of work on thorium-lanthanide separations. While establishing conditions for routine thorium-lanthanide separation using dibutyl ester (HDBP), they found that a promising fractionation of the lanthanides was possible by the use of such ester systems. On further investigation they found that (HDEHP) was preferable to (HDBP) because of its greater resistance to hydrolysis and lower aqueous solubility.

The quantitative representation of equilibrium, set up when an aqueous lanthanide, M^{3+}, reacts with a toluene solution of HDEHP may be represented as follows:

$$M^{3+} + 3(HY)_2 \rightleftharpoons M(HY_2)_3 + 3H^+ \qquad (9)$$

where $(HY)_2$ represents dimerised HDEHP.
Assuming only $M(HY_2)_3$ is extracted by the HDEHP-toluene phase, even in the presence of complexing agents like fluoride or oxalate in the aqueous phase, the distribution ratio ϕ_2 can be defined as

$$\phi_L = \frac{\{M(HY_2)_3\}_o}{\{M^{3+}\}} = k\,\frac{\{(HY)_2\}_o^3}{\{H^+\}^3} \qquad (10)$$

where k is the equilibrium constant of the reaction. From equation (10) it is evident that ϕ_L should show a direct third power dependence on (HDEHP) concentration in the organic phase and an inverse third power dependence on hydrogen-ion concentration in the aqueous phase. For constant (HDEHP) and hydrogen-ion concentrations, ϕ_L remains constant. It has previously been shown[12,13,14] that the equation above holds good for trivalent ions of lanthanides partitioning between solvents like HDEHP and aqueous perchlorate, chloride or nitrate solutions. During the course of the present investigation it was found that the above relation holds good in the presence of representative concentration of other ligands used in the course of the work described later. Thus, from preliminary experiments, HDEHP appears to be a suitable solvent.

The studies contemplated, however, require a reagent of high purity. HDEHP, as supplied by the manufacturer (Messrs. Kodak Ltd., Kirby, Lancashire, England) contained impurities such as alcohols, tri-alkyl phosphates, mono-alkyl phosphoric acid, polyphosphorous or pyrophosphorous compounds and metal contaminants. It can be free of all such impurities by a relatively easy method of purification.

Purification

Two purification procedures have been reported in the literature[15,16]. Both are essentially based on a procedure developed by Stewart and Crandel . In the present work the method of Schmitt and Blake was followed. The essential features of this method are, (a) treatment of the commercial mixture with hydrochloric acid to hydrolyse polymeric substances, (b) extraction of neutral impurities such as alcohols and tri-alkylphosphates from the sodium salt of HDEHP with petroleum ether and finally (c) liquid-liquid partition of the mono- and di-alkyl phosphoric acid between ethylene glycol and petroleum ether.

Reagents and solutions required

The experimental procedure adopted and developed during the course of the present work consisted of operations described below. Chemical substances used were of analytical reagent grade unless otherwise specified. Information pertaining to particular chemicals used has been recorded in parenthesis at relevant places in the text.

Preparation of stock solutions

(a) Background salt solution. An appropriate weight of sodium perchlorate to give an ionic strength of 0.5 or 1.0, as required, was dissolved in doubly-distilled carbon-dioxide-free water in a standard flask and the pH. adjusted to the desired value (in this case 3.60 ± 0.01) by using standard solutions of sodium hydroxide and perchloric acid. Alternatively and preferably the solution was prepared by neutralising appropriate volumes of standard sodium hydroxide and perchloric acid to give the desired ionic strength and pH. It was stored in screw-cap bottles and periodically checked for constancy of pH.

(b) Tracer solution. An adequate volume of the tracer was transferred to a standard flask and diluted with the background salt solution (a) so that two millilitres on further dilutions to twenty five millilitres gave an activity of nearly 10^4 counts per ten millilitres per minute in a G.M. liquid counter or nearly 2 x 10^4 counts per 2-5 ml. per minute in a scintillation counter. The pH. of the solution was adjusted to the required value, (3.60 ± 0.01) as usual.

(c) Ligand solution. Stock solutions of α-hydroxyisobutyrate, fluoride, sulphate and oxalate were prepared by the neutralisation of the corresponding acids in such a way that the ionic strength made up with sodiumperchlorate was 0.5 or 1.0, as desired, and the pH. 3.60 ± 0.01. α-hydroxyisobutyric acid was recrystallised twice from benzene before use. Doubly distilled carbon-dioxide-free water was used in the preparation of all the stocks.

(d) HDEHP solution. An approximately 0.5% $(\frac{v}{v})$ stock solution was prepared by diluting the purified acid with toluene. Further dilutions of the stock solution with toluene were made as required.

General method of equilibration. The distribution ratio, ϕ, of the selected lanthanide or actinide element between the two phases, HDEHP or resin, and the aqueous phase was determined by measuring the counting rate of the aqueous phase before (C_1) and after (C_2) equilibration. ϕ is then defined by the relation

$$\phi = \frac{(C_1 - C_2)v}{C_2\ m}$$

where m is the mass of the resin or the volume of the HDEHP solution and v is the volume of the aqueous phase (see page 49). In the systems containing resin, a small correction to the δ-factor is normally applied to v to account for uptake of water from the aqueous phase; it was applied in the course of this work when found necessary.

A series of aqueous solutions containing varying concentrations of the ligand of interest (α-hydroxyisobutyrate, fluoride, sulphate or oxalate), a fixed volume of the tracer solution (B) and different proportions of the medium solution (A) were prepared in such a way that each solution in the series corresponded to a particular ligand concentration and a fixed total ionic strength. The solutions were prepared in marked 25 ml. standard flasks and thoroughly mixed before equilibration.

For equilibrations with ion-exchange resin, the same volume of aqueous phase (15 ml.) from each solutions comprising the series was transferred to polythene capsules each containing the same weight of resin. The capsules were heat-sealed and attached to a rotating disc immersed in a thermostat at 25 ± 0.1°C and equilibrated for 18 to 24 hours.

In the solvent extraction procedure equilibrations were carried out in 50 ml. standard flasks instead of polythene capsules, and agitation was achieved in air at the laboratory temperature (24–25°C) by means of a mechanical shaker (Griffin flask shaker). After equilibration the phases were separated by centrifugation in both cases. For the liquid-liquid system checks were made for radioactive mass balance by measurement of the activity in both phases.

pH measurement. Measurement of pH were carried out by means of a Doran Universal pH meter, fitted with a glass calomel electrode system. In order to avoid inconvenient corrections, the calomel electrode was modified by changing the usual potassium chloride bridge for a saturated sodium chloride bridge. The meter was 'standardised' against 0.05 M potassium hydrogen phthalate.

Preliminary experimentation

Prior to the study of complex formation of the selected lanthanide or actinide element by the solvent extraction method using HDEHP, some preliminary investigations were carried out in order to establish satisfactory procedural conditions. This involved the study of partition behaviour of a chosen lanthanide between a representative aqueous phase and a toluene based HDEHP phase.

When experiments are conducted to ascertain the organic-aqueous distribution coefficient of a metal ion, it is generally desirable to determine the distribution ratio, ϕ_2, as a function of the hydrogen ion and ligand concentrations in the aqueous phase and

HDEHP in the organic phase. These investigations were carried out in the present work using cerium(III) as a metal tracer, and α-hydroxyisobutyrate as ligand. Experiments were also carried out to establish times required for the attainment of equilibrium. The possibility of a change in the concentration of ligand due to its partition in the organic phase was also investigated. The experimental details of these investigations are as follows:

Equilibrium time

In order to establish the time required for the attainment of equilibrium, partition of cerium(III) between 0.5 M sodium perchlorate containing representative amounts of desired ligand was followed as a function of time. A series of solutions, marked 1, 2, ... n, containing a fixed amount of tracer and ligand solutions and enough sodium perchlorate to give an ionic strength of 0.5 were prepared from appropriate solutions (A), (B) and (C). After thorough mixing of the components, the solutions were equilibrated for varying times, the phases separated and assayed radiometrically in the manner described (see page 49). The partition ratios obtained showed that in general equilibrium was reached within 20 minutes.

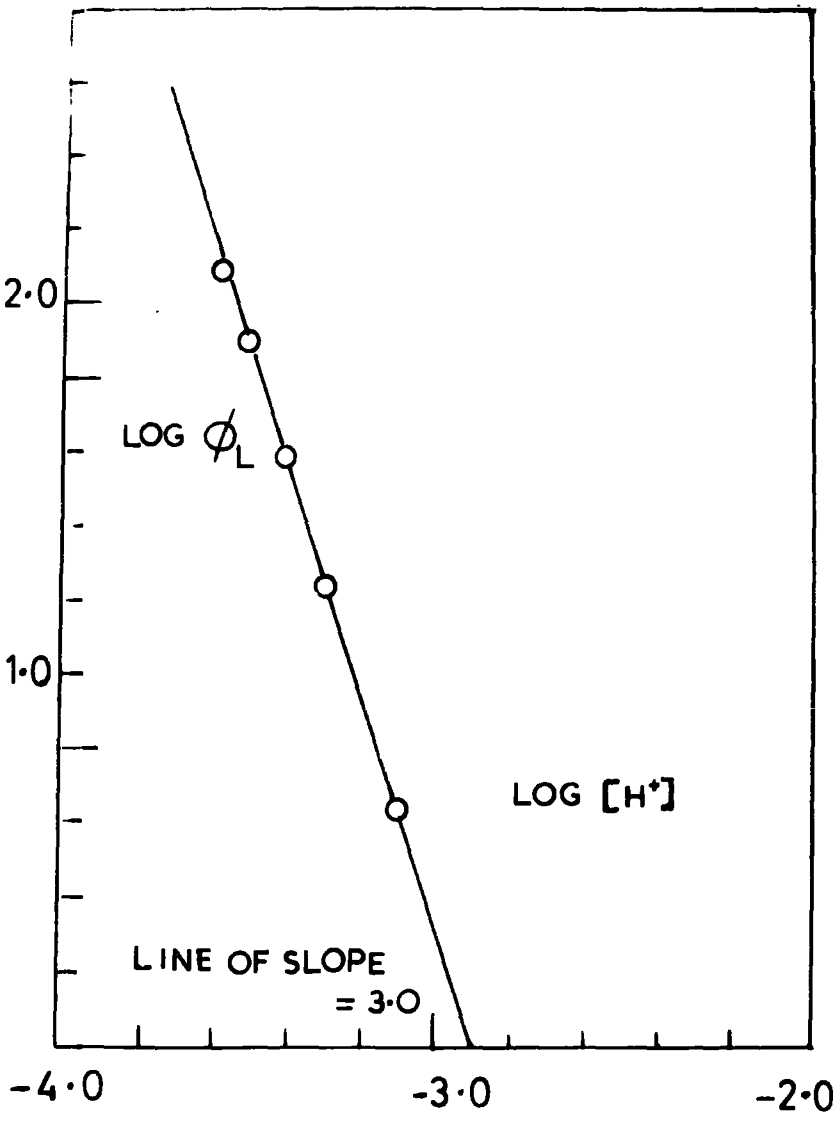

Fig II Hydrogen ion dependency of the extraction of Ce(III) into 0·5% (v/v) HDEHP (toluene) from NaClO$_4$ μ = 0·5

Effect of hydrogen ion concentration

To examine the effect of hydrogen ion concentration on ϕ_2 values, partition of cerium(III)-144 between 0.5 M sodium perchlorate and a 0.5% $(\frac{V}{V})$ HDEHP-toluene phase was followed as a function of hydrogen ion concentration in the aqueous phase. The method followed was essentially that described in the previous experiment except that each aqueous phase had a different hydrogen ion concentration, and the time of equilibration was fixed at 4 hours. The pH of each solution was measured after equilibration in order to take account of any pH change during the process of equilibration. The inverse third power dependency of ϕ_2 on hydrogen ion concentration of the aqueous phase was confirmed, (see fig. II).

'Free' ligand concentration

In order to study the change in the ligand concentration of an aqueous system due to possible partition of the ligand into the organic phase, the 'free' ligand of a representative aqueous phase was determined by a potentiometric titration method.

Three solutions, (A), (B) and (C), containing varying volumes of a standard ligand solution, a fixed volume of the tracer solution and enough of the back-ground salt to give the desired ionic strength were prepared in 25 ml. volumetric flasks. 15 ml. of each solution was mixed with an equal volume of pre-equilibrated 0.5% $(\frac{v}{v})$ HDEHP-toluene phase in 50 ml. standard flasks and equilibrated as before. The pH of each solution was measured by using the remainder of the aqueous solutions which were subsequently titrated potentiometrically under a nitrogen atmosphere, with standard sodium hydroxide. After equilibration the aqueous phases corresponding to each solution was titrated in the same way. The results obtained showed no partition of the ligand into the organic phase.

Effect of HDEHP concentration

The dependency of ϕ_{ℓ} on the HDEHP concentration in the toluene phase was examined by studying the partition of europium(III) from solutions of ionic strength 0.5 (maintained with sodium perchlorate) containing the representative concentrations of α-hydroxyisobutyrate, fluoride or oxalate ligands and HDEHP solutions of suitable concentrations in toluene.

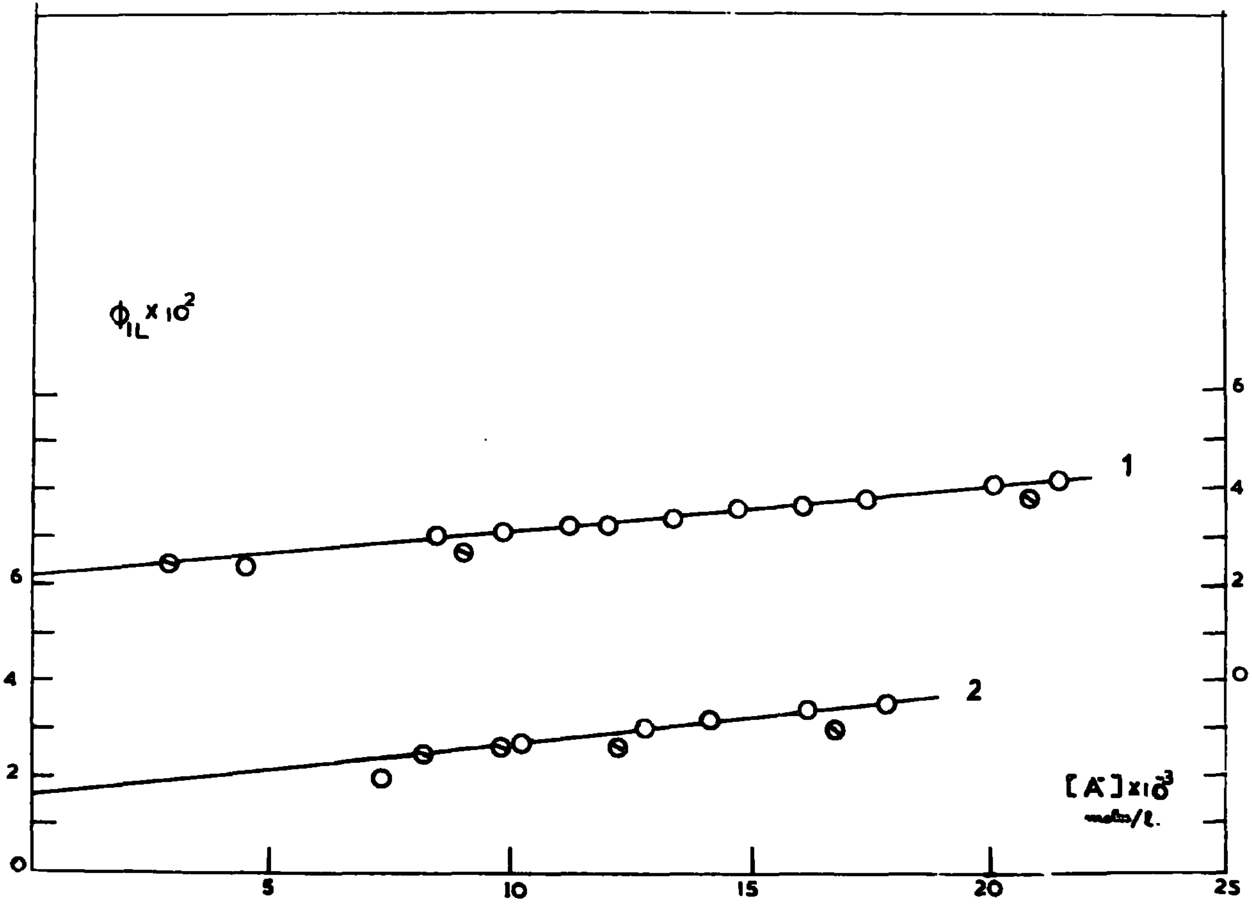

Fig III ϕ_{1} as a function of α-hydroxyisobutyrate concentration.
Curves I and 2 refer to cerium and lanthanum data respectively.
O refers to HDEHP distribution data from the present work.
⊖ refers to ion-exchange data (see text ref. 17)

The results will be discussed in chapter II along with other europium results. The effect of sulphate used as a ligand was studied using cerium-144 praesodymium-144.

Preliminary equilibrium constant measurements

Some preliminary measurements using lanthanum(III) and cerium(III) with α-hydroxyisobutyrate were carried out by the solvent extraction method described on the previous pages and the results compared with an ion-exchange study of the corresponding systems[17]. The results showed satisfactory agreement. Lanthanum-140 was isolated from barium-140 by a method due to Toshiyasu Kiba et al[18]. The comparative data are recorded in Fig.III

References - Chapter II

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CHAPTER III

THE UPTAKE OF EUROPIUM(III)-CATIONIC COMPLEXES WITH α-HYDROXY-ISO-BUTYRATE, FLUORIDE AND OXALATE LIGANDS BY A CATION-EXCHANGER

Introduction

The use of the ion-exchange method in the study of metal complexes in equilibrium systems, particularly where more than one cationic species from the solution enters the resin phase, is to be regarded with caution[1]. For, although a method of treating distribution data involving such an uptake has been developed[2], its limitations have also been increasingly realised. As pointed out in the introductory chapter of the present work, when the distribution of several partially complexed species is involved along with that of the 'free' metal ion, the relations connecting the measured quantities and equilibrium constants have to account for each distributing species in the system. Additional parameters ($\lambda_1, \lambda_2, \ldots\ldots \lambda_j$) are thus introduced into the equation defining the distribution ratio 'ϕ_R' (see Equation 42 page 35). Unfortunately, in the ion-exchange work, an independent measurement of each distribution parameter is not possible; only the 'free' metal ion may thus be examined. For the calculation of other ratios, reliance has to be made on the gross distribution data obtained for the metal ion in the presence of ligand. In doing so it is frequently necessary to apply unverified assumptions and to put undue reliance on the precision and other aspects of the experimental data. The study of an identical system by the solvent-extraction method, on the other hand, does not involve such difficulties provided the organic extractant used is selective in that it extracts only 'free' metal ions[3,4].

In the work to be described here, dilute solutions of 'HDEHP' in toluene have been used; this solvent system appears to extract only 'M^{n+}' and not '$MA^{(n-1)+}$, $MA_2^{(n-2)+}$, ……., $MA_j^{(n-j)+}$. This was the conclusion reached after suitable experiments with the limited number of systems examined in this work confirmed theoretical requirements. Keeping in view this selectivity of HDEHP a comparison can, therefore, be made with distribution obtained for the non-selective conventional cation-exchanger when a common aqueous system is studied by both the methods under identical aqueous phase conditions. This leads to a more direct measure of the uptake of partially complexed species by the cation-exchanger.

A new method based on the above principles was thus evolved for the study of the partition of partially complexed metal species by a cation-exchanger. This forms the subject matter for discussion in this chapter. The metal ion chosen in the experimental work was europium(III), and its interactions with α-hydroxy-iso-butyrate, fluoride and oxalate ligands were examined at a constant ionic strength of 0.5. Experimental data has been obtained on the potential use of this phosphoric acid in determining equilibrium constants and on the partition of europium partially complexed species between a cation-exchanger and an external aqueous phase.

Theory

Consider a system consisting of an aqueous phase containing metal cations, M^{n+}, $MA^{(n-1)+}$, ... $MA_j^{(n-j)+}$ (where M and A are the metal ion and the ligand respectively) and a HDEHP-toluene phase. Then, following the extraction mechanism of a trivalent metal by the HDEHP-toluene phase described before (see page 58), one can write the following general expression

$$M^{n+} + n(HY)_2 \rightleftharpoons M(HY_2)_n + n(H^+)$$

If the assumption that only $M(HY_2)_n$ distributes into the organic phase is true even in the presence of complex forming ligands in the aqueous phase, then

$$\phi = \frac{[M(HY_2)_n]_L}{[M^{n+}]_{aq}} = k\ \frac{[(MY_2)]_L^n}{[H^+]_{aq}^n}$$

where k is the equilibrium constant of the above reaction and subscript 'L' and 'aq' represent organic and aqueous phases respectively. ϕ should then show a direct n^th power dependence on HDEHP concentration in the toluene phase and an inverse n^th power dependence on hydrogen ion concentration in the aqueous phase. In the absence of a ligand derived from a weak acid the dependence on hydrogen ion can readily be checked. The dependence on HDEHP concentration in toluene must, however, be checked in the presence of ligands contemplated for the present equilibrium study. This has already been done[4] in the case of certain lanthanide and actinide elements partitioning between aqueous perchlorate, chloride or nitrate solutions and

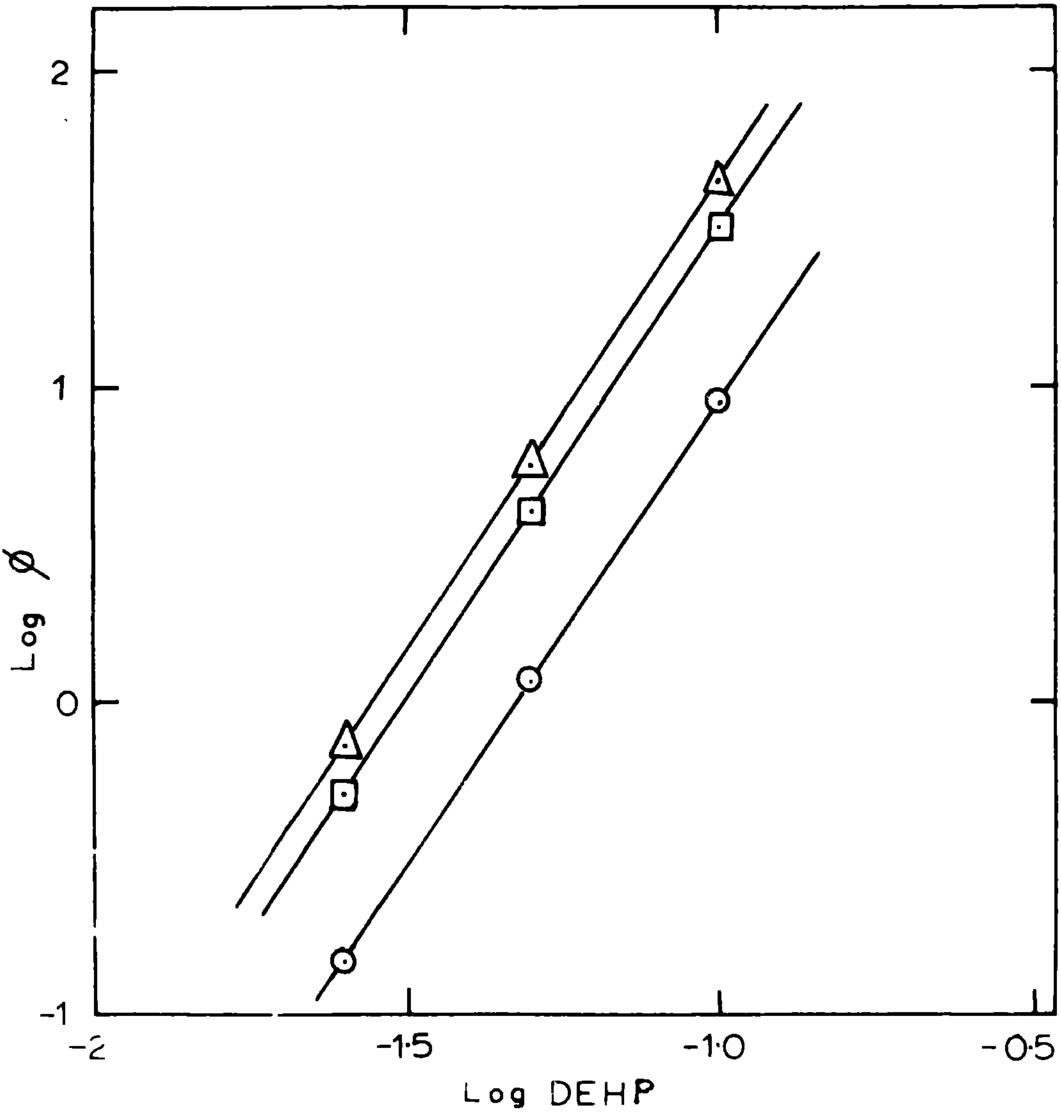

Fig. IV. The distribution, φ , of europium between an aqueous phase of ionic strength 0.5 containing ligand(I.7I X IO^{-4} M oxalate [△] I.49 X IO^{-3} M fluoride [□] , or I.29 X IO^{-2} M α-hydroxyisobutyrate [⊙] as a function of HDEHP concentration.

dilute solutions of HDEHP-like solvent systems.

In the course of the work described here it was found (see Fig.IV) that in the presence of constant and representative concentrations of each of the ligands used the third power dependence on HDEHP holds good within the limits of experimental error. Thus, it may be concluded (cf. page 58) that in the case of europium(III) only $Eu(HY_2)_3$ extracts into the toluene phase and europium complex by α-hydroxy-iso-butyrate, fluoride or oxalate does not partition. Applying this condition in general then

$$\phi_L = \lambda o/(1+\sum_1^j \beta_j (A^-)^j$$

Rearrangement of this relation gives

$$\phi_{1L} = \sum_1^j \beta_j (A^-)^{(j-1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

In the case of ion-exchange systems the species M^{n+}, $MA^{(n-1)+}$, ... $MA_j^{(n-j)+}$ may all, at least in principle, partition into the resin phase. The corresponding expression for ion-exchange systems will be

$$\phi_{1R} = \sum_1^j(\beta_j - \lambda_j^{'})(A^-)^{(j-1)}/(1 + \sum_1^j\lambda_j^{'}(A^-)^j) \ldots\ldots\ldots (2)$$

where $\lambda_j^{'} = \beta_j \frac{\lambda j}{\lambda^o}$

From equations (1) and (2) for $\lambda_j^{'} \geqslant o$, $\phi_{1L} \geqslant \phi_{1R}$ it follows that

$$(\phi_{1L}-\phi_{1R})(1 + \sum_1^j\lambda_j^{'}(A^-)^j) = (\sum_1^j\beta_j(A^-)^{(j-1)}(1 + \sum_1^j\lambda_j^{'}(A^-)^j) - \{\sum_1^j (\beta_j - \lambda_j^{'})(A^-)^{(j-1)}\} \ldots\ldots\ldots (3)$$

Rearranging equation (3) we have

$$(\phi_{1L} - \phi_{1R}) + (\phi_{1L} - \phi_{1R})(\sum_1^j\lambda_j^{'}(A^-)^j) = (1 + \sum_1^j\beta_j(A^-)^j)(\sum_1^j\lambda_j^{'}(A^-)^{(j-1)}) \ldots\ldots\ldots (4)$$

or $$\sum_1^j\lambda_j^{'}(A^-)^{(j-1)} = (\phi_{1L} - \phi_{1R})/\{(1 + \sum_1^j\beta_j(A^-)^j) - (\phi_{1L} - \phi_{1R})(A^-)\} \ldots\ldots\ldots (5)$$

From equation (1) we have $\phi_{1L} = \sum_1^j\beta_j(A^-)^{(j-1)}$ and substituting for ϕ_{1L} in (5) gives

$$\sum_1^j\lambda_j^{'} (A^-)^{(j-1)} = (\phi_{1L}-\phi_{1R})/(1 + \sum_1^j\beta_j(A^-)^j) - \{\sum_1^j\beta_j(A^-)^j - \phi_{1R}(A^-)\} \ldots\ldots\ldots (6)$$

Rearrangement of (6) thus gives

$$\sum_{1}^{j}\lambda_j'(A^-)^{(j-1)} = (\phi_{1L} - \phi_{1R})/(1 + \phi_{1R}(A^-)) \; ..... \qquad (7)$$

Thus λ_j' values may be computed directly from the equation (7). From appropriate values of β and $\overset{o}{\lambda}$ obtained for the ion-exchange resin, λ values are then calculated from the relation

$$\lambda_j = \frac{\lambda_0 \times \lambda_j'}{\beta_j} \qquad (7a)$$

Experimental

A general outline of the experimental procedure has been described in chapter II. In the present measurements similar procedures were adapted. More specific information concerning the measurements are given where relevant.

Radioactive tracer. An isotopic mixture of europium-152 and 154 having a high specific activity was obtained from the Radiochemical Centre, Amersham, England. It was dissolved in 1M hydrochloric acid. A solution in perchlorate of ionic strength 0.5 and pH. 3.60 was prepared in the manner described before. Two ml. of this solution after dilution to 25 ml. and 5 ml. counted in a well-type γ-scintillation counter had a counting rate of about 2 x 10^4 counts per minute. It was about 10^{-7} M in europium.

Ligand solutions. Separate stock solutions of α-hydroxy-iso-butyrate, fluoride and oxalate were prepared as described before (see page 61). Concentrations of total ligand species were 0.5000, 0.2000 and 0.01292 M in that order. As required, the ligand stock solutions were diluted with 0.5 M sodium perchlorate solution of pH. 3.60. α-hydroxy-iso-butyrate was kindly provided by A.E.R.E. Harwell, England.

di-(2-ethylhexyl)orthophosphoric acid. This reagent was obtained from Messrs. Kodak Ltd., Kirby, Lancashire. It was purified before use. Stock solutions of 0.025% and 0.04% $(\frac{V}{V})$ HDEHP concentrations were prepared by diluting the purified acid with toluene. Before the distribution measurements the diluted solutions were pre-equilibrated with equal volumes of 0.5 M sodium perchlorate solutions of pH. 3.60.

Ion-exchange resin. The resin, Zeo-Karb-225 (SRC15), 'Chromatographic Grade', 100-200 mesh having a nominal 8% cross-linking was obtained from The Permutit Company Ltd., London. Its treatment has been described in the general method (see page 55). The exchange capacity was 4.03 m equiv/g.

The methods of equilibrations and radioactive assay were similar to those described in chapter II. The pK values of α-hydroxyisobutyric acid and monohydrogen oxalate appropriate to the electrode system (cf. chapter II) at 25°C and ionic strength 0.5 were determined and checked over the ligand concentration ranges covered in the distribution studies. They were found to be constant at 3.61 and 3.51 respectively. For hydrofluoric acid the pK value of 2.91 taken from the literature[5] was found to be appropriate to this electrode system. A summary of pK values used in this work is given in Table I for convenient reference.

Treatment of data

α-hydroxy-iso-butyrate system. The results for the europium(III) α-hydroxy-iso-butyrate system obtained by the solvent-extraction and ion-exchange methods are recorded in Table 2. Using equation (7), the function

TABLE I

Measured 'dissociation' constants for the ligand systems used.

No.	Acid	Ionic strength of the medium	pK	Reference
1	α-hydroxy-iso-butyric	0.5000	3.61	p.w. 5
2	"	1.000	3.52	p.w.
3	Mono-hydrogen oxalate	0.5000	3.51	p.w.
4	Mono-hydrogen sulphate	0.5000	1.08	p.w. 6
5	Hydrofluoric	0.5000	2.91	p.w. 7

p.w. refers to the present work.

TABLE II - Cation-exchange and DEHP distribution data for the europium-α-hydroxy-isobutyrate system

$[A^-]\times10^{3}$ (mole/l.)	$\phi_{1R}\times10^{-3}$ (l./mole)	$\phi_{1L}\times10^{-3}$ (l./mole)	$\frac{\phi_{1L}-\phi_{1R}}{1+\phi_{1R}[A^-]}$ (l./mole)	$f\times10^{-5}$ ($l^2/mole^2$)	$\frac{\Delta f}{\Delta\phi_{1R}}$ (l./mole)	$g\times10^{7}$ ($l^3/mole^3$)
1.011	-	0.6421*	-	-	-	-
1.816	0.6196	-	-	2.44	-	7.10
2.528	-	0.8693*	-	-	-	-
3.633	0.7833	-	-	3.14	544	7.65
4.942	-	1.276*	-	-	-	-
5.056	-	1.162*	-	-	-	-
5.449	0.9363	-	-	3.87	520	8.86
7.265	1.033	-	-	4.43	531	9.87
7.908	-	1.670*	-	-	-	-
9.425	1.282	(1.867)	44.7	5.57	508	12.03
9.884	(1.310)	1.929*	44.4	-	-	-
11.86	(1.498)	2.211*	38.0	-	-	-
12.25	1.534	(2.265)	36.9	6.83	506	14.40
12.36	(1.548)	2.280	36.4	-	-	-
12.85	(1.620)	2.501*	40.4	-	-	-
14.83	(1.896)	2.729	28.6	-	-	-
15.08	1.936	(2.815)	29.1	8.73	497	19.00
15.82	(2.003)	3.079	32.9	-	-	-
17.30	(2.138)	3.398	33.2	-	-	-
18.68	2.267	(3.895)	37.6	10.39	497	21.20

TABLE II - continued

$[A^-]\mathrm{x}10^3$ (mole/l.)	$\phi_{1R}\mathrm{x}10^{-3}$ (l./mole)	$\phi_{1L}\mathrm{x}10^{-3}$ (l./mole)	$\frac{\phi_{1L}-\phi_{1R}}{1+\phi_{1R}[A^-]}$ (l./mole)	$f\mathrm{x}10^{-5}$ (l^2/$mole^2$)	$\frac{\Delta f}{\Delta\phi_{1R}}$ (l./mole)	$g\mathrm{x}10^7$ (l^3/$mole^3$)
18.77	(2.268)	3.929	38.1	-	-	-
19.77	(2.317)	4.097	38.0	-	-	-
21.75	2.414	(4.220)	33.8	11.19	501	22.63
22.24	(2.493)	4.252	31.2	-	-	-
24.71	2.902	5.685	38.3	13.56	498	27.23
27.68	3.393	-	-	15.96	486	31.78
30.64	3.917	-	-	18.47	494	36.65

* Distributions with approximately 0.025% (V/V) DEHP for which $k_0 = 7.701$; the remainder were got using approximately 0.04% DEHP, $k_0 = 37.11$ $\phi^\circ_{1R} = 500$ and $f^\circ = 1.6 \times 10^5$ were used in the calculations. ϕ_1 in parentheses were obtained by interpolation.

$\dfrac{'\phi_{1L} - \phi_{1R}'}{1 + \phi_{1R}(A^-)}$ has been calculated from these data and found to be approximately constant over the range of distributions where the difference $(\phi_{1L} - \phi_{1R})$ takes reasonably reliable numerical values. A mean value for λ'_1 obtained is (36.4 ± 1.1, Where the data did not permit direct use of ϕ_{1L} and corresponding ϕ_{1R} calculated from experimental distribution ratios, graphically interpolated ϕ_1 were used. From the data obtained for the solvent-extraction system, calculations of equilibrium constants by the application of equation (1) gives $\beta_1 = 520$. A least squares treatment then gives $\beta_2 = (1.2 \pm 0.1) \times 10^5$ and $\beta_3 = (2.5 \pm 0.4) \times 10^6$. This involved the assumption that $\left(\dfrac{\phi_1 L - \beta_1}{(A^-)}\right)$ is a linear function of (A^-). Reiteration using β_2 and β_3 to calculate a new β_1 value has been suggested in the literature[8], but it does not lead to an improvement nor does a least squares treatment taking three parameters in equation (1) and dispensing with the preliminary extrapolation.

The ion-exchange data were treated in the manner prescribed by Fronaeus[2] and others[9,10]. Following the equations derived in chapter I, ϕ_{1R} were plotted against corresponding (A^-) values and then ϕ_{1R} extrapolated to

A = o. This gives $\phi_{1R}^{o} = \beta_1 - \lambda_1'$ (see equation 48 page 36). From the relation $\phi_{1R}^{o} = \beta_1 - \lambda_1'$, another function '$f$' given by

$$f = \frac{\lambda\overset{o}{\phi}{}^{-1}[(\beta_1 \ -\lambda_1')(A^-)-1] + 1}{[A^-]^2} \tag{8}$$

was calculated (see for example equation 50 chapter I). It can be shown that

$$f = \frac{1^o/\phi^{-1}[((\beta_1-\lambda_1')(A^-)-1] + 1}{[A^-]^2} = \beta_1\phi_{1R} - x_2 + \lambda_2'\lambda_0\phi^{-1}\ldots \tag{9a}$$

where $x_a = (\beta a + \beta(a + 1)(A^-) + \beta(a + 2)(A^-)^2 + \ldots\ldots)$

Extrapolation of f plotted against (A^-) to $(A^-) = o$ gives f^o where

$$f^o = \beta_1\phi_{1R}^{o} - \beta_2 - \lambda_2' \tag{9b}$$

Then from the relation $\Delta f = f - f^o$ and $\Delta\phi_{1R} = \phi_{1R} - \phi_{1R}^{o}$ it follows that

$$\frac{\Delta f}{[A^{n-}]} = \beta_1\frac{\Delta\phi_{1R}}{[A^-]} + \phi_1(\lambda_2' + \lambda_3'(A^-)) + \lambda_3' - x_3 \tag{10a}$$

or rearranging

$$\beta_1 = \frac{\Delta f}{\Delta\phi_{1R}} + \frac{[A^-]}{\Delta\phi_{1R}}\left[x_3 - \phi_{1R}\lambda_2' + \lambda_3'\left(\frac{\lambda o}{\phi_R} - 2\right)\right] \tag{10b}$$

As pointed out before (cf. chapter I) a rough working measure of β_1 can be obtained from equation (10b) directly by calculating the quantity $\frac{\Delta f}{\Delta \phi_{1_R}}$ provided the values remain reasonably constant. This implies that the remaining terms in equation (10b) are negligible. Consideration of equation (10a) suggests that if a straight line plot can be obtained between $\frac{\Delta f}{[A^-]}$ and $\frac{\Delta \phi_{1_R}}{[A^-]}$ then the remaining terms in equation (10a) may be neglected and β_1 may, therefore, be obtained as the slope of the line. This, unfortunately, is a difficult test to apply, for in most distribution studies, including those described here, the data obtained are so bunched together that a linear plot is seldom obtained. In view of this, the α-hydroxyisobutyrate data obtained in this work were treated on the basis of equation (10b). Where Δf and $\Delta \phi_{1_R}$ were sufficiently large compared to f^o and $\phi_{1_R}^o$ good constancy was obtained for the rates (see Table II) and the mean (508 ± 5) was taken to be β_1.

For the calculation of β_2 and β_3, application of equation (56) page(58) was made. The function 'g' was found to be linear in ϕ_{1_R} and a least squares treatment gave the slope, $\beta_2 = (9.3 \pm 0.1) \times 10^4$. As is frequently the case the intercept lies close to the origin making the calculation of β_3 doubtful. According to Fronaeus[11] an estimate of λ_2' can be obtained from the relation

$$\frac{\beta_1{}^2}{\beta_2} = \frac{(\lambda_1')^2}{\lambda_2'} \qquad (11)$$

Taking the values for β_1 and β_2 from ion-exchange data and that for $\lambda_1' = 36.4$ from equation (7) gave $\lambda_2' = 4.8 \times 10^2$ from (11). In order to obtain β_3 equation (9a) was tried, and inclusion of the $\lambda_2\lambda_0\phi_R{}^{-1}$ term which was of the same order of magnitude as $(\beta_1\phi_{1_R} - f)$ lead to a sensibly constant value for $x_2 = (8.4 \pm 0.2) \times 10^4$ which was equated with β_2. It was therefore concluded that a meaningful estimate of β_3 could not be obtained from the ion-exchange data.

Since β_1 was calculated by ignoring all but one of the terms in equation (10b) it is of interest to estimate numerically the size of those remaining. Taking $x_3 = \beta_3 = 2.5 \times 10^6$ (from the DEHP data), $\lambda_2' = 4.8 \times 10^2$ and $\lambda_3' = 9.2 \times 10^2$ (obtained by the method leading to λ_2') values ranging from 6 to 28 were obtained. It is therefore not unreasonable in the present instance to ignore those terms particularly having regard to the constancy of $\frac{\Delta f}{\Delta \phi_{1R}}$ and the numerical uncertainty in the β_3, λ_2' and λ_3' data.

The fluoride system. The results obtained for this system are recorded in Table III. Experimentally derived and where required interpolated data were used. The β_1 and β_2 values for this system were obtained from HDEHP data directly by means of equation (1). From the plot of ϕ_{1L} against (A^-) and assuming that ϕ_{1L} was linear in (A^-) two complex fluoroeuropeum ions predominated and a least squares treatment gave $\beta_1 = (2.48 \pm 0.10) \times 10^3$ and $\beta_2 = (3.01 \pm 0.12) \times 10^6$. Both sets of data lead to $\lambda_1' = (4.94 \pm 0.22) \times 10^2$ and $\lambda_2' = (1.26 \pm 0.26) \times 10^5$ by equation (7). In view of such large numerical values for λ_1' and λ_2' relative to β_1 and β_2, consideration of equation (2) showed that it was somewhat fortuitous for ϕ_{1R} to appear to be a linear function of (A^-), (see fig. 5). It was therefore thought that extrapolation of the experimentally derived ϕ_{1R} plotted against (A^-) to $A = o$ would not be justified. Taking β_1 and β_2 from the HDEHP data and using equation (2) to calculate ϕ_{1R} for selected values of (A^-) it was found that the values for ϕ_{1R} turned downwards with

TABLE III - Cation exchange and DEHP distribution data for the europium-fluoride system.

$[A^-] \times 10^4$ (mole/l.)	$\phi_{1R} \times 10^{-3}$ (l./mole)	$\phi_{1L} \times 10^{-3}$ (l./mole)	$\frac{\phi_{1L}-\phi_{1R}}{1+\phi_{1R}[A^-]}$ (l./mole)	$f \times 10^{-6}$ ($l^2/mole^2$)	$\frac{\Delta f}{\Delta\phi_{1R}} \times 10^{-3}$ (l./mole)	$\beta_1 \times 10^{-3}$ (l./mole)
2.905	2.569	-	-	3.119	-	-
3.334	(2.585)	3.528	5.06	-	-	-
4.066	2.613	(3.720)	5.37	3.668	2.677	2.463
4.357	(2.627)	3.799	5.46	-	-	-
5.224	2.672	(4.036)	5.69	4.020	2.961	2.703
5.602	(2.691)	4.141	5.78	-	-	-
7.133	2.772	(4.498)	5.80	4.419	3.093	2.774
7.470	(2.801)	4.579	5.75	-	-	-
8.320	2.880	(4.997)	6.23	4.661	2.989	2.549
8.715	(2.903)	5.193	6.49	-	-	-
9.291	2.941	(5.346)	6.44	4.828	2.973	2.611
9.960	(2.986)	5.529	6.40	-	-	-
10.46	3.022	(5.596)	6.19	5.026	2.932	2.546
11.21	(3.074)	5.702	5.91	-	-	-
11.62	3.103	(5.903)	6.08	5.216	2.889	2.481
12.45	(3.116)	6.318	6.56	-	-	-
12.78	3.121	-	-	5.325	2.940	2.497

The approximately 0.025% ($^V/_V$) DEHP used had $k_0 = 8.209$.
$\phi^o_{1R} = 1.99 \times 10^3$ and $f^o = 2.00 \times 10^6$ were used in the calculations.
Interpolated data are given in parentheses.

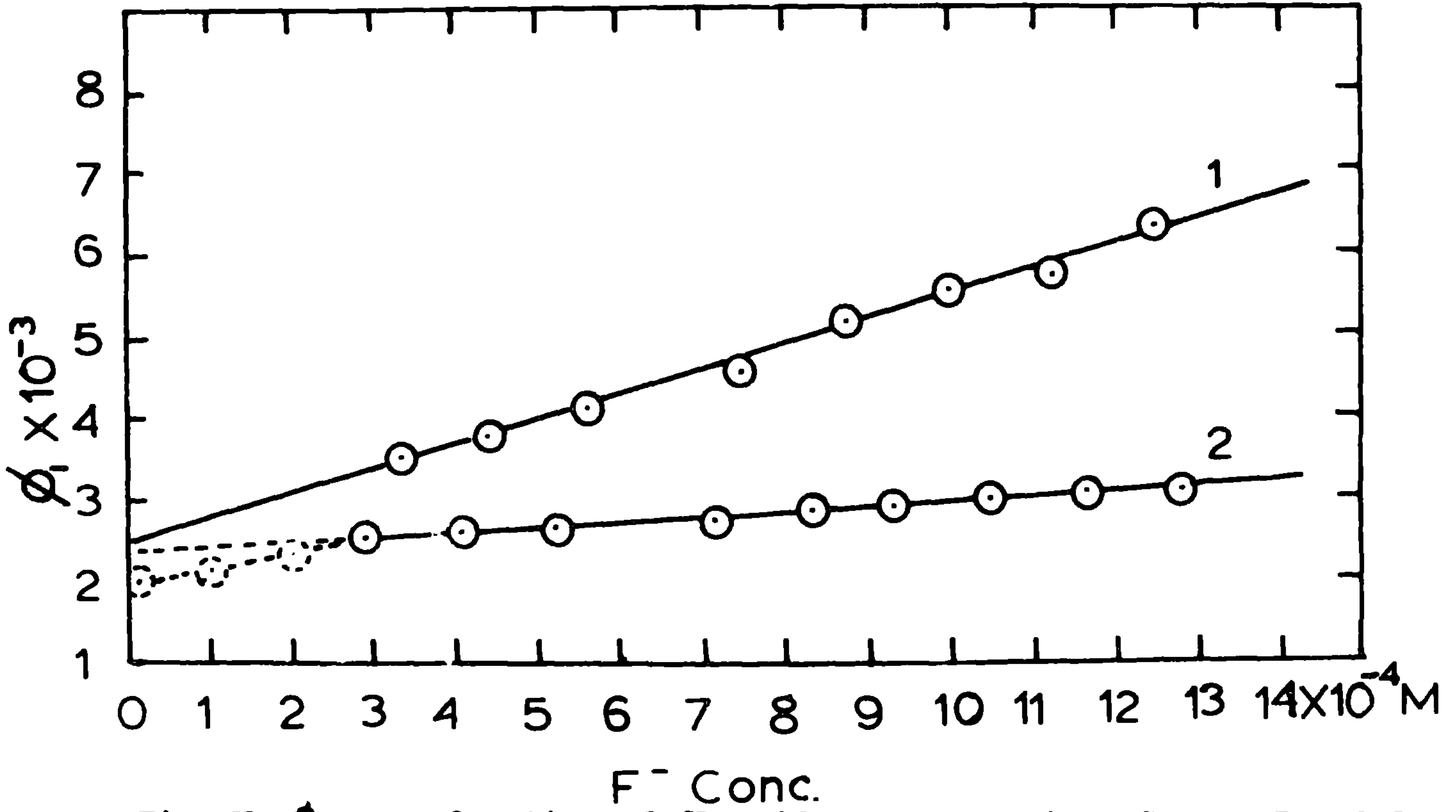

Fig. V. ϕ_1 as a function of fluoride concentration. Curves I and 2 refer to HDEHP and ion-exchange distribution respectively. Points enclosed by broken circles are calculated from Equation (see text) decreasing (A^-) reaching a limiting value around $\phi_{1R}^{o} = 1.99 \times 10^3$ (broken line, Fig.V). A linear extrapolation (by least squares) of the experimental data gave $\phi_{1R}^{o} = (2.37 \pm 0.06) \times 10^3$. With $\phi_{1R}^{o} = 1.99 \times 10^3$, $\frac{\Delta f}{\Delta\phi_{1R}}$ was calculated and when corrected individually for the

$$\frac{(A^-)}{\Delta\phi_{1R}^{-1}} \quad \phi_{1R}\lambda_2'$$

contribution (equation 10b), the β_1 values recorded in column 7 of the table were obtained. These lead to a mean $\beta_1 = (2.58 \pm 0.04) \times 10^3$ and equation (9b) then gave $\beta_2 = 3.0 \times 10^6$. Both β_1 and β_2 values were thus in good agreement with those derived from the HDEHP data alone.

A least squares treatment applied to the experimentally obtained ion-exchange data ignoring the distribution of partially complexed species gave $\beta_1 = (2.37 \pm 0.06) \times 10^3$ and $\beta_2 = (6.07 \pm 0.23) \times 10^5$. β_1 thus appeared to be in reasonable agreement and β_2 in poor agreement with corresponding values from HDEHP data. For the fluoride system good agreements between the values of the ratio $\frac{(\lambda_1')^2}{\lambda_2'}$ derived from equation (12) and directly from λ_1' and λ_2' was obtained. They were 2.04 and 1.94 respectively.

The oxalate system. Experimentally derived data for this system are recorded in Table III. Assuming that only two oxalato-europium complexes are formed under the experimental conditions employed, a least squares treatment of the data obtained by the solvent-extraction method gives $\beta_1 = (7.30 \pm 0.49) \times 10^4$ and $\beta_2 = (4.68 \pm 0.17) \times 10^8$. The comparative ion-exchange and HDEHP data for this system suggest that there is little,if any, real discernible difference (see Table III) between corresponding ϕ_1 values obtained from the two methods. It was concluded therefore that the partition of monoxalatoeuropium ions between the resin and the aqueous phases was negligible. A least squares treatment performed on the ion-exchange data gave $\beta_1 = (7.26 \pm 0.53) \times 10^4$ and $\beta_2 = (4.51 \pm 0.19) \times 10^8$.

It is seen from the table that for selected ligand values replicate ϕ_1 values were obtained and recorded accordingly. In the calculation mean ϕ_{1R} were used where replicate values exist. On the strength of the above assumption equation (10a) for this case reduces to $\beta_1 = \frac{\Delta f}{\Delta\phi_{1R}}$. A mean of $\frac{\Delta f}{\Delta\phi_{1R}}$ values thus leads to $\beta_1 = (7.37 \pm 0.02) \times 10^4$. It thus follows that $\beta_2 = 4.90 \times 10^8$ from equation (9b). In addition, the relation $f = \beta_1 \phi_{1_R} - \beta_2$ (from equation (9)) yields $\beta_1 = (7.30 \pm 0.01) \times 10^4$ and $\beta_2 = (4.45 \pm 0.03) \times 10^8$.

It may be concluded that in general the assumptions made in calculating parameters for the systems are reasonable since they lead to internal consistency in the calculated equilibrium constants. Further discussion of the results obtained is deferred to chapter VI.

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CHAPTER IV

THE STUDY OF THE COMPLEXES OF CERIUM(III) AND GADOLINIUM(III) WITH FLUORIDE, α-HYDROXY-ISO-BUTYRATE, SULPHATE AND OXALATE LIGANDS.

Introduction

The complexes of cerium(III) with fluoride, α-hydroxy-iso-butyrate and sulphate, and of gadolinium(III) with fluoride, sulphate and oxalate ligands have been studied by cation-exchange and separately by solvent-extraction methods under the same conditions as those used for similar studies involving these ligands and europium(III). The distribution coefficients for partially complexed species were thereby determined and equilibrium constants for the complexes formed were computed and various tests applied to the method of computation from ion-exchange distribution data. The present work is therefore an extension of the studies made with europium(III) in order to substantiate the results obtained previously for the uptake of partially complexed species of trivalent lanthanides by a cation-exchanger. In the course of the studies with europium(III) it was found that the order of the distribution of europium(III) species between the resin and the external aqueous phase was $Eu^{3+} > EuA^{(3-j)+} > EuA_2^{(3-2j)+}$ with differences in the ratios of successive distribution coefficients depending markedly on A^{j-}. It was, for instance, found that in the case of oxalate which carries two negative charges the absorption of $Eu(C_2O_4)^+$ was negligible compared to corresponding complex species involving fluoride or α-hydroxy-iso-butyrate ligands. It was thought desirable to supplement this observation; sulphate was chosen because of its importance in rare earth chemistry. Also in the case of cerium a much wider range of the ligand α-hydroxy-iso-butyrate was investigated in order to get information on MA_2^+ and MA_3 distributions; to facilitate this particular study a higher ionic strength (1.00) was used.

Experimental

The tracers used for the investigations described in the present chapter were cerium-144/praesodymium-144 and gadolinium-153 respectively. The experimental procedures adapted for equilibrations were essentially those used for europium (cf. Chapter III). The counting was done using an annular type G-M liquid counter (cerium-144/praesodymium) and a well type γ-scintillation counter (gadolinium). For the preparation of stock solutions of sulphate ligand, calculated amounts of standardised sulphuric acid were neutral~~l~~ized by standard sodium hydroxide in such a way that the ionic strength made up with sodium perchlorate was 0.5 and the pH 3.60. Neutral~~l~~ized sodium perchlorate solution was used throughout. For the monohydrogen sulphate ion a pK value of 1.08 taken from the literature[1] was found to be appropriate to this electrode system. pK for α-hydroxy-iso-butyric acid for an ionic strength of 1.0 in sodium perchlorate was determined and found to be 3.52. Experimental data are recorded in Table 1.

Experimental data and its treatment

Sulphate system. In order to investigate the sulphate complexes of cerium and gadolinium by the solvent-extraction method using HDEHP, dependence of M(III) extraction as a function of HDEHP concentration in the toluene phase in the presence of a constant and representative concentration of sulphate ligand in the aqueous phase was examined at constant pH (3.60). The expected third power dependence was observed as is deduced from the results contained in Table I(a). Since similar studies with europium(III) involving fluoride, α-hydroxy-iso-butyrate and oxalate ligands had shown a third power dependence (cf. Chapter III), thereby suggesting that only species of the form $Eu(HY_2)_3$ were extracted by the organic phase, it was assumed that gadolinium and cerium would show similar behaviour in the presence of these ligands.

The experimental data obtained for cerium(III) and gadolinium(III) sulphate complexes by ion-exchange and separately by the solvent-extraction method are recorded in Tables 2 and 3. The values of '$\phi_{,L}$' and '$\phi_{,R}$' plotted against corresponding values of $[A^-]$ give curves to which straight lines are readily fitted. Furthermore, for cerium(III) the data obtained separately by ion-exchange and solvent-extraction methods appear to be coincidental. It may be, therefore, concluded that distribution of monosulphate species in the ion-exchange resin system is negligible, under the experimental conditions used. Least squares treatments of the two sets of data separately, assuming the presence of $[Ce(SO_4)]^+$, $[Ce(SO_4)_2^-]$, as carried out for the europium oxalate system (cf. Chapter III), yields directly the β_1 and β_2 reported in Table 4, together with the corresponding errors.

In the case of gadolinium(III), again both sets of data may be represented by straight line curves suggesting the presence of two complex ions. In this case, however, there is a divergence of the curves with increasing ligand

TABLE 1 - Data for pK determination of α-hydroxy-iso-butyric acid in one molar sodium perchlorate solution

No.	Amount of acid g.	Concentration of alkali (sodium hydroxide) x10^2 mole/l.	Amount of sodium perchlorate g.	Total volume ml.	Free ligand concentration m.mole/l.	pH at equilibrium	Calculated pK values
1	0.0546	1.042	30.58	25.00	1.042	3.71	3.54
2	0.1061	2.028	30.55	"	2.028	3.64	3.52
3	0.1201	2.224	6.054	"	11.12	3.51	3.52
4	0.1794	3.423	6.018	"	17.11	3.55	3.52
5	0.2207	4.396	5.988	"	21.97	3.52	3.52
6	0.2663	5.106	2.905	"	51.06	3.52	3.52
7	0.5240	10.06	2.754	"	100.6	3.52	3.52
8	0.7939	15.25	2.594	"	152.5	3.52	3.52

A pK value of 3.52 for α-hydroxy-iso-butyric acid for μ = 1.0 (sodium perchlorate) was chosen.

TABLE 1(a) - K_D dependence on (HDEHP) concentration in toluene in the presence of 8.4×10^{-2} mole/1. sulphate in the aqueous phase of $\mu = 0.500$ and pH 3.60.

No.	(HDEHP) % ($^v/_v$) x10^2	K_D	K_D normalised	$\dfrac{(K_D - K_D^{=})}{\sigma}$
1	1.000	0.2220	0.2220	0.000
2	2.000	1.768	1.776	0.008
3	3.000	5.98	5.994	0.010
4	4.000	14.19	14.21	0.017

TABLE 2 - Cation-exchange and HDEHP data for the cerium-sulphate system

No.	$[A^{2-}] \times 10^{2}$ (mole/l.)	$\phi_{1R} \times 10^{-2}$ (l./mole)	$\phi_{1L} \times 10^{-2}$ (l./mole)
1	0.4080	0.8700	
2	1.224	1.022	0.9410
3	1.632	1.007	0.9910
4	2.040	-	1.029
5	2.448	1.058	1.017
6	2.856	1.078	-
7	3.264	1.068	0.9870
8	3.672	-	1.142
9	4.080	1.160	1.164
10	4.896	1.249	1.302 (1.330)
11	5.712	1.268	1.436
12	6.528	1.373	1.417
13	7.344	-	1.386
14	7.752	-	1.498
15	8.160	1.400	1.510
16	8.568	-	1.610
17	8.976	1.513	1.532
~~18~~	~~9.792~~	~~-~~	~~1.421~~

ϕ_{1L} were obtained using approximately 0.125% $(\frac{v}{v})$ HDEHP and ϕ_{1R} using 0.1000 g. of 8% (DVB) 100 - 200 mesh Zeo-Karb (SRC 15) resin for which $\lambda^{o} = 49.99\overset{150}{\times}$ at $\mu = 0.5$ ($NaClO_4$) and pH 3.60.

TABLE 3 - Cation-exchange and HDEHP data for the gadolinium sulphate system

No.	$[A^-] \times 10^2$ (mole/l.)	$\phi_{1R} \times 10^{-2}$ (l./mole)	$\phi_{1L} \times 10^{-2}$ (l./mole)	$\left[\frac{\phi_{1L} - \phi_{1R}}{1+\phi_{1R}[A^-]}\right]$ (l./mole)
1	0.8160	0.8430		
2	1.224		0.9607	
3	1.632	0.9001	0.9630	
4	2.448	1.005	1.070	
5	2.856		1.113	
6	3.264	1.047		
7	3.672		1.119	
8	4.080	1.055	1.129	
9	4.896	1.130	1.186	
10	5.712	1.187	1.424	3.05
11	6.528	1.268	1.507	2.58
12	7.344	1.321	1.529	1.94
13	8.160	1.359	1.579	1.82
			1.542	1.51
14	8.976	1.397	1.745	2.58
15	9.792	1.499		

ϕ_{1L} were obtained using approximately 0.025% ($\frac{v}{v}$) HDEHP and ϕ_{1R} using 0.1000 g. of 8% (DVB) 100 - 200 mesh Zeo-Karb-225 (SRC 15) resin at $\mu = 0.5$ ($NaClO_4$) and pH. 3.60.

TABLE 4 - Equilibrium constants for cerium and gadolinium sulphate complexes as calculated from the data obtained by cation-exchange and solvent-extraction partition.

Metal	Ligand	Method	Temp.	Ionic strength	β_1	β_2	λ'_1	λ'_2
Ce^{3+}	SO_4^{2-}	i. ex.	25±1°C	0.5($NaClO_4$)	(88.5±1.8)	(6.85±0.37)x10²	-	-
"	"	sol.extn.	"	"	(87.3±4.4)	(7.56±0.74)x10²	-	-
Gd^{3+}	"	i. ex.	25±1°C	"	(79.9±1.3)	(6.96±0.22)x10²	[2.25]*	-
"	"	sol.extn.	"	"	(80.1±3.7)	(9.88±0.70)x10²	-	-

* A mean value of λ'_1 for gadolinium sulphate system calculated from cation-exchange and HDEHP data for the ligand range (5.712 - 8.976)x 10^{-2} mole/l.

concentrations. A least squares treatment gives the values of β_1 and β_2 recorded in Table 4. The differences would suggest that 'λ_1'' has a value of about 2.25. For the calculation of 'λ_1'', values of ϕ_{1L} and ϕ_{1R} for the ligand range between 5.712×10^{-2} - 8.926×10^{-2} have been used.

Other ϕ_1L - ϕ_1R values are too small to merit serious consideration having regard to the size of likely errors. In view of the possible observational errors involved the significance of the numerical value for λ_1' must remain doubtful.

Fluoride systems. As was observed in the study of europium with fluoride a large difference was obtained between ϕ_{1L} and ϕ_{1R} at each ligand value for both cerium(III) and gadolinium(III). A good deal of spread was obtained in ϕ_{1L} for gadolinium(III) which however rises appreciably more steeply with increasing ligand than does for europium(III) and cerium(III). There is a possibility that above a ligand value of about 12.0×10^{-4} m/l ϕ_{1L} begins to level off. The β_1 and β_2 have therefore been calculated using all the data and also by just including ϕ_{1L} up to $[A^-] = 12.0 \times 10^{-4}$ m/l. The results are not markedly different (see Table 6(a)).

TABLE 5 - Cation-exchange and HDEHP data for cerium-fluoride system

No.	$[A^-]$x10^4 (mole/l.)	ϕ_{1L}x10^{-3} (l./mole)	ϕ_{1R}x10^{-3} (l./mole)	$(\phi_{1L}-\phi_{1R})/[1+\phi_{1R}(A^-)]$ x10^{-2} (l./mole)
1	1.993	1.474	-	-
2	2.657	1.525	0.6184	7.79
3	3.322	1.834	(0.6990)	9.21
4	3.986	1.767	0.7792	7.54
5	4.650	1.689	(0.07924)	6.55
6	5.315	1.938	0.8053	7.93
7	6.643	2.023	0.7707	8.28
8	7.972	2.190	0.6512	10.1
9	9.304	2.479	0.6925	10.9
10	10.63	2.535	0.7611	9.81
11	11.96	(2.549)	0.7095	9.95
12	13.29	2.556	0.8141	8.37
13	14.62	(2.748)	0.8253	8.71
14	15.94	(2.935)	0.7742	9.67
15	16.96	3.081	(0.8263)	9.40
16	17.27	(3.028)	0.8425	8.91
17	18.60	2.836	-	-

ϕ_{1L} (1 - 5) were obtained using 0.025% ($\frac{v}{v}$) HDEHP for which K^o = 0.7827; the remainder were obtained using 0.04% ($\frac{v}{v}$) HDEHP for which K^o = 3.768.

ϕ_{1R} were obtained using 0.2000 g. of 8% (DVB), 100 - 200 mesh Zeo-Karb-225 (SRC) resin for which λ^o = (80.21 ± 1.22)X75

Values in parenthesis indicate those obtained by interpolation.

TABLE 6 - Cation-exchange and HDEHP data for gadolinium-fluoride system

No.	$[A^-]\times10^4$ (mole/l.)	$\phi_{1L}\times10^{-3}$ (l./mole)	$\phi_{1R}\times10^{-3}$ (l./mole)	$\phi_{1L}-\phi_{1R}/[1+\phi_{1R}(A^-)\times 10^{-3}$ (l./mole)
1	2.657	3.786	2.066	1.110
2	3.986	4.822	2.133	1.45
3	5.315	5.325	2.275	1.38
4	6.643	6.042	2.343	1.45
5	6.772	6.418	(2.339)	1.58
6	7.972	(7.133)	2.294	1.71
7	9.300	(7.933)	2.420	1.70
8	10.63	8.001	2.372	1.60
9	10.76	8.704	(2.383)	1.77
10	11.96	8.420	2.495	1.49
11	12.08	7.733	(2.482)	1.56
12	13.29	(8.918)	2.365	1.58
13	14.62	9.124	2.425	1.47
14	14.74	9.776	(2.413)	1.62
15	15.94	(10.21)	2.268	1.72
16	16.07	10.27	(2.303)	1.70
17	17.27	-	2.636	-

ϕ_{1L} values were obtained using approximately 0.025% $(\frac{v}{v})$ HDEHP for which $K^o = 21.12$; ϕ_{1R} were obtained using 0.1000 g. of resin for which $\lambda^o = (28.46)\times/150$ The values in parenthesis were obtained by interpolation.

TABLE 6(a) - Equilibrium constants of cerium and gadolinium fluoride complexes calculated from the cation-exchange and HDEHP data

Metal	Ligand	Ionic strength	β_1	β_2	λ_1'	λ_2'	λ_1	λ_2
Ce^{3+}	F^-	0.5($NaClO_4$)	$(1.41\pm0.08)\times10^3$	$(9.07\pm0.78)\times10^5$	$(7.90\pm0.60)\times10^2$	$(1.02\pm0.55)\times10^5$	3380	677.
					$[8.88\pm0.27]\times10^2$		[3780]	
Gd^{3+}	F^-	0.5($NaClO_4$)	$(2.67\pm0.27)\times10^3$	$(5.17\pm0.32)^{*}\times10^6$	$(1.22\pm0.12)^{*}\times10^3$	$(3.90\pm1.4)^{*}\times10^5$	1950*	321*
			$(3.05\pm0.28)\times10^3$	$(4.60\pm0.26)^{**}\times10^6$	$(1.32\pm0.09)^{**}\times10^3$	$(2.37\pm0.81)^{**}\times10^5$	[2500]	220**
					$[1.56\pm0.04]\times10^3$		~~[1446]~~	

* values obtained by taking first eleven values of λ_1', (Table 6, column 5).

** values obtained by taking all the values of λ_1', (Table 6, column 5).

[ ] values in square brackets give mean λ_1' and λ_1, assuming only MF^{2+} partitions under the experimental conditions used.

Both cerium and gadolinium solvent-extraction data were treated in the same manner as the corresponding europium data in order to obtain β_1 and β_2. The results are given in Table 6(a). It may be noted that in the case of the ion-exchange data for gadolinium(III) ϕ_{1_R} appears to be turning downwards towards the lower end of the ligand range investigated as was predicted by calculations for europium (cf. Chapter III). For the calculation of λ_1' and λ_2' for corresponding cerium and gadolinium systems similar calculations were carried out as described before (see page 78). They are reported in Table 6(a). Alternatively λ_1' values have been obtained by averaging the values for

$$\frac{\phi_{1_L} - \phi_{1_R}}{1 + \phi_{1_R}[A^-]} \quad ;$$

of course this would imply that only the first complex exchanges in addition to the free metal ion.

Oxalate systems. As for europium the differences between ϕ_{1_L} and ϕ_{1_R} can be regarded as being insignificant. In each case the data are adequately represented by straight lines giving β_1 and β_2 values recorded in Table 7(b). The data obtained by both ion-exchange and solvent-extraction methods are recorded in Table 7.

TABLE 7 - Cation-exchange and HDEHP data for the gadolinium oxalate system

No.	$[A^-] \times 10^5$ (mole/l.)	$\phi_{1_L} \times 10^{-4}$ (l./mole)	$\phi_{1_R} \times 10^{-4}$ (l./mole)
1	2.452	7.353	6.721
2	4.904	8.012	7.732
3	6.183	9.413	-
4	8.290	9.533	11.14
5	10.31	9.367	-
6	12.37	10.72	12.26
7	14.43	11.99	13.06
8	17.16	12.77	-
9	19.62	14.39	14.55
10	21.02	-	16.52
11	22.67	16.86	16.70
12	24.73	17.26	17.98

ϕ_{1_L} were obtained using approximately 0.020% $(\frac{v}{v})$ HDEHP; K° = (13.79 ± 0.55) and ϕ_{1_R} using 0.1000 g of 8% (DVB) 100 - 200 mesh Zeo-Karb-225 (SRC) resin at μ = 0.5 ($NaClO_4$) and pH 3.60. λ° for the resin = (24.46 ± 0.17)X150.

TABLE 7(b) - Equilibrium constants for gadolinium oxalate complexes calculated from cation-exchange and HDEHP data

Metal	Ligand	Method	Temp.	Ionic strength	β_1	β_2
Gd^{3+}	$C_2O_4{}^{2-}$	i. ex.	25±1°C	0.5($NaClO_4$)	$(5.96\pm0.47)\times10^4$	$(4.83\pm0.29)\times10^8$
Gd^{3+}	$C_2O_4{}^{2-}$	sol.extn.	25±1°C	0.5($NaClO_4$)	$(5.75\pm0.42)\times10^4$	$(4.50\pm0.28)\times10^8$

TABLE 8 - Cation-exchange and HDEHP data for the cerium-α-hydroxyiso-butyrate system

o.	$[A^-]\times10^2$ (mole/l.)	$\phi_{1L}\times10^{-3}$ (l./mole)	$\phi_{1R}\times10^{-3}$ (l./mole)	$\frac{\phi_{1L}-\phi_{1R}}{1+\phi_{1R}[A^-]}$ (l./mole)	$f\times10^{-5}$ ($l^2/(mole)^2$)	$\frac{\Delta f}{\Delta\phi_{1R}}$ (l./mole)	$g\times10^{-6}$ ($l^3/mole^3$)
1	1.000	0.3587	-	-	-	-	-
2	1.020	(0.3603)	0.3251	8.156	0.6592	232.2	2.833
3	2.000	0.4509	(0.4053)	5.008	-	-	-
4	2.103	(0.4651)	0.4138	5.288	0.8723	236.2	3.742
5	3.000	0.5859	(0.5226)	3.795	-	-	-
6	3.102	(0.5978)	0.5354	3.543	1.144	231.1	4.820
7	4.653	(0.7939)	0.7578	0.9956	1.646	227.7	6.834
8	5.180	0.8619	(0.8366)	0.5706	-	-	-
9	5.687	(1.024)	0.9132	2.093	2.000	228.6	8.252
0	6.000	1.127	(0.9512)	3.027	-	-	-
1	6.865	(1.293)	1.056	3.224	2.387	235.8	9.877
2	7.000	1.319	(1.084)	3.056	-	-	-
3	8.985	(2.080)	1.525	4.021	3.396	228.4	13.83
4	9.000	2.084	(1.527)	4.024	-	-	-
5	10.04	(2.583)	1.820	4.152	4.270	225.0	16.70
6	10.57	(2.838)	2.061	3.551	4.615	228.1	18.71
7	12.00	3.521	(2.630)	2.814	-	-	-
8	12.68	(4.185)	2.905	3.465	6.555	228.6	26.49
9	13.00	4.403	(3.047)	3.414	-	-	-
0	13.50	4.630	(3.275)	3.058	-	-	-
1	14.27	(5.196)	3.625	3.031	8.173	227.8	32.93
2	14.50	5.364	(3.850)	2.706	-	-	-
3	15.33	(5.959)	4.697	1.750	10.61	227.8	42.69
4	17.00	7.187	-	-	-	-	-

$_L$ were obtained using approximately % ($\frac{v}{v}$) HDEHP for which k_0 = 122.03 ±
$_R$ = 230 and f^o = 4.50 x 10^4 were used in the calculations. ϕ_1 in
arentheses were obtained by interpolation. Both sets of data were
otained at μ = 1.0 ($NaClO_4$) and pH 3.60 λ^o for the resin = 31.96x30.

TABLE 8(b) - Equilibrium constants for cerium-α-hydroxyisobutyrate complexes as calculated from the data obtained by the ion-exchange and solvent extraction methods

Metal	Ligand	Method	Temp.	Ionic strength	β_1	β_2	β_3	β_4	λ'_1	λ'_2
Ce^{3+}	α-hydroxy-iso-butyrate	i.ex.*	25±1°C	1.0($NaClO_4$)	226	0.88×10^4	-	-	[3.16]	-
Ce^{3+}	"	soln. extn.**	25±1°C	"	235	0.88×10^4	7.0×10^7	8×10^5	-	-

[ ] mean of λ'_1 values for observations 9 to 23.

* β_1 obtained from a $\frac{\Delta f}{[A^-]}$ vs $\frac{\Delta \phi_{1R}}{[A^-]}$ plot; β_2 obtained from g plotted against ϕ_{1R}.

** β_2, β_3, β_4 obtained by iterative and graphical methods (see text).

α-hydroxy-iso-butyrate systems

As for europium, the data obtained for cerium indicate that $\phi_{1_L} - \phi_{1_R}$ diverges as $[A^-]$ is increased. Further, ϕ_{1_L}, at the higher end of the ligand range rises steeply with increasing $[A^-]$. Since the data at the lower ligand end is rather scanty, precise extrapolation to $[A^-] = 0$ on the basis of data alone would prove difficult. An estimate of $\phi_1^o = 235$ was made having regard to published values for β_1. Considerable weight was given to the work of Powell et al[2], in choosing this value. But since the ionic strength in his measurement is different, consideration was also given to unpublished distribution measurements performed in this laboratory[3].

Assuming the relation

$$\phi_{1_L} = \beta_1 + \beta_2[A^-] + \beta_3[A^-]^2 + \beta_4[A^-]^3 + \ldots\ldots\ldots \quad (1)$$

is applicable and knowing β_1 the function

$$X_1 = \frac{\phi_{1L} - \beta_1}{[A^-]} = \beta_2 + \beta_3[A^-] + \beta_4[A^-]^2 + \ldots\ldots\ldots \quad (2)$$

was calculated and the left hand side plotted against ligand then showed the presence of a fourth complex $[CeA_4]^-$ since the curve is clearly non-linear. The β_2 and β_3 values were estimated from the intercept and limiting slope of this curve at the lower ligand end.

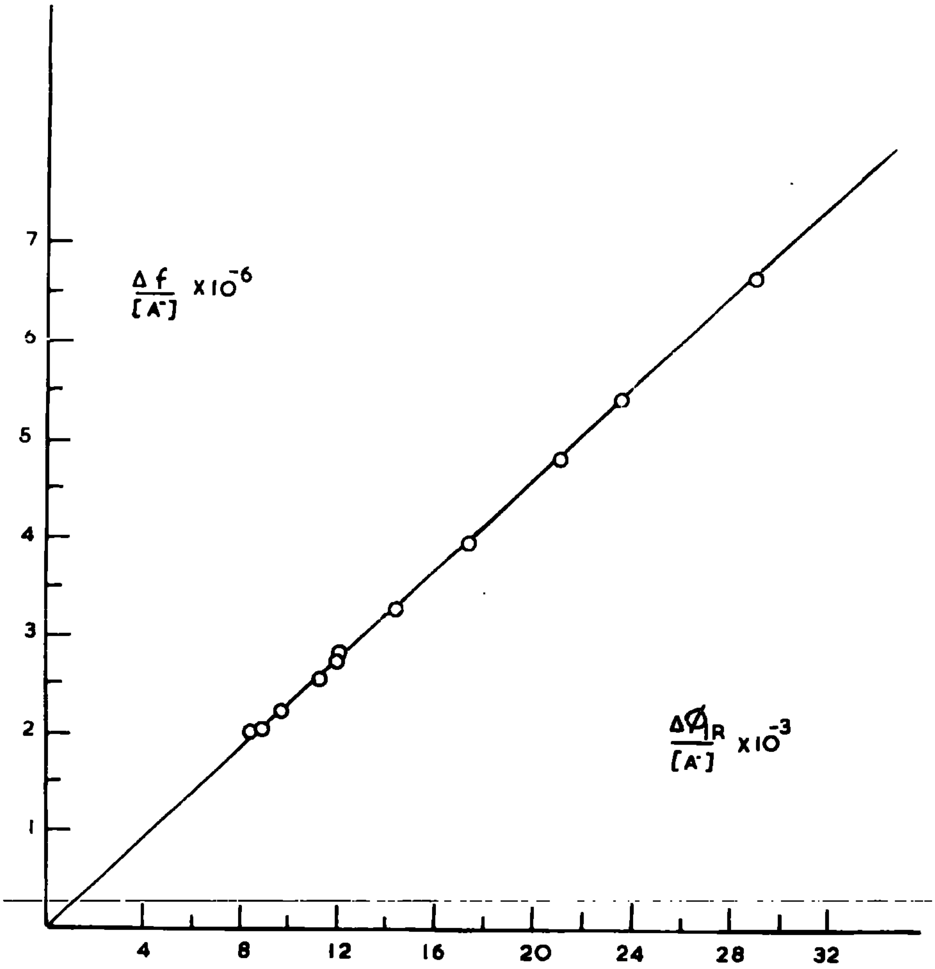

Fig v) The cation-exchange measurement of the cerium α-hydroxyisobutyrate system. $\Delta f.[A^-]^{-1}$ is presented as a function of $\Delta \phi_{1R}\ [A^-]^{-1}$ for α-hydroxyisobutyrate cocentrations between 10 and 150 mM. The slope of the line gives β_1

Knowing β_2, another function

$$X_2 = \left[\frac{X_1 - \beta_2}{[A^-]}\right] = \beta_3 + \beta_4 [A^-] + \dots\dots\dots \qquad (3)$$

was calculated giving a new value for β_3 and a value for β_4. The new value for β_3 and the value for β_4 were then put into equation (2) giving an improved β_2 value which was then used in equation (3) to refine β_3 and β_4 values. At this stage X_2 plotted against $[A^-]$ gave a good straight line, and further iteration did not effect any improvement in the fit obtained by applying these β_2, β_3 and β_4 values to the data. These values are given in Table 8(b). The function

$$\frac{(\phi_{1L} - \phi_{1R})}{1 + \phi_{1R}[A^-]}$$

was obtained and found to be substantially constant over that range of the measurement. As for europium the ion-exchange data relating to Ce(III) was treated by Fronaeus's method. ϕ_1^o was obtained having regard to λ_1' calculated as above and the previously chosen β_1; on this basis $\phi_{1R}^o = 230$ was decided upon. It is consistent with the reported experimental data. $\frac{\Delta f}{\Delta \phi_{1R}}$ is constant (Table 8) and a plot of $\frac{\Delta f}{[A^-]}$ against $\frac{\Delta \phi_{1R}}{[A^-]}$ shows a linear relationship between $\frac{\Delta f}{[A^-]}$ and $\frac{\Delta \phi_{1R}}{[A^-]}$ (Fig VI). The slope of this line gives β_1 reported in Table 8(b). This value is in

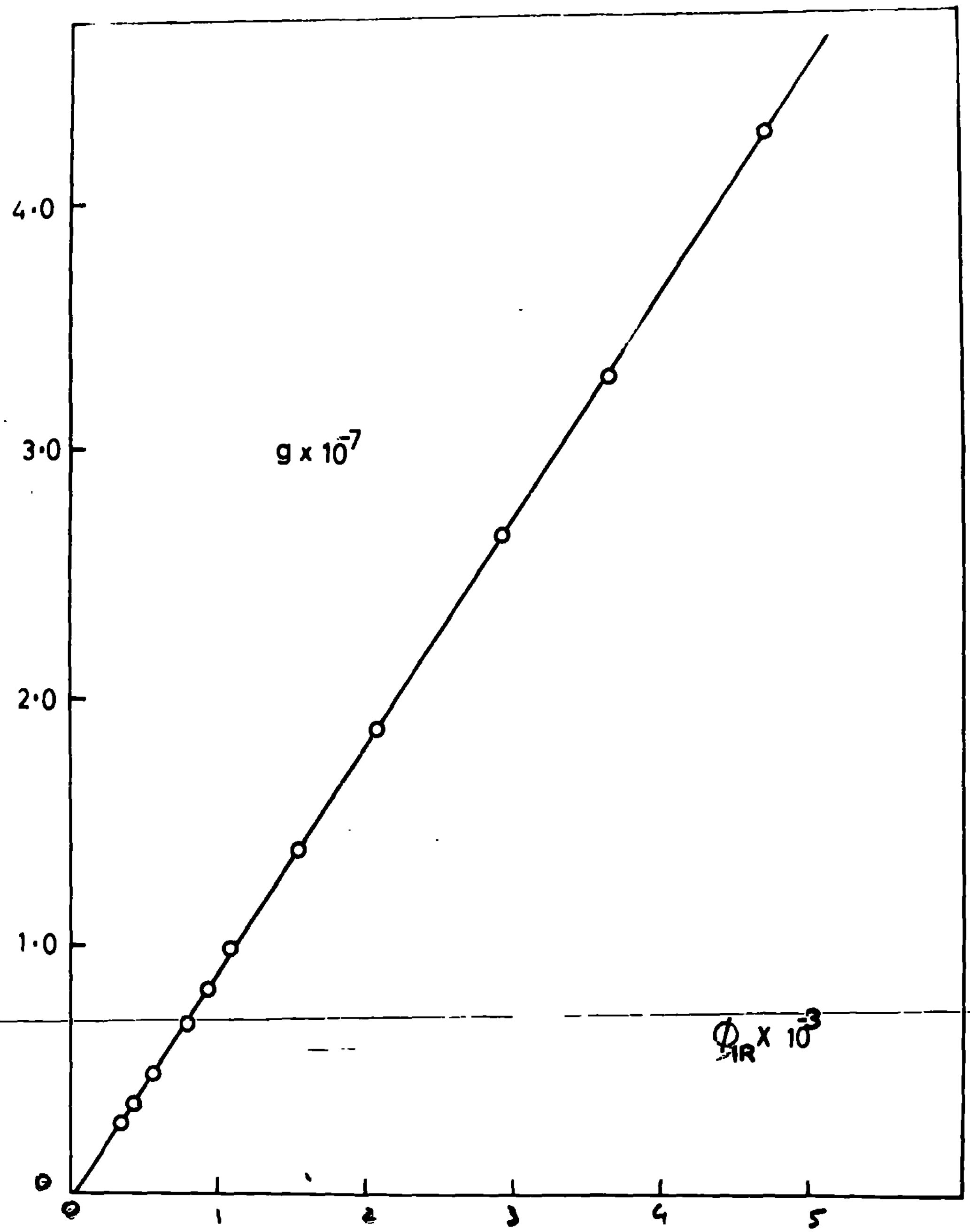

Fig VII The cation-exchange measurements on the Cerium-α-hydroxy-iso-butyrate system. g is represented as a function of ϕ_{IR} for α-hydroxy-iso-butyrate concentrations between 10 and 150mm. The slope of the line gives β_2.

good agreement with an average of $\frac{\Delta f}{\Delta \phi_{1R}}$ values calculated from equation 10(b) (see Chapter III). In this case where liquid-liquid data clearly shows the presence of a fourth complex, it is of some interest to examine ion-exchange data by the Fronaeus treatment in order to find out whether or not it predicts the same degree of complexation. This test should be possible using equation (56) (cf. Chapter III), to calculate 'g'. In order to predict the presence of a fourth complex 'g' should be a non-linear function of ϕ_{1R}. The data presented in fig. VII, clearly shows 'g' to be linear in ϕ_{1R}. Thus, this treatment does not appear to be sufficiently adequate on extension to systems involving a fourth step in complexation even to indicate its existance qualitatively.

References - Chapter IV

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CHAPTER V

Some Americium(III) and Curium(III) Complexes

Introduction

Although in the past, data on the complex formation of corresponding lanthanide and actinide elements have been obtained,[1,2] in few instances have they been acquired using the same method for both metal ions in the pair.[3,4] Such studies are desirable from the point of view of separation of these elements from each other and in order to attempt a rigorous comparison of their behaviour. The great majority of work on the complexes of lanthanides has been done by generally reliable potentiometric methods which, unfortunately, are not applicable for similar studies with many of the actinide elements. Most of the radioisotopes of the higher actinide elements have short half-lives and as a consequence high specific activities. If used for such studies in milligramme quantities their decay would produce complicated radiolytic effects and thereby make the measurements difficult to interpret. Even with relatively long lived isotopes of the rarer actinides one is obliged to make measurements at very low concentrations on conservation grounds since only trace amounts may be available. The production of isotopically pure nuclides is very expensive and occasionally the isolation of an isotopically pure nuclide of interest may be well-nigh impossible.

As has been pointed out before, partition methods are well suited to such studies. These methods can be worked at tracer levels and valuable information can, generally, be obtained without undue labour. The present chapter covers the study of some complexes of americium(III) and curium(III) by ion-exchange and solvent-extraction methods. The solvent-extraction method has proved most useful from the point of view of the radioactive assay of samples containing α-emitting nuclides. The higher actinides are frequently α-unstable and radioactive assay of samples containing nuclides of medium half-life can be hazardous and present problems in handling unless present in very small amounts. A liquid-scintillation method of counting has been discussed and it has been shown that it is particularly useful for the sort of measurement where high concentrations of salts are present in the aqueous phase to maintain constant ionic strength. The counting of α-emitting solid sources would be inefficient, present difficulties in source preparation and also perhaps be a health hazard.

The development of methods for the liquid-scintillation counting of americium-241 and curium-244 are described and results given for equilibrium constants in selected aqueous systems.

Experimental

The radioisotopes chosen were americium-241 and curium-244. Americium-241 is readily obtainable and of the three longer lived isotopes of the element (Am^{241}, $t_{\frac{1}{2}} = 458y$; Am^{242}, $t_{\frac{1}{2}} = 100y$; and Am^{243}, $t_{\frac{1}{2}} = 7600y$), Am^{241} is obtained isotopically pure and is an example where the concept of fixed atomic weight is valid. Also americium-241 has been used for the study of the majority of known chemical and physical facts regarding americium[5]. The isotope curium-244 has had particular utility for such studies since it can also be obtained in a good degree of purity, and by virtue of its half-life of 19 years it has a specific activity some forty times smaller than curium-242. Curium-242 emits $\sim 7 \times 10^{12}$ α-particles per milligramme per minute which would decompose[6] an aqueous solution of curium producing compounds like hydrogenperoxide and as a consequence make aqueous solution studies of complex formation meaningless (cf. page 95). The americium was obtained from the Radioisotope Centre, Amersham, England, dissolved in 0.1 M nitric acid solution. The curium was obtained from A.E.R.E. Harwell, England. Prior to the preparation of the stock solutions of the tracers, their purity was checked on a multichannel analyser. The procedures adopted for the preparation of other requisite stock solutions were similar to those described before. In the case of curium an alternative method of equilibrating a radioactive HDEHP-phase with an initially barren aqueous phase containing the complexing ligand was followed. This was necessitated because of difficulties arising from α-counting and has been described in detail later in the text.

α-counting by the liquid-scintillation method

The higher actinides are mostly α-unstable and occasionally there is little or no γ-emission, for example, curium-244. It is, therefore, desirable to have a method that is capable of permitting the samples to be counted by α-counting procedures. Counting of α-particles effectively requires preparation of good α-sources which must be thin, preferably weightless. This is because alpha particles have a short range in matter. Preparation of such sources, however, without an elaborate initial separation scheme will be unworkable for the type of measurements described here because of the high concentrations of salts present.

Also there are difficulties associated with the counter to be used. The counter window or other material through which the α-particles must pass should be thin and it is preferable to use windowless counters for such purposes[7]. The alternative is a liquid-scintillation counting method. Liquid scintillation counting methods have been widely used for the radioactive assay of soft β-emitters like carbon-14 and tritium[8,9,10,11,12]. Comprehensive reviews on the subject have been appearing at regular intervals[13,14]. Although counting by the liquid-scintillation method is equally applicable to β- and α-radiations, relatively little work has been done on the counting of α-particles by this method. Alpha particles, on the other hand, possess a definite advantage over β-particles, namely their higher energy which results in the production of large scintillation effects. This eliminates difficulties due to phosphorescence and interference from electrical noise in the electronics associated with the counting. However, working with a liquid scintillation counting method presents problems and it has its limitations. The foremost difficulty encountered with counting of α-emitting cations relates to the successful solubilization and dispersion within the scintillation media. One has to utilise chemical substances which do not result in the formation of colour or other form of light quenching. This is because the usual liquid-scintillation mixtures are organic based and do not readily assimilate water or aqueous solutions containing inorganic salts. Water exerts a rather strong quenching action: with 24% water the original light intensity drops by more than 70% in a solution of PPO in purified dioxan[15]. The choice of solvent to be used, therefore, constitutes one of the major problems in the application of liquid-scintillators to the counting of polar substances. A great deal of work in the field has, indeed, been directed towards developing mixed solvent systems in order to improve the measurement of aqueous samples. The different mixed solvent systems which have been developed in recent years have been reviewed by Rapkin[16]. In general, alcohols, such as methanol or ethanol, ethers, such as dioxan, and naphthalene are among the main substances which are being incorporated for the counting of water or aqueous mixtures in most of the solvent systems which have been studied. Various complexing and extracting agents have been used to solubilise different inorganic ions[17,18,19,20].

In the work to be described here, α-particles of the nuclides americium-241 and curium-244, were counted by means of a single photomultiplier liquid-scintillation counter assembly with high signal-to-noise ratio, using a scintillation mixture consisting of 10 g. PPO (2,5-diphenyloxazole), 0.5 g POPOP (1,4-bis-2-(5-phenyloxazole))benzene, 5 g naphthalene and 170 ml cellosolve per litre of dioxane. PPO and POPOP were obtained from Nuclear Enterprises (G.B.) Limited, Edinburgh, Scotland. The naphthalene was microanalytical grade from Hopkins and Williams Ltd. The cellosolve and dioxane were ordinary grade reagents from Hopkins and Williams Ltd.

The above mixture was found to be well suited to the assimilation of aqueous solutions to the extent of 15% ($\frac{v}{v}$). Prior to the actual measurements, however, several checks on the stability of the resultant mixture of scintillation and aqueous solutions were carried out in the presence of all the ligands anticipated to be used in the proposed measurements. In a recent article, Erdtmann[21] has shown that cations, if brought into a scintillator liquid, do not always form stable solutions. K. Joon and P.A. Deurloo[22] found similar difficulties in solubilising plutonium. They used a scintillation mixture similar to that used in the present work. Their mixture composed of 7 g of PPO, 0.3 g of dimethyl POPOP and 100 grammes of naphthalene per litre of dioxan. During the course of the present work, no such difficulties were observed. The counting rate of a sample was constant for over 8 weeks. A detailed study, however, revealed that whereas no loss of activity occurred in the presence of aqueous solutions consisting of sodium-perchlorate-sodium fluoride and sodium-perchlorate-α-hydroxyisobutyrate systems, instantaneous loss of radioactivity was observed due to precipitation if sulphate or oxalate salts were present along with the sodium perchlorate.

It is interesting to note that such systems were still found to give reproducable results, if care was taken to let the precipitates settle down or if they were evenly dispersed throughout the scintillation mixtures. In the literature, a technique called "suspension counting" has been reported. It was observed by Davidson[23] that barium carbonate suspensions looking "opaque and bizarre" with all sizes of clumps of precipitate, nevertheless counted reproducibly. Our observations seem to confirm his views. Also, the suggestion of Gjone et al[24] that suspension counting may lead to inaccurate results if low energy β-particles are counted. This follows because particles emitted within the precipitate are absorbed to a varying degree depending on the particle size which may differ from one sample to the other. Similar conclusions appear to be valid in the case of high energy α-particles. It was observed during the course of the present work that two samples containing the same amounts of precipitate gave different counting rates if the particle sizes of the precipitates were different. Provided that fine crystals could be produced by means of breaking the larger ones, reproducible counting rates could be obtained.

In order to avoid such risks, an alternative method of counting the nuclide in an organic medium was used in the present work. Curium-244 was counted in this manner. Since americium could be counted by γ-scintillation counter, no problem was encountered in the study of sulphate and oxalate complexes. HDEHP-toluene solutions carrying curium or americium activities readily mix with the proposed scintillation mixture forming a stable homogeneous solution which gives reproducible results. This then formed the basis of the method for the work on the curium-sulphate system.

Treatment of data

Sulphate systems. Ion-exchange data for the americium-sulphate system and HDEHP data for the curium-sulphate system are recorded in Tables 3 and 1 respectively. Previous work on corresponding lanthanide-sulphate systems had shown that the distribution of the mono-sulphate lanthanide ion into the resin, under the experimental conditions used, was negligible and, therefore, either the ion-exchange or the HDEHP-extraction method could be used with equal advantage. However, the ion-exchange method is more convenient to handle and hence the americium sulphate system was studied by the cation-exchange method. Also, since americium-241 has a useful γ-ray, a γ-scintillation counter could be used for the radioactive assay of samples instead of the proposed liquid scintillation method which, due to precipitation (cf. page 102) difficulties, cannot conveniently be used for counting aqueous samples. Curium-244, being devoid of any γ-emission, was studied by the HDEHP-extraction method. β_1 and β_2 values were calculated using the least squares method for both sets of data. A plot of ϕ_{1R} or ϕ_{1L} against $[A^-]$ gives curves to which straight lines can readily be fitted suggesting that there are not more than two complexes formed under the conditions of the experiments used. The β_1 and β_2 values for both the metal systems have been recorded in table-5

Oxalate system. Cation-exchange data for americium-oxalate systems were obtained in the usual way and they are recorded in table 2 . As for the corresponding lanthanide, Eu^{3+}, the data are readily fitted to a straight line suggesting only two complexes. The values for β_1 and β_2, obtained by the least squares method along with the standard errors on the results, are recorded in table-5 . The discussion of results obtained is, however, deferred until the main discussion of the work described in this thesis.

Fluoride system. Some preliminary measurements carried out on the americium-fluoride system by both the ion-exchange and the solvent-extraction method, in general, confirmed the pattern observed for corresponding lanthanide systems. The ion-exchange study of the fluoride system gives rather low ϕ_{1_R} values suggesting that the distribution of AmF^{2+} and $AmF_2{}^{+}$ ions is very large under the experimental conditions used. It is suggested that this measurement should be supplemented by solvent-extraction data on the system. The ϕ_{1_R} values obtained by the ion-exchange method were determined by γ- and also by α-counting of the same samples; the results are recorded in table -4 for comparison.

TABLE I - HDEHP data for the curium(III)-sulphate system

No.	$[A^-]$ (mole/l.)	ϕ_L	$\phi_{1L} \times 10^{-1}$ (l/mole)
1	0.8160	15.64	7.524
2	1.632	11.60	7.206
3	2.448	8.783	7.655
4	3.264	7.161	7.735
5	4.080	5.520	8.757
6	4.896	4.673	8.990
7	5.712	3.468	10.99
8	6.528	3.366	9.956
9	7.344	2.934	10.350
10	8.160	2.709	10.19
11	8.976	2.433	10.44
12	9.972	2.127	10.90

ϕ_{1L} were obtained by using approximately 0.125 $(\frac{V}{V})$ HDEHP-toluene solution at $\mu = 0.5$, pH. 3.60 for which k^o (average of four values) of 25.24 was determined.

TABLE I - Collected values for the equilibrium constants (α-hydroxy-isobutyrate systems).

Metal	Ligand	Method	Temp. °C	Ionic strength	β_1	β_2	β_3	β_4	Ref.
Ce^{3+}	α-hydroxy-isobutyrate	i. ex.	25 ± 0.1	1.0	226	0.88×10^4	-	-	(p.w.)
		sol.extn.	24 - 25	1.0	235	0.88×10^4	7.0×10^4	8×10^5	(p.w.)
		Pot.	25	0.5	234	1.02×10^4	-	-	(1)
		Pot.	25	2.0	270	2.079×10^4	2.079×10^5	-	(3)
		gl.	20	0.1	630	5.495×10^4	8.709×10^5	-	(2)
Eu^{3+}		i.ex.	25 ± 0.1	0.5	508	9.3×10^4	-	-	(p.w.)
		sol.extn.	24 - 25	0.5	520	1.2×10^5	2.5×10^6	-	(p.w.)
		Pot.	25	0.5	513	8.32×10^4	8.13×10^5	-	(1)
		Pot.	25	2.0	503	8.75×10^4	3.33×10^6	-	(3)
		gl.	20	0.1	1230	3.47×10^5	2.1×10^7	-	(2)

For all the data quoted ionic strength was maintained with sodium perchlorate. i. ex. = ion-exchange; sol. extn. = liquid-liquid extraction; Pot. = potentiometric; gl. = glass-electrode.

TABLE II - Collected values for equilibrium constants (Fluoride Systems).

Metal	Ligand	Method	Temp. °C	Ionic strength	β_1	β_2	Ref.
Ce^{3+}	F^-	sol. extn.	24 - 25	0.5	1.41×10^3	9.07×10^5	(p.w.)
		i. ex.	25 ± 0.1	0.5	-	-	(p.w.)
		red.	25	0.5	1.29×10^3	-	(15,16)
		i. ex.	25	0	1.0×10^4	-	(31)
Eu^{3+}	F^-	sol. extn.	24 - 25	0.5	2.48×10^3	3.01×10^6	(p.w.)
		i. ex.	25 ± 0.1	0.5	-	-	(p.w.)
Gd^{3+}	F^-	sol. extn.	24 - 25	0.5	2.67×10^3	5.17×10^6	(p.w.)
		i. ex.	25 ± 0.1	0.5	-	-	(p.w.)
		red.	25	0.5	2.34×10^3	-	(15,16)
Am^{3+}	F^-	i. ex.	25 ± 0.1	0.5	-	-	(p.w.)

For all the data ionic strength was maintained with sodium perchlorate. i. ex. = ion-exchange; sol. extn. = liquid-liquid extraction; red. = redox; p.w. = present work.

TABLE II - Cation-exchange data for the americium-oxalate system

No.	$[A^-] \times 10^5$ (mole/l.)	ϕ_{1R}	$\phi_{1R} \times 10^{-4}$ (l./mole)
1	2.117	17.48	6.840
2	4.234	9.674	8.085
3	6.351	6.334	9.062
4	8.468	4.459	10.15
5	10.58	3.347	11.13
6	12.70	2.630	12.02
7	14.82	2.094	13.11
8	16.94	1.807	13.47
9	19.05	1.539	14.07
10	21.17	1.287	15.23
11	23.29	1.142	15.66
12	25.40	1.014	16.22

ϕ_{1R} values were obtained using 0.1000 g. of 8% (DVB), 100 - 200 mesh, Zeo-Karb-225, (SRC-15) resin at $\mu = 0.5$ pH. 360 for which an average λ° (8 values) of (42.79 ± 0.2051) x150 was determined.

TABLE III - Cation-exchange data for the americium(III) sulphate system

No.	$[A^-] \times 10^2$ (mole/l.)	ϕ_R	$\phi_{1R} \times 10^{-1}$ (l./mole)
1	0.8160	27.11	7.083
2	1.632	18.04	8.407
3	2.448	13.81	8.566
4	3.264	10.41	9.534
5	4.080	8.285	10.21
6	4.896	6.829	10.75
7	5.712	5.774	11.22
8	6.528	5.112	11.29
9	7.344	4.392	11.90
10	8.160	3.744	12.78
11	8.976	3.554	12.30
12	9.972	3.077	13.18

ϕ_{1R} values were obtained using 0.1000 g of 8% (DVB), 100 - 200 mesh, Zeo-Karb-225 (SRC-15) resin at $\mu = 0.5$ pH. 360 for which an average λ° (8 values) of (42.79 ± 0.2051) X150 was determined.

TABLE III - Collected values for the equilibrium constants (oxalate system).

Metal	Ligand	Method	Temp.	Ionic strength	β_1	β_2	Ref.
Eu^{3+}	$C_2O_4{}^{2-}$	i. ex.	25 ± 0.1	0.5	7.26×10^4	4.51×10^8	(p.w.)
		sol.extn.	24 - 25	0.5	7.30×10^4	4.68×10^8	(p.w.)
		sol.extn.	25	1	5.89×10^4	5.25×10^8	(17)
		i. ex.	25	0.5	6.4×10^4	3.7×10^8	(18)
Gd^{3+}		i. ex.	25 ± 0.1	0.5	5.95×10^4	4.82×10^8	(p.w.)
		sol.extn.	24 - 25	0.5	5.75×10^4	4.49×10^8	(p.w.)
Am^{3+}		i. ex.	25 ± 0.1	0.5	6.58×10^4	4.00×10^8	(p.w.)
		sol.extn.	25	1	4.26×10^4	2.23×10^8	(17)

TABLE IV - Cation-exchange data for americium(III)-fluoride system

No.	$[A^-] \times 10^4$ (mole/l.)	$\phi^{*}_{R} \times 10^{-1}$	$\phi^{**}_{R} \times 10^{-1}$	$\phi^{*}_{1R} \times 10^{-2}$ (l./mole)	$\phi^{**}_{1R} \times 10^{-2}$ (l./mole)
1	3.984	41.96	46.16	3.238	1.235
2	5.316	34.64	41.53	6.909	3.127
3	7.968	36.59	34.37	3.690	5.134
4	9.296	34.51	30.55	4.001	6.296
5	11.95	29.94	30.11	4.870	5.090
6	13.28	29.03	31.23	4.752	4.147
7	15.94	28.79	27.47	4.046	4.788
8	17.26	27.14	26.21	4.316	4.911
9	19.92	25.61	26.15	4.262	4.277
10	21.25	23.83	24.55	4.645	4.578
11	22.57	24.06	24.70	4.289	4.255
12	24.70	21.48	23.71	4.879	4.221

* ϕ_R and ϕ_{1R} obtained by α-counting.

** ϕ_R and ϕ_{1R} obtained by γ-counting.

ϕ_R and ϕ_{1R} values were obtained using 0.1000 g. of 8% (DVB) 100 - 200 mesh Zeo-Karb-225 (SRC-15) resin at μ = 0.5 ($NaClO_4$) and pH. 360. The λ° calculated from data obtained by α-counting was 47.37 × 150 (average of 4 values); λ° obtained by γ-counting was 48.43 × 150 (average of 4 values).

TABLE IV - Cation-exchange and DEHP distribution data for the europium-oxalate system.

	$[A^{2-}]\mathrm{x}10^4$ (mole/l.)	$\phi_{1R}\mathrm{x}10^{-4}$ (l./mole)	$\phi_{1L}\mathrm{x}10^{-4}$ (l./mole)	$\frac{\Delta f}{\Delta\phi_{1R}}\mathrm{x}10^{-4}$ (l./mole)
1.	0.5703	9.858 9.607 10.41	10.07	7.418
2.	0.8555	11.48 11.04	11.88	7.385
3.	1.141	12.18 12.19	11.85	7.597
4.	1.426	14.13 12.98	14.76	7.394
5.	1.711	14.84 15.53	15.51	7.347
6.	1.996	-	15.42	-
7.	2.281	17.58 16.35	17.73	7.377
8.	2.567	19.76	20.59	7.310
9.	2.852	21.90 19.74	20.75	7.318
10.	3.137	-	20.60	-
11.	3.422	22.56 20.40	22.96	7.360
12.	3.707	25.33 22.82	24.72	7.328
13.	3.992	23.87	26.11	7.351
14.	4.275	-	27.98	-
15.	4.563	-	29.19	7.309

ϕ_{1L} for Nos. 1, 4, 5, 7, 9, 11, 13 and 14 were obtained using approximately 0.025% ($^V/_V$) DEHP for which k_0 = 8.002, the remainder with 0.04% DEHP, k_0 = 42.45. ϕ^0_{1R} = 7.30 x 10^4 and f^0 = 4.84 x 10^9 were used in the calculations.

TABLE IV - Collected values for the equilibrium constants (sulphate system).

Metal	Ligand	Method	Temp. °C	Ionic strength	β_1	β_2	Ref.
Ce^{3+}	SO_4^{2-}	i. ex.	25 ± 0.1	0.5	88.5	6.85 x 10^2	(p.w.)
		sol. extn.	24 - 25	0.5	87.2	7.56 x 10^2	(p.w.)
		i. ex.	25	1	43.0	2.20 x 10^2	(24)
		i. ex.	0	0.5	60.0	-	(25)
		i. ex.		0.5	56.2	7.94 x 10^2	(26)
Eu^{3+}		i. ex.	26 ± 1	1 - 1.3	34	2.50 x 10^2	(27)
		sol. extn.		0.1	171	-	(29)
		sol. extn.	25	1	34	4.89 x 10^2	(17)
Gd^{3+}		sol. extn.	24 - 25	0.5	80.1	9.8 x 10^2	(p.w.)
		i. ex.	25 ± 0.1	0.5	79.8	6.95 x 10^2	(p.w.)
Am^{3+}		i. ex.	25 ± 0.1	0.5	72.8	6.2 x 10^2	(p.w.)
		i. ex.	25	0.75	60.0	1.3 x 10^2	(30)
		i. ex.	25	1.5	58.0	-	(30)
		i. ex.	26 ± 1	1 - 1.3	31	3.0 x 10^2	(27)
		sol. extn.	25	1	37	4.57 x 10^2	(17)
Cm^{3+}		sol. extn.	24 - 25	0.5	69	4.3 x 10^2	(p.w.)

TABLE V - Collected equilibrium constants for the americium(III) and curium(III) complexes

Metal	Ligand	Method	μ	β_1	β_2
Am^{3+}	SO_4^{2-}	i. ex.	0.5($NaClO_4$)	$(7.28 \pm 0.252) \times 10$	$(6.25 \pm 0.418) \times 10^2$
Am^{3+}	$C_2O_4^{2-}$	i. ex.	0.5($NaClO_4$)	$(6.58 \pm 0.230) \times 10^4$	$(4.00 \pm 0.148) \times 10^8$
Cm^{3+}	SO_4^{2-}	sol.extn.	0.5($NaClO_4$)	$(6.91 \pm 0.372) \times 10$	$(4.36 \pm 0.617) \times 10^2$

TABLE-VI Ion-exchange distribution coefficients for 'free' and partly complexed species.

Metal	Ligand	λ_0	λ_1	$\frac{\lambda_1}{\lambda_0}$	λ_2	$\frac{\lambda_2}{\lambda_1} \times 10$
Ce^{3+}	α-hydroxy-isobutyrate	460	6.16×2	1.34×10^{-2}	-	-
Eu^{3+}	"	276.9×15	19.4×15	7.00×10^{-2}	-	-
Ce^{3+}	Fluoride	401×15	224.5×15 $[253] \times 15$	5.59×10^{-1}, $[6.29] \times 10^{-1}$,	45.1×15 -	2.01 -
Eu^{3+}	"	276.9×15	55.2×15	1.99×10^{-1}	11.6×15	2.10
Gd^{3+}	"	284.6×15	$130^{*} \times 15$ $123^{**} \times 15$ $[146] \times 15$	$4.57^{*} \times 10^{-1}$, $4.32^{**} \times 10^{-1}$, $[5.13] \times 10^{-1}$	$21.5^{*} \times 15$ $14.7^{**} \times 15$ -	1.65^{*} 1.19^{**} -
Eu^{3+}	Oxalate	276.9×15	$< 2 \times 10^{-1} \times 15$	-	-	-
Gd^{3+}	$SO_4{}^{2-}$	300.8×15	$[8.49]^{\dagger} \times 15$	0.033		

* Values obtained by taking first eleven values of λ_1', (Table 6, column 5).

** Values obtained by taking all the values of λ_1', (Table 6, column 5).

[ ] Values in square brackets give λ_1'; assuming only MF^{2+} partitions under the experimental conditions used.

† λ_1 obtained from a mean value of λ_1' for gadolinium sulphate system calculated from cation-exchange and HDEHP data for the ligand range $(5.712 - 8.976) \times 10^{-2}$ mole/l.

References - Chapter V

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CHAPTER VI

DISCUSSION OF RESULTS

A summary of all the results obtained in this work is presented along with relevant published data in Tables I - IV. To facilitate intercomparison, data for particular ligands appear in separate tables. The information obtained on the distribution of partially complexed cations into ion-exchange resins, are discussed separately. The method of calculation and other relevant treatment of data obtained from both ion-exchange and solvent-extraction methods of investigation has already been discussed in previous chapters (see chapters I, III, IV and V).

It is evident from the data given in Tables I - IV that equilibrium constant values for the systems investigated by the two methods are generally in satisfactory agreement with each other where a comparison can be made. From the details of data recorded and discussed in relevant chapters, it also emerges that the solvent-extraction method has definite advantages over the ion-exchange method in general, where more than two complexes are involved and, in particular, where the distribution of partially complexed cationic species into the resin phase cannot be ignored. As has been pointed out earlier (see pages 71-75) from the combination of both methods a new method has been developed which on one hand makes it feasible to determine the equilibrium constants of partially complexed cations successfully, and on the other hand provides valuable information regarding operation of the ion-exchange technique. The scope of this method will be discussed later along with information on equilibrium constants of partially complexed cationic species.

The results obtained in this work are hereafter discussed individually system by system and in relation to each other.

α-hydroxy-isobutyrate systems

The equilibrium constant values for the α-hydroxy-isobutyrate complexes of cerium(III) and europium(III) obtained by both ion-exchange and solvent-extraction methods have been recorded in Table I along with other published values. An intercomparison of β_n values obtained by the two methods with each other and with that of Stagg and Powell[1] obtained by a potentiometric method shows that agreement is good provided the differences in the experimental conditions such as ionic strength and pH are taken into consideration. Complexes of lanthanide with α-hydroxy-isobutyric acid have been investigated rather extensively in recent years[1-5]. A striking feature of complex formation by rare earth cations is that appreciably stable complexes are obtained only when strongly chelating ligands are involved and more specially when the ligands contain highly electro-negative donor atoms like oxygen. For the formation of stable complexes involving d-type transition metals, participation of the 'd' electrons in metal-ligand bond formation is an important factor. This generally takes place through ligand field stabilization and hybridization of metal electronic orbitals and overlap of these hybrid orbitals with appropriate ligand orbitals. In the case of rare-earths the '$4f$'orbitals are effectively shielded from interactions with ligand orbitals by electrons in the '5s' and '5p' orbitals. It is, therefore, reasonable to conclude that if hybridization is to occur, it must of necessity involve[6] normally unoccupied high energy orbitals (e.g. 5d and 6p) thus allowing the ligand to retain in large measure control over the 'donated' electrons. This leads to essentially ionic type interactions. Thus, with rare-earth cations involving most ligands, significant cation-ligand interactions are largely electrostatic in character and complex species formed by these cations compare more closely with those derived from calcium, strontium and barium[7,8,9]. Magnetic moment measurements of the tripositive ions[10,11] and measurements by spectroscopic methods[12,13] lend support to this view. For example, no significant effects upon the values of the permanent magnetic moments of these ions, attributable to metal-ligand interactions, have been observed. This points to the absence of significant ligand field interactions between ligand and '$4f$' orbitals. Similarly, the positions of the sharply defined, characteristic absorption bands in the ultra violet and visible regions remaining nearly unaltered in the presence of ligand points to the same conclusions.

Under these circumstances both cation size and difference in the sizes of the several cations are of importance. Indeed, from published values for the equilibrium constants for the lanthanides which have been studied so far involving α-hydroxy-isobutyrate ligands, it appears that these confirm the general view that for a given oxidation state the values of equilibrium constants increase from cation to cation as the cation radius decreases. Also one notes that the equilibrium constants for a particular rare-earth and ligand increase as the ionic strength of the medium, in which these have been examined increases. This appears to apply when comparing results for the same or for different methods. The values obtained in this work confirm these observations. The work reported by Choppin et al[3], however, gave results which differ as far as the trend associated with the numerical values of the equilibrium constants and ionic strength is concerned. In the case of values reported for cerium(III) complexes as obtained in the present work the following points are worthy of mention. Firstly, an ionic strength of 1.0 was used in order to extend the measurement to a higher ligand concentration range and indeed the data support the formation of a fourth complex (see Table-I). Recently, evidence in support of four complexes for selected rare-earths and ligands having similar functional groups has come forward in the literature[14]. Unfortunately, a direct comparison for β_4 is not possible for lack of published data specifically for cerium(III). Calabro and Curro have investigated complexes of lanthanum, praseodymium and gadolinium with lactate ligand and reported four complexes. The successive β values reported are $\beta_1 = 158$, $\beta_2 = 6.030 \times 10^3$, $\beta_3 = 64.250 \times 10^3$, $\beta_4 \sim 2.2 \times 10^5$ for lanthanum, and $\beta_1 = 290$, $\beta_2 = 18.400 \times 10^3$, $\beta_3 = 250.000 \times 10^3$, $\beta_4 \sim 2 \times 10^6$ for praseodymium. In view of the fact that cerium lies between these two elements and that stabilities of corresponding lactate and α-hydroxy-isobutyrate complexes are nearly similar, the β values resulting from this work are in satisfactory agreement.

Fluoride system

The equilibrium constant values for the fluoride complexes of cerium(III), europium(III) and gadolinium(III) are reported in Table 2 . The data obtained on americium(III)-fluoride by the ion-exchange method are discussed separately (see page 105 chapter V). The β_n values for cerium and gadolinium obtained by the solvent-extraction method in this work are in good agreement with those reported by Kury et al[15,16]

Their values were obtained by a redox-method based upon the competition between the rare-earth ions and Fe(III) ions in a ferrous-ferric concentration cell. The β_n values for europium(III)-fluoride complexes can be compared with those of gadolinium obtained in the present work as well as with those given by Kuvy et al. The agreement is satisfactory within the scope of the experimental measurements. As explained in chapters III and IV, β_n values for cerium, europium and gadolinium were evaluated by a least squares treatment of HDEHP data in general. This treatment is based on the assumption that within the range of fluoride ligand concentration investigated, two complexes of the rare-earths concerned predominate and, therefore, $\phi_1 L$ values for all the three systems are, in general, a linear function of $[A^-]$. As to the values obtained by the ion-exchange method a direct extrapolation of experimentally derived ϕ_{1R} values to $[A^-] = o$ cannot be made with much confidence for reasons already explained in chapter III dealing with the europium work (see page 82).

Oxalate systems

The equilibrium constants for europium(III), gadolinium(III) and americium(III) reported in Table 5 are in agreement with relevant published values. Also, it is evident from Table 3 , that β_n values for europium and gadolinium obtained separately by ion-exchange and solvent-extraction methods agree with each other. This lends support to the hypothesis that for systems where distribution of partially complexed cationic species is insignificant β_n values obtained by the ion-exchange method should essentially be the same as those obtained by a suitable solvent-extraction method for corresponding experimental conditions. Recently Sekine[17] has reported work on lanthanum, europium and americium oxalate complexes by a solvent-extraction method. That the values for europium ($\beta_1 = 7.26 \times 10^4$) and americium ($\beta_1 = 6.58 \times 10^4$, $\beta_2 = 4.00 \times 10^8$) from the present work are somewhat higher than those reported by Sekine ($\beta_1 = 5.89 \times 10^4$) and ($\beta_1 = 4.26 \times 10^4$, $\beta_2 = 2.23 \times 10^8$) for corresponding systems in that order, is in agreement with the general observation regarding the trend between β_n values and ionic strength (μ) of the medium in which measurements have been made. Indeed, the fact that values for europium systems reported from the present work are in better agreement with those of Kerechuk and Paramonova[18] lends further support to this observed trend. It is interesting to note that β_n values reported for americium from the present work are, in general, similar to those reported for europium and gadolinium. The ratio of β_1 values for the pair europium/americium and gadolinium/americium has been calculated from the present data and is recorded in Table V.

Table V

Ligand	β_1Eu(III)/β_1Am(III)
Oxalate	1.01

Ligand	β_1Gd(III)/β_1Am(III)
Oxalate	0.901

It is evident from the above table that the values of the ratios obtained from the present work is close to unity, thus showing a parallel in the chemistry of the lanthanides and actinides. That for the pair Gd(III)/Am(III) the value is less than unity is, however, consistent with the observation that at gadolinium generally a decrease in the stability of complexes occurs. Curious as it might seem the fact is that for all ligands which have been studied, the gadolinium complex is less stable than would be expected from the simple electrostatic model[13]. This behaviour has been called the "gadolinium break", and cannot be explained, as was originally attempted[19] by assuming a steric effect, since it is apparent in complexes with ligands for which there should be no steric interference[20].

Sulphate systems

As for oxalate two sulphate complexes have been assumed to form within the range of ligand concentrations investigated. Agreement between values obtained by the solvent-extraction and the ion-exchange methods is good for cerium and europium, but there is a discrepancy between the gadolinium values. The equilibrium constant values are recorded in Table-4 along with other published work. The difference in the magnitude of β_n values when compared with some of the other published values are consistent with those expected from differences in ionic strength of the medium.

One interesting feature that emerges when β_n values are compared for sulphate complexes for a number of elements in the rare-earth and actinide series is their remarkable constancy provided experimental conditions are the same throughout. This is evident from the values reported in Table-4 , both from the present work and from other sources. Although no definite conclusions can be drawn due to inadequate data available for either series of elements the nature of the complex species giving rise to the distribution data observed is somewhat intriguing. Firstly the question arises as to whether or not sulphate forms a complex with the cations concerned. That the equilibrium constants reported for sulphate complexes are low favours the view that sulphate anions do not form inner-sphere complexes at all. Raman studies provide no evidence for inner-sphere complexes[21].

The question of whether or not sulphate forms inner-sphere complexes is, however, not simple to answer. The situation is complicated by difficulties in deciding whether or not any association of ions involves displacement of first-sphere ligands (H_2O). Smithson and Williams[22] suggest that if the d-d spectral transitions in a transition metal ion, occurring in the visible range, are not affected then outer-sphere complexes are formed. On this basis $CoSO_4$ is an outer-sphere complex and CoS_2O_3 an inner-sphere one. This is confirmed by the work of Posey and Taube[23]. As to the rare-earth ions the situation is not clear enough to enable any definite conclusions to be reached. Under these circumstances the significance of the equilibrium constants reported in this and other work must remain in doubt.

Ion-exchange Distribution Coefficients for "free" and partly complexed species

Distribution coefficients, λ_j, for the ion-exchanger calculated from appropriate β_j and λ'_n values, where $j = 1,2, \ldots\ldots$ (see also equation (7a) page 75 chapter-3) are recorded in Table 6 along with λ_0 values. It is evident that for intercomparison the data are insufficient and do not suggest any definite trend. Moreover, λ_j depends upon λ_0, β_j and λ_j values and consequently errors in the latter constants affect λ_j values to a very considerable extent. This fact alone makes it unwise to draw definite conclusions. The data, however, suggest that for ligands fluoride and α-hydroxy-isobutyrate the ion-exchange method is inadequate. For oxalate on the other hand both solvent-extraction and ion-exchange methods can be used with equal advantage. The data are henceforth discussed separately for individual ligands.

For α-hydroxy-isobutyrate λ_0 is greater than λ_1 by factors in the region of 74 and 14 for cerium(III) and europium(III) respectively. There is thus a considerable reduction in the size of the distribution coefficient on going from "free" aquated rare-earth ions through successive stages of complex formation. This further means that the resin phase contains species predominantly of low ligand number relative to the solution phase. If one considers this fact from the 'exchange' process point of view also, the results reported appear to be consistent. Exchange involving a cation-exchanger shows considerable selectivity as the charge of the cation increases; this is a well known phenomenon. Also, as successive stages of complex formation are reached the distribution of partially complexed species like MA^{2+} and MA_2^{+} compared with the aquated rare-earth ion, $M^{3+}(nH_2O)$, comes into conflict with other features of the ion-exchange process, such as steric hindrance. This manifests itself by virtue of the work to be done in expanding the resin phase (swelling energy) in order to accommodate larger ions. That such an effect will be considerable in the case of two α-hydroxy-isobutyrate ligands bound to the metal atom is consistent with the observations on oxalate systems. They show that both the charge and the size of the exchanging species take part in the exchange process. Recently, Brücher and Szarvas[24], have reported elution studies of trace lanthanides using a diffusion coefficient measurement method. They observe from ammonium lactate studies that as soon as a certain ligand concentration (about 0.1 M) in the eluent is reached the displacement of the rare-earth ion predominantly takes place in the form,

$$\overline{MA}^{2+} + 2NH_4^+ \rightleftharpoons MA^{2+} + \overline{2NH_4}^+ ,$$

where a bar on a species in the preceding relation indicates species in the resin phase. They further conclude that the quantity of a rare-earth ion in the M^{3+} form displaced by ammonium ions may be neglected compared to those displaced in the MA^{2+} form. The results reported in the present work are consistent with the above observations. For instance, consider the data recorded in Table 6(a):

Table 6(a)

Metal ion	λ_0/λ_1	MA^{2+}/M^{3+} at		
		0.01[A^-] m/l.	0.1M/l.[A^-]	0.5 M/l.[A^-]
Ce(III)	74.3	2.35	23.5	117.5
Eu(III)	14.2	5.2	52	260

In Table 6(a), column three contains ratios of MA^{2+} to M^{3+} in the aqueous phase at concentrations 0.01 to 0.5 m/l. of the ligand. It is evident from the numerical values of these ratios that at high concentrations where

$MA^{2+}/_{M}3+ > \frac{\lambda_0}{\lambda_1}$ exchange of the metal precedes predominantly by the exchange of MA^{2+}. The results of this work are therefore in at least semiquantitative agreement with those of Brücher and Szarvas.

For fluoride systems the results suggest that the distribution of partially complexed species in the resin phase is by no means insignificant compared to that of the 'free' metal ions. This is probably due to a size effect. The α-hydroxy-isobutyrate ligand is presumably large compared with the water molecules it displaces on complex formation. There is therefore not only a reduction in charge of one unit, but the increased ion size will require more work (swelling energy) to be done against the resin structure in order to accommodate it in that phase. (For sufficiently large ions a 'sieve effect' may also come into play.) The effect of charge is probably considerable since the α-hydroxy-isobutyrate and oxalate ligands are similar in size but mono-complex formation with the latter reduces the charge by 2, and comparison suggests that λ_1 for the latter is smaller by a factor of at least 10. Fluoride on the other hand is relatively much the smallest ligand of the four studied and although the bond to the metal ion is likely to be largely ionic, positively charged fluoro-rare-earth ions in solution are unlikely to be much different in size from 'free' aquated rare-earth ions; evidence which again points to the significance of ion charge reduction in determining λ. A qualitative explanation for these observations is obtained by regarding the ion-exchanger as a Donnan membrane system. In order to maintain metal-ligand complexes within the resin phase, free ligand is necessary. The Donnan treatment leads to the conclusion that anions are largely excluded from the resin phase provided the internal electrolytic concentration which normally depends on cross-linking is higher than the external. Also, the higher the anion charge, the greater is its degree of exclusion. Since a polystyrene-sulphonic acid type resin having 8 to 10% cross-linking may be expected to have an internal counter ion concentration in the region of 5 M, under the conditions whereby most equilibrium studies are carried out, including those described here, free anionic ligand will be at a considerably lower concentration within the resin than without. Thus, it may be concluded that for such ligands, the expectation is that distribution of their positively charged metal complexes between a cation-exchanger and external solution will be small relative to the distribution of the 'free' metal ion.

References - Chapter VI (Discussion)

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