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"RADIOCHEMICAL AND OTHER STUDIES OF SELECTED RARE EARTHS AND ACTINIDES IN SOLUTION"

THESIS

presented in candidature for the degree

of

DOCTOR OF PHILOSOPHY

in the

University of Kent at Canterbury

by

ABDUL AZIZ, M.Sc.(Peshawar)

MEMORANDUM

The work described in this thesis was carried out in the University Chemical Laboratory, University of Kent at Canterbury, between October 1966 and October 1969 under the supervision of Dr. S.J. Lyle, Senior 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 conclusion of other authors in relevant studies, 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.

A. AZIZ

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SUMMARY

The association of fluoride, sulphate, oxalate, hydroxide, propionate, lactate, alaninate and pyruvate ligands with trivalent rare earths, actinides, scandium and indium in aqueous solution has been studied. Partition into di-2-ethylhexylphosphoric acid (HDEHP) in toluene and a polystyrene type 8% cross-linked cation-exchanger (Zeo Karb-225) was employed. From the studies of the extraction of yttrium, trivalent lanthanides and actinides from aqueous fluoride $[F^-]$ into HDEHP, (H_2D_2), it has been deduced that for $[F^-] = (0.1 - 4.0)10^{-3}$M and pH = 3.60 substances other than $M(HD_2)_3$ contribute appreciably to the metal ~~ion, M^{3+}_{aq}~~, distribution. From known equilibrium constants for aqueous fluoro metal complexes of Y^{3+}, it was concluded that under the prevailing experimental conditions, a substance of the form $MF_3.3H_xD_x$ (where x is an unknown integer) also extracts. A method was thus evolved whereby distribution data alone were made to yield equilibrium constants for the stepwise formation of the first three complexes for La^{3+}, Ac^{3+}, Am^{3+} and Cm^{3+} at $\mu = 0.500$ $(NaClO_4)$. Under similar conditions it was observed that Sc^{3+} and In^{3+} extract overwhelmingly as $M(HD_2)_3$ and $\beta_1 - \beta_4$ are obtained in good agreement with published values. Tests which throw light on the nature and number of the principal metal species which extract, are described. β_1 and β_2 values were only reported for Ce^{3+}, Eu^{3+} and Gd^{3+} fluoride systems because of limited distribution data. 1:1 and 1:2 metal-ligand complexes were formed with sulphate and oxalate over the range of ligand studied by HDEHP extraction methods. Only $M(HD_2)_3$ extracts when these ligands and lactate, pyruvate and alaninate are present in the aqueous phase. The equilibrium constant for sulphato and oxalato complexes for Ac^{3+}, La^{3+}, Eu^{3+}, Am^{3+}, Cm^{3+} and In^{3+} at $\mu = 0.500$ were reported. The application of liquid-scintillation counting to such partition studies with α-emitters is discussed. The interaction of lactate, alaninate and pyruvate with Am^{3+} and Eu^{3+} at an ionic strength of 2.000 in aqueous solution were also studied by the HDEHP extraction method. The stability constants, $\beta_1 - \beta_3$, for these systems in addition to europium propionate studied by a potentiometric titration method were reported.

Using the equilibrium data from the HDEHP extraction method the distribution of positively charged cationic complexes partitioning into the cation-exchanger has been studied and compared with distributions for the 'free' metal ions. Partition of trivalent rare earths, actinides, indium and scandium from fluoride and sulphate solutions have been examined. The results show the partition of $M(SO_4{}^{+})_{aq}$, MF^{2+}_{aq} and $MF_2{}^{+}{}_{aq}$ into the resin. Except for

Sc^{3+} and In^{3+} where only M^{3+}_{aq} and MF^{2+}_{aq} partition~~s~~ into the resin, detailed study with Y^{3+}, La^{3+}, Am^{3+}, Cm^{3+} showed that $MF^{+}_{2\,aq}$ participates in cation-exchange more than MF^{2+}_{aq}, but apparently to a lesser extent than M^{3+}_{aq}.

HDEHP in toluene and the cation exchange resin have also been examined for the measurement of equilibrium constants for hydrolytic reaction in very dilute aqueous solutions of In^{3+} and La^{3+} at constant ionic strength $\mu = 3.000$. HDEHP provides a satisfactory means of measurement for In^{3+} but not La^{3+} which necessitates working at such low hydrogen ion concentrations, $\leq 10^{-8}$M, as to cause HDEHP to partially transfer to the aqueous phase. Secondary metal ion exchange by the cation exchanger prevented a satisfactory analysis of the partition data from this source.

An 'Orion' fluoride-sensitive membrane electrode has been examined critically for the measurement of metal-fluoride association in aqueous solutions, with a calomel reference electrode and sodium chloride salt bridge. Measurements were made with Mg^{2+}, Ca^{2+}, Sc^{3+}, Fe^{3+}, Eu^{3+} and Gd^{3+} at 25°C; Y^{3+}_{aq} and H^{+}_{aq} were studied at 15, 25 and 35°C and enthalpy and entropy changes calculated. The electrode is limited to solutions 10^{-6}M or greater in free $[F^{-}]_{aq}$, with a consequent limitation on the magnitude of the first-association constant to $\leq 10^{6}$.

Further limitations are imposed by the insolubility of most metal fluoride salts. The electrode is less sensitive than the iron(III)-iron(II) electrode system, but is much more convenient. Good agreement with the results from other methods was obtained.

The results obtained are discussed and compared where possible with existing data, mechanistic explanations and theories.

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CHAPTER I

INTRODUCTION

Several theories have been advanced over the last 100 years or so to explain the behaviour of ions in solution. The ionisation theory attributed to Arrhenius[1] postulated that electrolytes are completely dissociated into their constituent ions in the limit of infinite dilution; the equivalent conductance of the free ions is independent of concentration and the equilibrium between the ions and the undissociated molecules giving rise to them conforms to the law of mass action[2]. It is now known that the original postulate is invalid since the mobility of the free ions decrease with increasing concentration owing to interaction between ions of opposite charge.

In 1920 the specific ion interaction theory was advanced by Brønsted[3]; it was based on the postulation that chemical interaction is limited to that between ions of opposite sign. The first statistical theory of the behaviour of electrolytes in solutions, the interionic attraction theory, was that developed by Debye and Hückel[4] and its application has been remarkably successful in interpreting the appropriate properties of very dilute solutions. From the theory it is sought to calculate the average potential energy of a given ion in solution due to all the other ions, assuming the medium to have the dielectric constant of the pure solvent. Strong electrolytes assumed to be completely dissociated into ions at all concentrations in solution showed deviations from the behaviour predicted by this theory; the discrepancies are ascribed to electrical interactions between ions at sufficiently high concentrations. In dilute solution of a binary electrolyte the chemical potential of the solute, U, is adequately described thermodynamically by the equation

$$U = U^{o} + RT \ln C + RT \ln \gamma_{\pm} \qquad (1.1)$$

where U^{o} is the standard chemical potential, C the molal concentration and $\gamma_{\pm}$ is the mean molal activity coefficient of the electrolyte. The extra free energy represented by third term on the right hand side of equation (1.1) mainly reflects the energy of interaction due to the electrical charges on the ions.

Debye and Hückel calculated the electrostatic contribution of ions to the free energy and the mean molal activity coefficient of the ions by the limiting law

$$\log f_{\pm} = -|Z_{+}Z_{-}|A\mu^{\frac{1}{2}} \qquad (1.2)$$

where $\mu(=\frac{1}{2}\Sigma C_{i}Z_{i}^{2})$ is the ionic strength (C_i being the concentration and Z_i the charge on the ion i) and A is a constant from the Debye and Hückel theory. For an aqueous solution at 25°C the activity coefficient of a Z-valent ion becomes

$$\log f_Z = -0.509\ Z^2\ \mu^{\frac{1}{2}} \qquad (1.3)$$

On considering the finite sizes of the ions the modified ionic activity coefficient is

$$\log f_Z = \frac{-AZ^2\mu^{\frac{1}{2}}}{1 + Ba\ \mu^{\frac{1}{2}}} \qquad (1.4)$$

where B is another constant such that

$$10^8\ B = \frac{(8\Pi Ne^2)^{\frac{1}{2}}}{(10^3 K\epsilon T)^{\frac{1}{2}}} \qquad (1.5)$$

and "a" may be thought of as the mean effective diameter of the ions in the solution or as the distance of closest approach. Other workers, e.g. Davies[5], have used the full Debye-Hückel expression with an additional linear term introduced as an empirical correction to allow for the short range ion-solvent interactions

$$\log f_Z = -\frac{AZ^2\ \mu^{\frac{1}{2}}}{1 + Ba\ \mu^{\frac{1}{2}}} + c'I \qquad (1.6)$$

The proposed formula of Davies with $c = 0.2$ has the form of the modified Debye-Hückel equation suggested by Guggenheim[6]. It corresponds to one with an "a" value in equation (1.4) of 4.2 - 4.4°A for 2-2 electrolytes up to $\mu = 0.1$. It has been shown that the equation is in good agreement with the actual values of mean ionic activity coefficients for dilute solution of 1-1, 1-2 and 2-1 electrolytes.

Ion association or complex formation

In an electrolyte although there is a continual interchange of ions, nevertheless the possibility exists for formation of what amounts to a new entity in the solution, the ion pair, persisting through a number of collisions with solvent molecules. This 'species' was first recognised by Bjerrum[7] in 1926. Thus in discussing the properties of a weak electrolyte in solution, we may have in addition to the free ions and possible undissociated neutral molecules, ion pairs in which the ions are separated by one or more solvent molecules. When the ions interact directly, i.e. where solvent molecules do not separate them, they are considered to have formed a complex ion or molecular species. Ion association in a solution of an electrolyte M_pL_n may be expressed by the equilibrium

$$M^{n+} + L^{-p} \rightleftharpoons ML^{(n-p)+} \qquad (1.7)$$

The activity of the species in solution are related to K, the thermodynamic constant, by the relation

$$K = \frac{a_{ML^{(n-p)+}}}{a_{M^{n+}}\, a_{L^{p-}}} \qquad (1.8)$$

where 'a' represents activity.

By introducing the activity coefficient terms, f, into this expression

$$K = \frac{[ML^{(n-p)+}]}{[M^{n+}][L^{-p}]} \cdot \frac{f_{ML^{(n-p)+}}}{f_{M^{n+}} \, f_{L^{-p}}} \qquad (1.9)$$

or

$$K = Kc \cdot \frac{f_{ML^{(n-p)+}}}{f_{M^{n+}} \, f_{L^{-p}}} \qquad (1.10)$$

where Kc is the 'concentration quotient'. Terms in square brackets represent concentrations. Thus the evaluation of K requires a knowledge of the values of the activity coefficients of the various species. By substituting activity coefficients from equation (1.6) into equation (1.10) we obtained

$$\log K = \log Kc + \frac{(\Delta Z^2)A\mu^{\frac{1}{2}}}{1+Ba\mu^{\frac{1}{2}}} - c'\mu \qquad (1.11)$$

where ΔZ^2 is the difference between the square of the ionic charge on $ML^{(n-p)+}$ and the sum of the squares of the charges on M^{n+} and L^{-p}. Values for thermodynamic association constants ($\mu = 0.0$ M) are calculated using this equation.

The question arises as to how close the ions have to be to each other before they can be considered to have lost their thermodynamic independence. This problem was tackled by Bjerrum[7] who, from purely electrostatic considerations defined a distance $q = -Z_+Z_-e^2/a\epsilon KT$

between the oppositely charged ions within which they are to be considered as being associated into ion pairs and he postulated the now classical equation for the association constant.

$$K = \frac{4\Pi N}{1000} \int_a^q \exp\left[\frac{-Z_+Z_-e^2}{\epsilon rKT}\right] r^2 dr \qquad (1.12)$$

where r is the distance between the centres of the two ions. The Bjerrum equation predicts greater ion pair formation the higher the valencies Z_+ and Z_- and the smaller the dielectric constant ϵ of the medium. This is in qualitative agreement with experimental results. The theory has been criticised however, because of the somewhat arbitrary cut-off distance q which must be imposed in order to make possible the solution of the divergent integral in equation (1.12) and it has now largely been superseded by the proposals of Denison and Ramsey[8] and Fuoss and Kraus[9]. These workers argued that the association constant must be given, to a first approximation, by the equation

$$\ln K = \ln K^o - Z_+Z_-e^2/a\epsilon KT \qquad (1.13)$$

and regarded only those ions in actual contact as forming ion-pairs. In this way the difficulty encountered by Bjerrum of considering ions not in physical contact as those constituting ion-pairs is avoided. K^o in equation

(1.13) is the association constant for two uncharged particles in the solution.

The limiting form of the Debye-Hückel equation at low concentrations has also been derived in several other ways in the theories of e.g. Kirkwood and Poirier[10] and Mayer[11]. In all these theories formidable mathematical problems make it very difficult to proceed beyond the limiting law stage, and only for the cluster theory of Mayer[11] has it been possible to provide some basis for comparison of theory and experiment. Considerable advances have been made by Friedman[12] and his associates who have developed a theory of ionic solutions based upon the cluster model. The main difficulty in all this work is the problem of finding a satisfactory physical picture or model for the system which is in accord with the mathematical description.

There are currently two main approaches to studies of ion association or complex formation. In one, the derivation of 'true' or thermodynamic association constants is one of the major goals. This improves the restriction that measurements must be confined to very dilute concentrations where Debye-Hückel theory is valid or where any error arising from concentration effects are kept to a minimum. The restriction imposed often means that accurate measurements can only be obtained by sensitive methods and the use of very pure substances since the calculations depend on rather small differences in the measurements or on the concentration of ion pairs or complexes derived from them. In much of this work only the first product of ion association, namely the interaction of cations and anions in a 1:1 ratio is considered.

The second approach with which workers in the Scandanavian countries are particularly associated, permits the study of a wide range of cation:anion ratios, keeping the total ionic strength constant. In this way the presence of significant concentrations of the major associating species leads to further stages of association than are usually revealed from thermodynamic studies. Of necessity, the total ionic strength is kept high so that the evaluation of 'true' thermodynamic constants using appropriate theoretically or empirically based relations as discussed earlier is frequently precluded. In addition it is assumed that ion association or complex formation between the 'inert' salt that is used to maintain a constant ionic strength and the ions of the electrolyte under investigation is negligible.

The interaction between a hydrated metal ion, M^{n+}_{aq}, and an anion, L^{p-}_{aq}, or a neutral ligand may involve a number of solvated species which participate in a series of equilibria represented by

$$M^{n+}_{aq} + L^{p-}_{aq} \rightleftharpoons \left(M^{n+}_{aq},L^{p-}_{aq}\right) \rightleftharpoons \left(M^{n+}H_2OL^{p-}\right)_{aq} + xH_2O$$

$$\rightleftharpoons \left(ML^{(n-p)+}\right)_{aq} + (x+1)H_2O \qquad \ldots. \; (1.14)$$

Thus the ion-pairs formed in the solution need not be identical, and we can make a formal distinction between outer and inner sphere species. In the former, one or at most two, solvent molecules are interposed between the interacting ions, whilst in the latter, the ions are adjacent to one another. Different methods are used to recognise these alternatives in the determination of association constants. In place of the terms 'outer sphere' and 'inner sphere' many workers[5,13] have used ion-pair and complex respectively to distinguish between the two types of species. In an ion-pair the bonding is entirely due to the long-range electrostatic forces between the oppositely charged ions whereas in complexes, short range or covalent forces can contribute to the stability. Taube and Posey[14], Eigen and Tamm[15], and Atkinson and Kor[16] experimentally obtained evidence for such ion-pairs and complexes in their studies of bivalent metal sulphates in water.

In the association of a metal cation and an anion the concentrations can be selected so that essentially only mononuclear species (containing one metal ion) are formed in the solution. The present investigation is mainly concerned with such cases in aqueous solution. The formation of hydrolytic and polynuclear (containing more than one metal ion) species following especially from the work of Sillén and his associates has been adequately summarised by Rossotti[17,18]. The association constants for a number of metal ion complexes of the mononuclear type were studied in the laboratories of Abbey and Bodlander[19] and N. and J. Bjerrum[20] in the first two decades of this century. A comprehensive table of the stability constants of metal ions with inorganic and organic ligand, has been compiled by Sillen and Martell[21].

Ion-association, following Bjerrum[20], can be regarded as a stepwise process involving the equilibria

$$\begin{array}{ccccc} M^{n+} & + & L^{p-} & \overset{K_1}{\rightleftharpoons} & ML^{(n-p)+} \\ ML^{(n-p)+} & + & L^{p-} & \overset{K_2}{\rightleftharpoons} & ML_2^{(n-2p)+} \\ \vdots & & \vdots & & \vdots \\ ML_{m-1}^{(n-(m-1)p)+} & + & L^{p-} & \overset{K_m}{\rightleftharpoons} & ML_m^{(n-mp)+} \end{array} \qquad (1.15)$$

In these equations associated water is omitted, m is the maximum coordination number of metal ion M^{n+} and K_1, K_2 ... K_m are the stepwise formation constants. The overall stability constant β_m, can be defined according to

$$\beta_m = \frac{[ML_m^{(n-mp)+}]}{[M^{n+}][L^{-p}]^m} \qquad (1.16)$$

and is related to stepwise formation constants, K_m,

$$K_m = \frac{[ML_m{}^{(n-pm)+}]}{[ML_{m-1}][L^{-p}]} \qquad (1.17)$$

by

$$\beta_m = K_1 \cdot K_2 \cdot K_3 \ \ldots . \ K_m \qquad (1.18)$$

In practice, $\bar{n}$, "the ligand number", that is the average number of ligands L bound to each M is measured. Omitting the charges for convenience

$$\bar{n} = \frac{\text{concentration of ligand bound to metal}}{\text{total metal concentration}} \qquad (1.19)$$

$$= \frac{[ML] + 2[ML_2] + 3[ML_3] + \cdots}{[M] + [ML] + [ML_2] + [ML_3] + \cdots} \qquad (1.20)$$

$$= \frac{\sum_{o}^{m} m\beta_m[L]^m}{1 + \sum_{o}^{m} \beta_m[L]^m} \qquad (1.21)$$

$$= \frac{\beta_1[L] + 2\beta_2[L]^2 + 3\beta_3[L]^3 + \ldots m\beta_m[L]^m}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \ldots \beta_m[L]^m} \qquad (1.22)$$

On rearrangement,

$$\frac{\bar{n}}{(1-\bar{n})[L]} = \beta_1 + \frac{2-\bar{n}}{1-\bar{n}}\beta_2[L] + \frac{3-\bar{n}}{1-\bar{n}}\beta_3[L]^2 + \ldots . \qquad (1.23)$$

Computation of stability constants from experimental data

Monk[22] and Rossotti[18] have discussed available methods of computation; these depend upon the $\bar{n}$, [L], [M] or $[ML_m]$ parameters measured. Bjerrum[20] has devised a number of methods, some of which give approximate answers, which may then be used to obtain more accurate values by refined treatments.

There are two methods of solving equation (1.21). One method involves a least square treatment of $\bar{n}$ and [L] preferably with the aid of an electronic digital computer. The use of appropriate computer programmes greatly simplifies the calculation burden. The second method was developed by Fronaeus[23] from earlier studies by Bjerrum[20].

Dividing equation (1.21) by [L] gives

$$\frac{\bar{n}}{[L]} = \frac{\sum\limits_{m=1}^{m} m\beta_m[L]^{m-1}}{1 + \sum\limits_{m=1}^{m} \beta_m[L]^m} \qquad (1.24)$$

If we assume that

$$X = \sum_{m=1}^{m} \beta_m[L]^m \qquad (1.25)$$

then equation (1.24) becomes

$$\frac{\bar{n}}{[L]} = \frac{dX}{X} \qquad (1.26)$$

which on integration yields

$$\ln X([L]_j) = \int_o^{[L]_j} \frac{\bar{n}}{[L]}\, d[L] \qquad (1.27)$$

Numerical and graphical integration of equation (1.27) gives the corresponding values of X and [L]. The quantities β_1, β_2 ... β_m can be calculated by extrapolation to [L] = o for the functions X_1, X_2, ... X_m when these are defined as

$$X_1 = \frac{X-1}{[L]} = \beta_1 + \beta_2[L] + \beta_3[L]^2 + \ldots \beta_m[L]^{m-1} \quad (1.28)$$

$$X_{m-1} = \frac{X_{m-1} - \beta_{m-2}}{[L]} = \beta_{m-1} + \beta_m[L] \quad (1.29)$$

These methods where $\bar{n}$ and [L] are determined for the measurement of stability constants, however, do not differentiate between ion pairs and complexes in the system under study.

Determination of stability constants

In planning a study of a particular complexing system there are some general points to be considered. In the first place it is possible to use a number of complementary physical methods such as spectrophotometry and potentiometry thus simplifying considerably the calculations of the concentrations of ionic species. Secondly we must decide whether to study the system at low concentrations so that activity corrections can be made in the calculation of thermodynamic association constants, or whether to use a medium of constant ionic strength. The choice will depend upon how the results are to be related to work done on similar systems of interest perhaps by other workers.

Methods of studying chemical equilibria have been discussed by Rossotti[18] under the following headings.

1. Methods that determine the concentration of individual species, e.g. potentiometry, polarography and partition methods.
2. Methods based on colligative properties, e.g. cryoscopy and ebullioscopy.
3. Methods that involve the study of physical properties, e.g. spectrophotometry (Raman, N.M.R. and U.V.), magnetic susceptibility, conductance, enthalpy change in chemical reaction.
4. Other methods like electrophoresis, dielectric polarization, ultrasonic absorption, dialysis and light scattering.

Methods from group 1 have been widely used for the measurement of successive equilibrium constants. Potentiometry and the partition methods are discussed here at some length because in the present investigation these techniques were used.

Potentiometric method

Numerous potentiometric methods have been applied to measurements of chemical equilibrium. The methods are divided into two types. In the first type 'free' metal ion is determined, e.g. using an amalgam electrode which responds directly[24,25] or indirectly[26] to metal ions, or redox electrodes[20,27]. Free ligand, [L], which can be measured directly using electrodes reversible to anions, for example halides, sulphates or oxalates, constitute the second type. An indirect procedure involving competition of M^{n+} with hydrogen ions or chosen auxiliary metal ions is convenient for ligands which are conjugate bases of weak acids. The value of [L] is calculated from the measurement of hydrogen ion concentration, provided that the stability constants of various acids H_jL have previously been determined.

Potentiometric concentration probes, using hydrogen[28], quinhydrone[29], or glass electrodes[30] are best, but acid-base indicators have also been used[31] for hydrogen ion measurement. The method was first used in the study of metal amines by Bjerrum[20], who kept the total concentration of dissociable hydrogen ion in the system constant, and varied the hydrogen ion concentration, [H], by changing the concentration of the total ligand species. However, a wide variation of [H] and hence of [L] and a conservation of ligand is possible in the Calvin-Wilson modification[32], in which total ligand concentration is kept constant, but [H] varied by the addition of acid or alkali. Either procedure is conveniently carried out titrimetrically. Care should be taken to avoid the range of [H] in which metal ion is hydrolysed or ligand is partially decomposed.

Systems which contain auxiliary metal ion giving rise to competition for ligand have also been used widely. They are particularly convenient when the free concentration of the auxiliary species can be determined potentiometrically. Brosset and Orring[27,33], and later Connick and Tsao[34] and Wilson and Taube[35] have used iron(III) as an auxiliary ion in studies of metal fluoro complexes. Copper(II)[36], silver(I)[25], and mercury(II)[37] have also been used as auxiliary ions in potentiometric studies of metal complexes.

Partition methods

Ion exchange, liquid-liquid extraction and solubility measurements are the three partition methods widely applied to chemical equilibrium studies. The solubility method is the oldest of these; measurements are limited, however, by the fact that in saturated solutions there is only one degree of freedom in the concentration of the components, whereas in unsaturated solutions there are two. The solubility measurement cannot provide information on the state of aggregation in the solution phase. Because of this limitation the method has not been used in the present study. Ion exchange and liquid-liquid extraction methods are now mainly employed especially in conjunction with radioactive tracers.

Ion exchange

Ion exchange materials particularly of the synthetic organic type, have been increasingly used in elucidating information about equilibria in solution and the apparent composition of the association products which form in ionic solutions. Much of the work reported up to 1953 dealing with the application of cation exchange resins and radioisotopes as tracers for obtaining stability constants has been reviewed by Schubert[38]. Marcus[39,40] has also summarised results of studies of ion-pair and complex formation by ion exchange methods.

The equilibrium established when a cation exchange resin in say the sodium form Na^+X^- is in contact with a solution containing M^{n+} ions, may be written

$$nNaX + M^{n+} \rightleftharpoons MX_n + nNa^+ \qquad (1.30)$$

and the equilibrium quotient at constant ionic strength

$$k = [M^{n+}]_R[Na^+]/[M^{n+}][Na^+]_R \qquad (1.31)$$

where $[\,]_R$ represents concentration in the resin phase expressed in suitable units such as mole g^{-1} of dry resin. Addition of an anion L^{-p} capable of interacting with M^{n+} will cause a redistribution of free M^{n+} ions between the resin and the solution by an amount which is quantitatively related to the extent to which M^{n+} is bound by the anion.

Fronaeus[41] developed a graphical solution applicable to systems of the type $M^{2+} - L^{-}$, where M^{2+} and the first complex are taken up by the cation exchanger. By assuming that the higher complexes neutral or negative in electrical charge do not take part in exchange, he obtained association constants for the formation of copper(II) and nickel(II)-acetate species which agreed with those obtained by a potentiometric method. The method for computing association constants if several complexes are formed is difficult but considerable simplification is possible if radiotracer concentrations of M^{n+} ion (say $\lesssim 10^{-7} Ml^{-1}$) can be used. Under such conditions and with the aqueous phase maintained at a constant ionic strength with a relatively large $[Na^{+}]$, both $[Na^{+}]_R$ and $[Na^{+}]$ are effectively constant and an experimentally determinable distribution coefficient, l, for M^{n+} between resin and solution may be defined by

$$l = \frac{k[Na^{+}]_R}{[Na^{+}]} = \frac{[M^{n+}]_R}{[M^{n+}]} \qquad (1.32)$$

If l_o and l_i are the values of distribution coefficients in the absence and presence of ligand L^{-p} respectively, all other conditions being identical, then

$$l_i \left[[M^{n+}] + [ML^{n-p}] + [ML_2{}^{(n-2p)}] + \ldots \right] = [M^{n+}]_R \qquad (1.33)$$

and

$$l_o\,[M^{n+}] = [M^{n+}]_R \qquad (1.34)$$

so that

$$\frac{l_o}{l_i} = 1 + \beta_1[L] + \beta_2[L]^2 + \ldots\ldots \qquad (1.35)$$

where β_m has the usual meaning and can be obtained from experimental data for $(\frac{l_o}{l_i} - 1)/[L]$ as a function of $[L]$, after making appropriate corrections for the uptake of solvent and swelling of the resin[39]. The model becomes complicated when the complex cationic or perhaps even neutral (in charge) species also partake in the exchange process. Suppose the positively charged complex species are also exchanging into the resin phase and assuming the absence of neutral or negatively charged species in the resin phase we get the distribution, ϕ_R, of the metal ion M^{n+}

$$\phi_R = \frac{[M^{n+}]_R + [ML^{(n-p)+}]_R + [ML_2{}^{(n-2p)+}]_R + \dots}{[M^{n+}] + [ML^{(n-p)+}] + [ML_2{}^{(n-2p)+}] + \dots} \quad (1.36)$$

In the limiting case, that is in the absence of ligand,

$$\phi_R = \phi_R^o = l_o = \frac{[M^{n+}]_R}{[M^{n+}]} \quad (1.37)$$

The distribution of the m^{th} partially complexed species into the resin phase can be defined as

$$l_m = \frac{[ML_m^{(n-mp)+}]_R}{[ML_m^{(n-mp)+}]} \quad (1.38).$$

and
$$\phi_R = \frac{l_o[M^{n+}] + l_1[ML^{(n-p)+}] + l_2[ML_2{}^{(n-2p)+}] + \dots}{[M^{n+}] + [ML^{(n-p)+}] + [ML_2{}^{(n-2p)+}] + \dots} \quad (1.39)$$

$$= l_o \frac{1 + \frac{\beta_1 l_1}{l_o}[L] + \frac{\beta_2 l_2}{l_o}[L]^2 + \dots\dots}{1 + \beta_1[L] + \beta_2[L]^2 + \dots} \quad (1.40)$$

let $$l'_m = \frac{\beta_m l_m}{l_o} \qquad (1.41)$$

and rearranging

$$\left(\frac{l_o}{\phi_R} - 1\right)/[L] = \phi_{1R} = \frac{(\beta_1 - l'_1) + (\beta_2 - l'_2)[L] + (\beta_3 - l'_3)[L]^2 + \ldots}{1 + l'_1[L] + l'_2[L]^2 + l'_3[L]^3 + \ldots.} \qquad (1.42)$$

It is seen that the determination of β_m needs the values of parameters l'_m or vice versa. Values for β_n obtained by other methods can be used to calculate l'_m and therefore l_m. The direct determination of β_m values from the ion exchange data alone was carried out by a procedure used by Fronaeus[41]. He defined the terms f and g in order to establish a method of computation.

$$f = \left(\frac{l_o}{\phi_R}\right)[(\beta_1 - l'_1)[L] - 1]/[L]^2 \qquad (1.43)$$

and $$g = [f - \beta_1\phi_{1R} + l_o\phi_R^{-1}(\beta_2 - l'_2)]/[L] \qquad (1.44)$$

The ion exchange method in general suffers from the large number of parameters which may be needed for an adequate description of the partition of the metal species.

Liquid-liquid extraction

The partition of a solute between an aqueous solution and an immiscible organic solvent may be used to investigate equilibria in solution. If ion-association occurs in the aqueous phase due to the presence of a ligand anion and assuming that only an uncharged species is present in the organic phase a study of the effect of ligand concentration on the partition equilibrium will yield the stability constants for the metal-ligand species. The range of extractant for use with aqueous phases is extremely wide and is continually being extended. A number of accounts[42-44] of the extraction of various metal ions with many different extractants have been published. Irving and coworkers[42] gave the quantitative treatment for metal complex equilibria in solvent extraction where account was made for all possible sorts of species partaking in the equilibrium.

Connick and McVey[45] gave an important variant of the method using an organic solvent containing a strong complexing agent, HD, capable of forming inner complexes with the metal ion but itself negligibly soluble in the aqueous phase. The distribution of the metal ion, M^{n+}, between aqueous and organic phases was then measured at various concentrations of an added ligand, L^{p-}, with which the metal formed complexes.

If it is assumed that the metal exists wholly in the form of the complex, MD_n, in the organic phase, the results can be used to calculate the stability constant of complexes between M^{n+} and ligand L^{p-} according to the following procedure. Assuming the extraction is a proton transfer reaction and that partially complexed species are not extracted into the organic phase.

$$M^{n+} + nHD \overset{K}{\rightleftharpoons} MD_n + nH^+ \qquad (1.45)$$

where K is the equilibrium constant for the reaction. The distribution coefficient, ϕ_L, for M^{n+} can be defined as

$$\phi_L = \frac{[MD_n]}{[M^{n+}] + [ML^{(n-p)+}] + [ML_2^{(n-2p)+}] + \ldots} \qquad (1.46)$$

Substituting for

$$[MD_n], [ML^{(n-p)+}], [ML_2^{(n-2p)+}], \ldots.$$

we get

$$\phi_L = \frac{K[M^{n+}][HD]^n[H^+]^{-n}}{[M^{n+}] + \beta_1[M^{n+}][L^{-p}] + \beta_2[M^{n+}][L^{-p}]^2 + \ldots} \qquad (1.47)$$

In the absence of the ligand ($[L^{-p}] = o$)

$$\phi_L = \phi_L^o = k^o = K[M^{n+}][HD]^n[H^+]^{-n} \qquad (1.48)$$

On substitution and rearrangement

$$\left(\frac{k^o}{\phi_L} - 1\right)/[L^{-p}] = \phi_{1L} = \beta_1 + \beta_2[L^{-p}] + \beta_3[L^{-p}]^2 + \ldots \quad (1.49)$$

From the graphical analysis of the plot of ϕ_{1L} against $[L^{-p}]$ or by a least square treatment one can calculate the stability constants $\beta_m (m = 1,2,3 \ldots)$ of metal complexes in the aqueous solution using equation (1.49).

A number of complexes of thorium with organic and inorganic ligands have been investigated[46,47] by employing as extractant a benzene solution of thenoyltrifluoroacetone (TTA). Peppard and his associates[48,49] have made similar studies on chloride and nitrate ion complexes with a number of lanthanides and actinides, where phosphoric acid esters in toluene were used as extractants. Choppin and Unrein[50], and Lyle and Naqvi[51] used dinonylnaphthalene sulphonic acid and di-2-ethylhexylphosphoric acid respectively as extracting agents in the study of lanthanide and actinide complexes with a variety of charged ligands.

Outline of the present work

Initially the work undertaken consisted of making improvements to partition methods in the measurement of stepwise stability constants for metal ions in aqueous solutions maintained at constant ionic strength. The metal ions of main interest were lanthanides and trivalent actinides. The methods were to be developed primarily for measurements on metal ion systems where radioactivity made it difficult or impossible, because of radiolytic effects, to work at appreciable metal concentrations. The ligands used were those of the 'hard' donor type[52-56], like fluoride and oxygen containing anions, which form strong complexes or ion-pairs with the hard trivalent lanthanide and actinide acceptors. Both inorganic and organic oxygen containing ligands (e.g. sulphate, hydroxyl, oxalate, propionate, lactate, alaninate and pyruvate) were used in this study. Fluoro complexes were of particular interest because of the limited existing data which was confined to equilibrium values for the first complex only for these classes of metal ion.

A liquid-liquid extraction method using di-2-ethylhexylphosphoric acid (HDEHP)-toluene solution was mainly used in the work undertaken. The extraction behaviour of the trivalent metal ions into HDEHP-toluene solution was critically examined. Yttrium-, scandium- and indium-fluoride systems for which reliable stability constant data is available in the literature were especially studied to provide checks on the liquid-liquid extraction method developed to measure the stability constants for the other metals. A cation-exchanger, Zeo Karb-225, was also used to study the distribution behaviour of trivalent rare earths, actinides, scandium and indium in their partition into this resin from an aqueous solution containing fluoride, sulphate, oxalate and hydroxide ligands. The data thus obtained was combined with that from the liquid-liquid partition experiments in order to get information about the ion-exchange distribution of partially complexed metal cations relative to the corresponding aquo cations.

During the course of the present work a fluoride ion sensitive membrane electrode[57] became available commercially. It was examined as part of a suitable cell for the measurement of the equilibrium constants of a range of metal ions (rare earths, scandium, iron(III), magnesium and calcium) to determine its limitations in this field. A comparison was made with the iron(II)-iron(III) half-cell for this purpose. These electrodes were examined in order to obtain a check on equilibrium constants derived from distribution measurements with HDEHP. By measuring stability constants for the hydrogen- and yttrium-fluoride systems as a function of temperature enthalpy and entropy changes were obtained for comparison with recently[58] published values which are not consistent with earlier[59] but fragmentry studies.

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CHAPTER II

Potentiometric methods in the study of metal-fluoride complex formation

INTRODUCTION

The fluoride ion membrane electrode was discovered recently by Frant and Ross[1] and it has been found applicable in the course of the present work to the measurement of free fluoride ion in a solution containing metal ions.

The essential component of a fluoride ion membrane electrode is a single crystal of lanthanum fluoride doped with europium(II), in the form of a disc about 1 cm in diameter and a few millimetres thick, cemented into the end of a polyvinyl chloride plastic tube (Fig. 2.1). A commercial version of the electrode is available from Orion Research Inc., Cambridge, Mass., U.S.A. The internal solution is typically a mixture of 0.1M sodium fluoride and 0.1M sodium chloride although other concentrations of fluoride and chloride ions may be employed to adjust the range of operating potential. The potential of the internal silver-silver chloride electrode is fixed by the chloride ion activity, and the fluoride ion activity controls the potential of the inner surface of the lanthanum fluoride membrane. When the electrode is

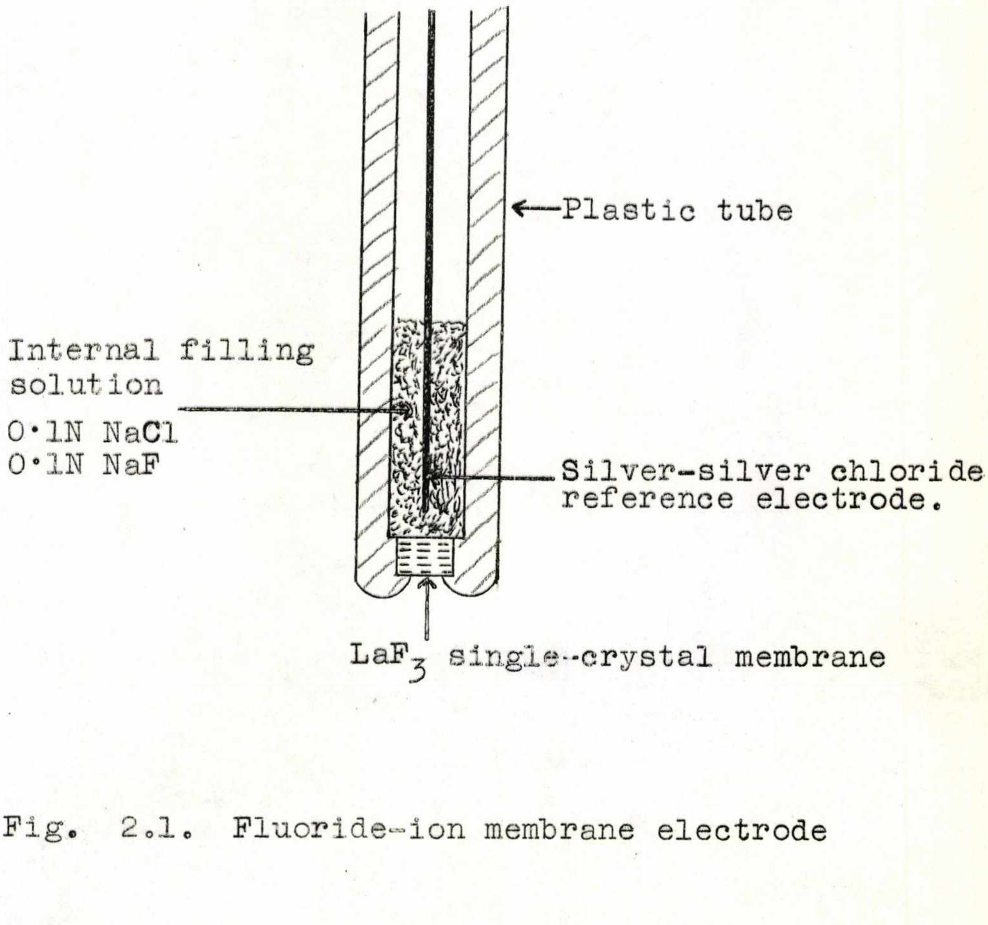


Fig. 2.1. Fluoride-ion membrane electrode

immersed in a fluoride solution an electrical potential difference is established across the membrane, the magnitude of which depends on the ratio of fluoride ion activities in the inner and outer solutions. When this electrode is paired with a reference electrode, e.g. calomel, the e.m.f., E, of the cell,

$$Ag|AgCl|Na^+Cl^-,F^-|La(Eu(II))F_3|\text{test solution}|NaCl_{(sat)}|Hg_2Cl_2|Hg$$

is given by a Nernst type relation

$$E = \text{constant} - \frac{RT}{F}\ln a_{F^-} \qquad (2.1)$$

where a_{F^-} is the fluoride ion activity.

Mesmer[2] and Frant and Ross[1] observed that the common anions, chloride, nitrate, acid carbonate and sulphate do not interfere in the functioning of the electrode. Lingane[3] first studied the application of the electrode to end-point detection in the titration of fluoride ion with thorium, lanthanum and calcium and later he showed[4] that phosphate and acetate are without effect on its performance. Srinivasan and Rechnitz[5] demonstrated that the electrode has a high response to fluoride activity (a_{F^-}) in highly acidic media. Vanderborgh[6] on the other hand examined the electrode for the measurement of the association of hydrogen and fluoride ions in a sodium perchlorate media at an ionic strength $\mu = 1.000$. The results demonstrate the application of this electrode to such measurements at high ionic strengths without interference from the perchlorate ion.

The metal ion systems investigated are, in the main, those for which equilibrium constants have previously been measured by other methods. They cover a range of metal ions (magnesium, calcium, scandium, iron(III), yttrium, europium(III) and gadolinium) sufficient to indicate the limitations arising from the extend of ion-ion interaction. The yttrium fluoride and hydrogen fluoride systems were studied at 15°, 25° and 35°C and enthalpy and entropy changes were obtained applicable to the conditions of measurement.

Another method used was that described by Brosset and Orring[7], whereby ionic interaction involving the fluoride ion were studied by making use of the effect on the known iron(III)-fluoride equilibria on the ferrous-ferric electrode potential. This, the so-called ferri method, was employed mainly to measure equilibrium constants for yttrium fluoride system as a contribution to the work described in Chapter III for obtaining reliable equilibrium data. A less detailed study was also carried out on the iron(III) fluoride system.

EXPERIMENTAL

Chemicals

All the chemical substances used were of reagent grade. The stock solutions of sodium fluoride and sodium perchlorate were prepared by neutralising the appropriate volumes of corresponding standard acid and alkali. Sodium fluoride solution was stored in a polythene bottle. The (III) oxides of the rare-earths, gadolinium, europium, yttrium and scandium supplied by Koch-Light, Colnbrook, England, all of 3N quality or better, were heated to remove carbonate before dissolution in perchloric acid to give standard solutions. The rare earth metal ion concentration was determined[8] by EDTA titration using xylenol orange as indicator and a buffer of pH 5.2. Iron, of high purity, in the form of granules (British Chemical Standard No. 149/2) was supplied by the Bureau of Analysed Samples, Ltd., Newham Hall, Middlesbrough. The iron was dissolved in perchloric acid and converted to the (III) state by adding a little nitric acid. The iron content in the solution was determined by (i) EDTA titration[8] and (ii) Potassium dichromate titration after reducing the (II) state with tin(II) chloride. Calcium and magnesium perchlorate solutions were prepared by dissolution of 'Specpure' calcium carbonate and magnesium oxide (from Johnson, Mathey and Co. Ltd., Hatton Garden, London) separately in perchloric acid.

The solutions were boiled to remove carbon dioxide completely before further dilution with carbon dioxide free doubly distilled water. The magnesium and calcium contents were checked by EDTA titration method[8]. Stock solutions 10^{-2}M in metal ion (except Mg and Ca which were 0.1 and 0.2M respectively) were made up to an ionic strength of 0.500 using sodium perchlorate. The solutions were adjusted to the required pH by the addition of small increments of very dilute sodium hydroxide to avoid metal hydroxide precipitation.

Apparatus

An Orion model 94-09 fluoride indicator electrode was used. This has an electrical resistance only a little less than most glass electrodes and it is therefore suitable for use with the potentiometer from a pH meter. A calomel electrode immersed in a bridging solution of saturated sodium chloride served as reference electrode. The e.m.f. was measured using a Derritron pH meter fitted with an external spot galvanometer for improved null point detection.

The cell consisted of a polypropylene beaker of about 250 mls capacity surrounded by a jacket for the circulation of water at a constant temperature. The solution was agitated by a mechanical 'minipack' stirrer made of 'teflon'. Measurements were carried out in a cell atmosphere of nitrogen and all the surfaces in contact with the cell solution were constructed from substances substantially inert to fluoride.

In the 'ferri' method the apparatus consisted of three identical polypropylene vessels of 250 ml capacity each fitted with a five-hole rubber bung (for insertion of the platinum electrode, stirrer, and agar salt bridge and inlets for titration and for nitrogen gas). The three half-cells (Fig. 2.2) bridged by 1.6M sodium perchlorate in agar-agar in an effort to minimise electrical resistance and liquid junction potentials, were placed in a thermostatted bath with temperature control to ± 0.1°C. The solutions were agitated by a 'minipack' mechanical stirrer controlled by a power unit. All surfaces in contact with the solution (body of stirrers, inlet for gas, etc.) were made of fluoride inert materials. Increments of titrant were added by micropipette. The electrodes made from high quality platinum sheet and wire were cleaned with dilute nitric acid before use and they were stored in distilled water when not in use. The nitrogen atmosphere above the solutions prevented aerobic oxidation of iron(II). The e.m.f. was measured using a thermocouple potentiometer, type P4, (Croydon Precision Instrument Co. Ltd., England), with an external spot galvanometer for improved null

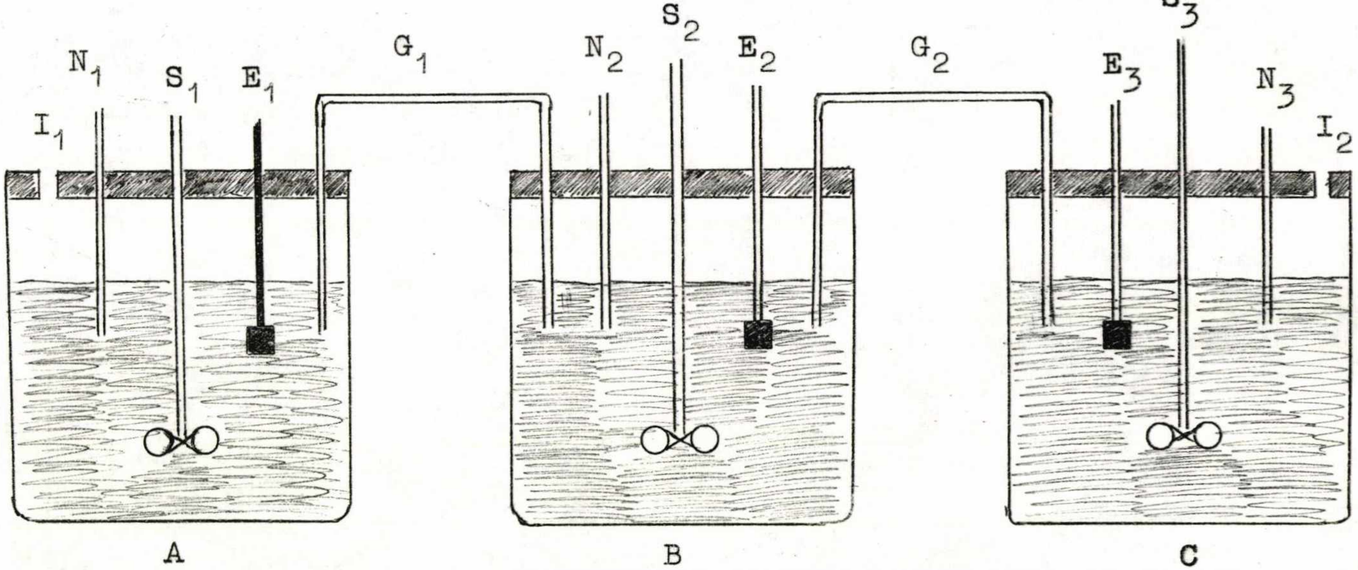


Fig. 2.2. A, B, and C are polypropylene beakers.
N_1, N_2 and N_3 are the inlets for nitrogen.
S_1, S_2 and S_3 are the stirrers.
E_1, E_2 and E_3 are the platinum electrodes.
G_1 and G_2 are the agar-agar salt bridges.
I_1 and I_2 are the inlets for micro pipette and outlets for nitrogen gas.

point detection. A change in e.m.f. of 0.02 mV can be measured accurately on this potentiometer. The potentiometer was checked against a standard cell from time to time during an experiment.

The method using the fluoride ion membrane electrode

The metal ion solution (100 ml) in sodium perchlorate at the required ionic strength and pH was placed in the cell and after establishment of constant temperature aliquot portions (0.1 - 1.0 ml) of fluoride solution, having the same pH, ionic strength and temperature as that of the cell solution, were added. A series of e.m.f. measurements were made with the addition of fluoride solution. Any change in pH of the solution in the cell at the end of a series of measurements was noted and if warranted a subsidiary experiment was performed to determine the change over the range of addition of fluoride ion. Three similar runs were made for each metal-fluoride ion system.

The cell was calibrated for direct fluoride ion concentration measurement by determining the e.m.f. for various known fluoride concentrations at the required pH and ionic strength or by titrating the fluoride solution against sodium perchlorate solution in the absence of the metal ion being studied but otherwise keeping all the conditions the same.

The method using the 'ferri' method

The half-cells consisted of the following solutions:

(A) $NaClO_4$, $HClO_4$, $Fe(ClO_4)_2$, $Fe(ClO_4)_3$

(B) $NaClO_4$, $HClO_4$, $Fe(ClO_4)_2$, $Fe(ClO_4)_3$

(C) $NaClO_4$, $HClO_4$, $Fe(ClO_4)_2$, $Fe(ClO_4)_3$, $M(ClO_4)_3$

where M is the metal ion under study. In all the measurements made here the $Fe(ClO_4)_2$ and $Fe(ClO_4)_3$ concentrations were 4.25×10^{-4}M and 4.75×10^{-4}M respectively and the $HClO_4$ concentration was $(1-3) \times 10^{-2}$M. Steps were taken to maintain constant ionic strength between the three half-cells. Aliquot parts of a solution of sodium fluoride (0.5M) at the temperature of the cells were added by micropipette to half-cells (A) and (C) and the e.m.f. was measured until constant (about five minutes). The stirrers were left on while adding the titrant and reading the e.m.f. The differences in e.m.f. of half-cells (A) and (C) arise because of the formation of complexes of ferric fluoride in half-cell (A) and of $MF_m^{(n-mp)}$ and ferric fluoride complexes in half-cell (C).

RESULTS and DISCUSSION

Fluoride ion membrane electrode method

Two typical calibration curves, obtained with the electrode employed in the present study are given in Fig. 2.3. The calibration curve I was obtained by measuring the e.m.f. of various standard fluoride solutions and curve II obtained by titrating sodium perchlorate (100 ml) with 10^{-2}M fluoride solution. Calibration runs were thus performed before and after every main experiment and at different temperatures as required. Because the ionic strength of all the solutions was kept constant, the potentiometric readings could be directly converted to concentration values. In the calculation of the free fluoride ion concentration, $[F]_f$, at pH 3.60, allowance was made for the presence of HF using the K_{HF} (the dissociation constant of HF = $\frac{[H][F]}{[HF]}$) value determined in separate experiments by this electrode system.

The slope of the curves obtained by least squares analysis of the data were in the range 58.5 ± 1.0 mV, i.e. the mean tended to be somewhat lower than the theoretical Nernstian value (59.16 mV) but nevertheless in agreement with the findings of other workers[6]. The discrepancy may arise from a small gradual change in the activity of the fluoride ion over the range of measurements

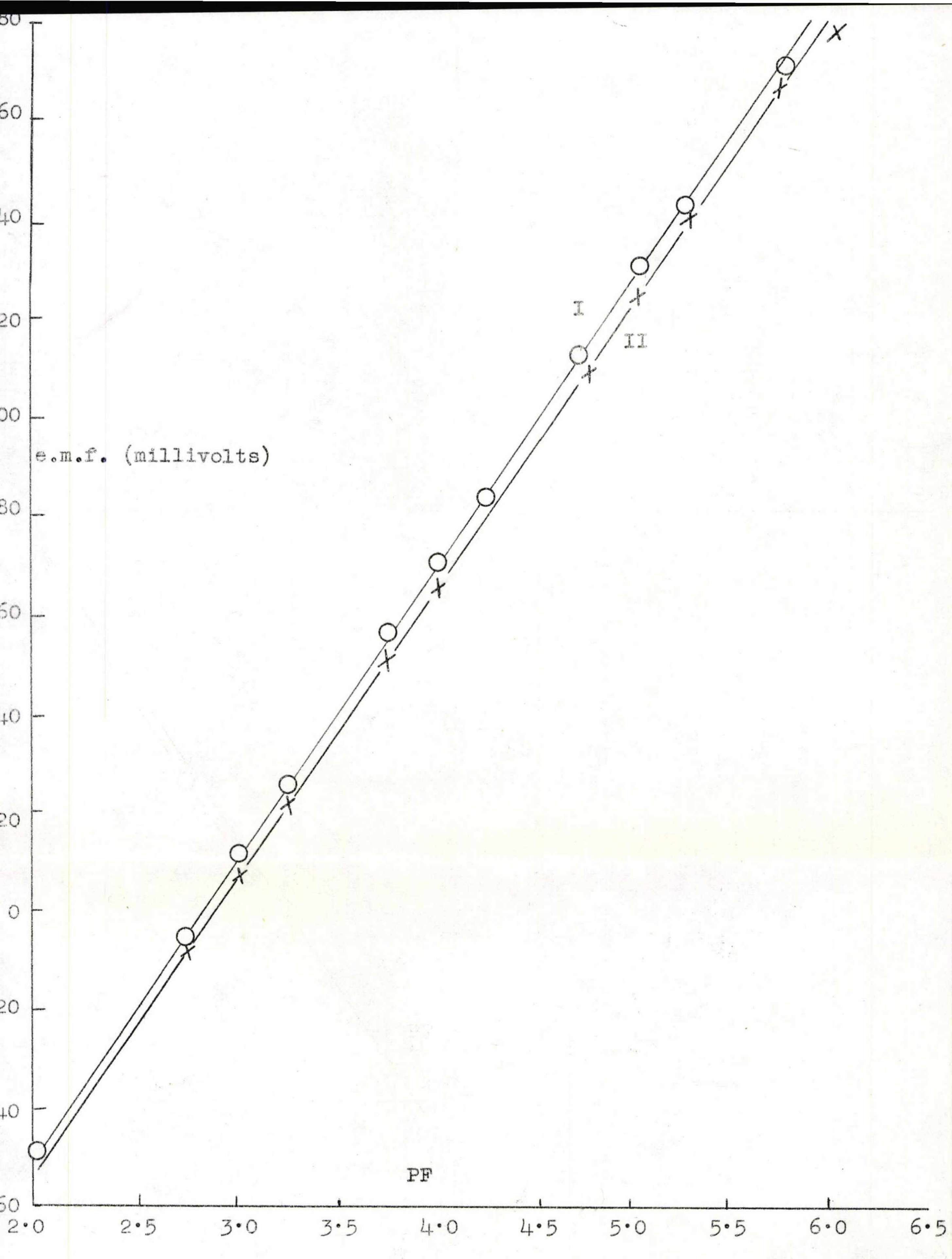


Fig. 2.3. Calibration curve for Fluoride ion electrode. Curve I represents the measure of e.m.f. of standard fluoride solutions. Curve II represents the titration of sodium perchlorate with 10^{-2}M fluoride solution. The two curves were constructed at different times.

$[F^-]_f = 10^{-6} - 10^{-2}$M. The e.m.f. of the cell was quite stable and reproducible to within a few tenths of a millivolt over several hours. Changes of several millivolts were however noted over two to three months. The drift in e.m.f. may depend upon the nature of the cations present in the solution, e.g. alkaline earth metal ions caused a -ive drift when the electrode was immersed for several hours. It was thought that subsequent immersion in thorium perchlorate solution restored the original stability in this case.

The titration of the chosen metal ion with sodium fluoride solution was carried out at constant hydrogen ion activity. The total fluoride, $[F^-]_t$, added, the measured free fluoride, $[F^-]_f$ from the cell e.m.f. and the calibration curve then permitted the calculation of the average number of ligands per metal ion, $\bar{n}$, from

$$\bar{n} = \frac{[F^-]_t - [F^-]_f}{[M^{+n}]_t} \qquad (2.2)$$

where $[M]_t$ is the total metal concentration in the solution. The quantity $[F^-]_t$ and $[M^{+n}]_t$ were corrected for the small volume changes which are introduced by addition of the standard fluoride solution. $\bar{n}$ is related to successive stability constants, β_m, by

$$\bar{n} = \frac{\beta_1[F^-]_f + 2\beta_2[F^-]_f^2 + 3\beta_3[F^-]_f^3 + \cdots\cdots}{1 + \beta_1[F^-]_f + \beta_2[F^-]_f^2 + \beta_3[F^-]_f^3 + \cdots} \qquad (2.3)$$

$\beta_1, \beta_2, \beta_3$ ..... were calculated according to well established methods[9,10] (Chapter I).

The hydrogen-fluoride ion system

The association constants for hydrogen and fluoride ion interaction in sodium perchlorate at $\mu = 0.500$ were measured by potentiometric titration using the fluoride ion membrane electrode at 15, 25 and 35°C with the results recorded in Tables 2.1 - 2.4. The calibration of the electrode before and after each run at the particular temperature was also carried out at pH = 5.00 where fluoride in solution is essentially for practical purposes free of association with hydrogen ions.

Only formation of hydrogen fluoride was observed over the range of hydrogen ion activity used as shown by the constancy of k_{HF} and therefore β_H ($= \frac{1}{k_{HF}}$) values at a particular temperature. Agreement with the previously recorded values are good (Table 2.4). The enthalpy, ΔH, and entropy, ΔS, changes accompanying 'protonation' were calculated from the van't Hoff isochore and the relation $\Delta G = \Delta H - T\Delta S$. The results are in satisfactory agreement with published values (Table 2.5).

The gadolinium-fluoride ion system

Fig. 2.4 represents the three main experimental runs attempted with gadolinium at different metal ion concentrations. As seen from Table 2.6 only β_1 is obtained

TABLE 2.1

The hydrogen-fluoride system

$\mu = 0.500$; $T = 15.00 \pm 0.05^\circ C$

$[F^-]_t = 1.00 \times 10^{-5}M.$

pH	e.m.f. in millivolts	$[F^-]_f \times 10^6$	$[HF] \times 10^6$	$K_{HF} \times 10^3$
3.60	120	8.710	1.290	1.695
3.46	122	7.943	2.057	1.339
3.05	129	6.166	3.834	1.433
2.50	146	3.090	6.910	1.414
2.35	152	2.455	7.545	1.452
2.20	159	1.862	8.138	1.443

TABLE 2.2

The hydrogen-fluoride system

$\mu = 0.500$; $T = 25.00 \pm 0.05^{\circ}C$

$[F^-]_t = 1.00 \times 10^{-5}M$.

pH	e.m.f. in millivolts	$[F^-]_f \times 10^6$	$[HF] \times 10^6$	$K_{HF} \times 10^3$
3.60	121	8.318	1.682	1.242
3.42	123	7.586	2.414	1.195
3.00	131	5.495	4.505	1.218
2.50	148	2.754	7.246	1.202
2.40	152	2.344	7.656	1.219
2.28	159	1.778	8.222	1.303

TABLE 2.3

The hydrogen-fluoride system

$\mu = 0.500$, $T = 35.00 \pm 0.05°C$

$[F^-]_t = 1.00 \times 10^{-5}M$.

pH	e.m.f. in millivolts	$[F]_f \times 10^6$	$[HF] \times 10^6$	$K_{HF} \times 10^3$
3.60	126	8.128	1.872	1.090
3.41	129	7.244	2.756	1.022
3.25	132	6.457	3.543	1.025
3.07	136	5.495	4.505	1.038
2.56	154	2.630	7.370	0.983

TABLE 2.4

The association constant for hydrogen-fluoride system in aqueous $NaClO_4$ (0.500M) at different temperatures

Temperature °C	Method	$\beta_H \times 10^{-2}$	Ref.
15.00 ± 0.05	F.I.M.E.	6.97 ± 0.04	p.w.
	Sp	7.08	11
25.00 ± 0.05	F.I.M.E.	8.14 ± 0.10	p.w.
	Sp	8.13	11
35.00 ± 0.05	F.I.M.E.	9.70 ± 0.16	p.w.
	Sp	10.00	11

F.I.M.E. = fluoride ion membrane electrode method.

Sp = spectrophotometric method;

p.w. = present work.

The value of β_H was taken as the mean of the values quoted in Tables 2.1, 2.2 and 2.3. The errors are the standard errors of the mean.

TABLE 2.5

Free energy, enthalpy and entropy changes for HF formation from $H^+_{(aq)}$ and $F^-_{(aq)}$ at $\mu = 0.500$ ($NaClO_4$) and 25.00 ± 0.05°C

Method	ΔH_1	ΔG_1	ΔS_1	Ref.
F.I.M.E.	3.11 ± 0.09	-3.97	23.75	p.w.
Sp	3.06	-3.97	22.00	11
Cal	2.60	-3.96	22.00	12

Sp = spectrophotometric; Cal = calorimetric value for ΔH.

For other abbreviations see the footnote to Table 2.4.

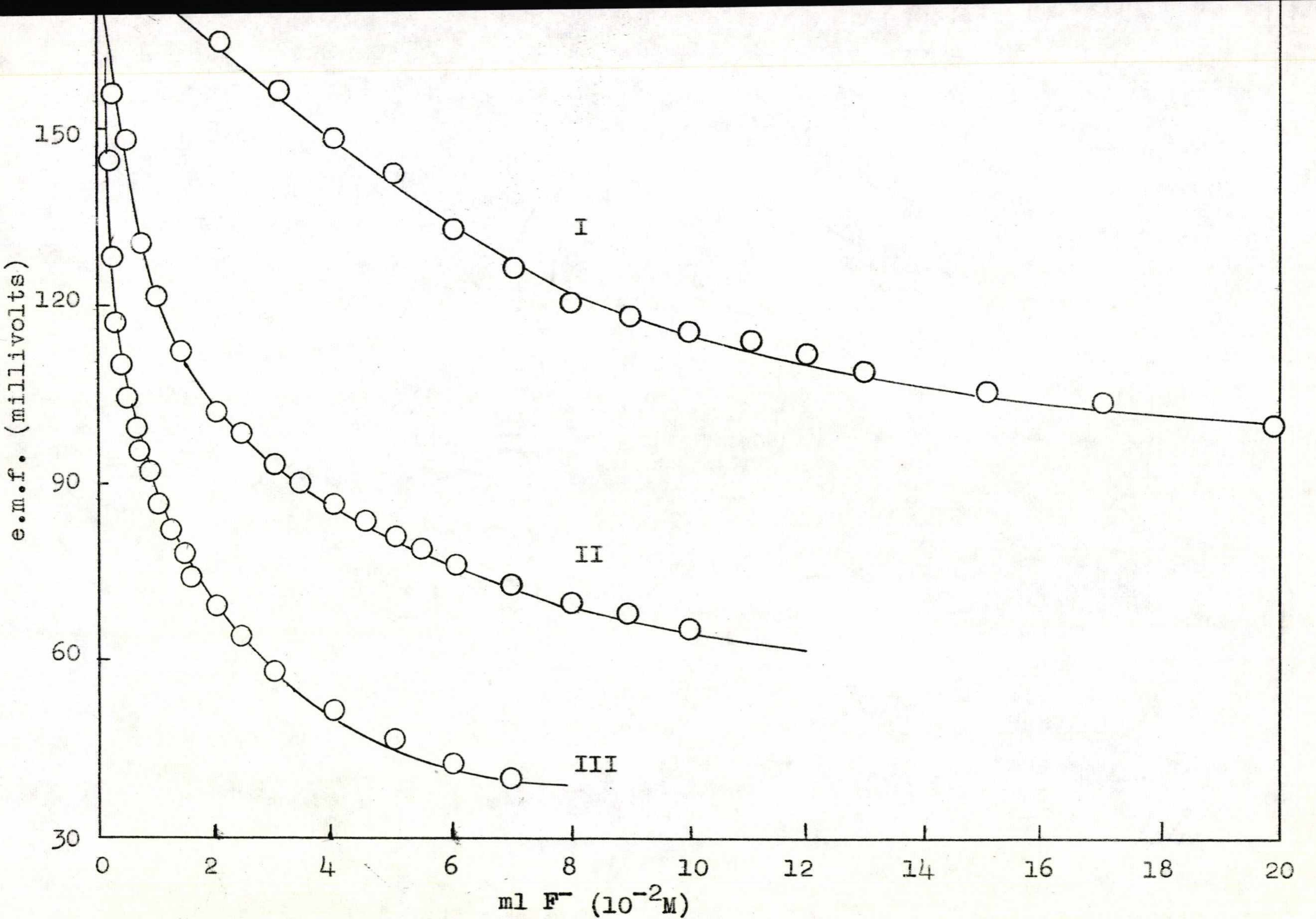


Fig. 2.4. Titration of 100ml of gadolinium (III), with 10^{-2}M fluoride ion each at pH = 3·60, μ = 0·500 ($NaClO_4$) and 25·00 ± 0·05°C. The initial gadolinium concentrations were 2·021 x 10^{-2}M (curve I) 2·021 x 10^{-3}M (curve II) and 2·021 x 10^{-4}M (curve III).

TABLE 2.6

The gadolinium-fluoride system

pH = 3.60; μ = 0.500; T = 25.00 ± 0.05°C

Run I		Run II		Run III	
$[M]_{initial} = 2.021 \times 10^{-4}$M		$[M]_{initial} = 2.021 \times 10^{-3}$M		$[M]_{initial} = 2.021 \times 10^{-2}$M	
$[F] \times 10^5$	$\bar{n}$	$[F] \times 10^5$	$\bar{n}$	$[F] \times 10^5$	$\bar{n}$
0.5623	0.0132	1.000	0.0238	1.096	0.0282
1.096	0.0278	1.413	0.0340	1.445	0.0321
1.660	0.0409	1.995	0.0475	1.549	0.0362
2.188	0.0557	3.020	0.0669	1.778	0.0401
2.818	0.0653	3.548	0.0806	1.862	0.0442
3.388	0.0779	4.169	0.1020	1.995	0.0482
3.890	0.0938	4.898	0.1147	2.239	0.0522
4.467	0.1059	5.623	0.1354		
5.623	0.1299	6.166	0.1530		
6.761	0.1545	6.918	0.1695		
7.762	0.1858	7.586	0.1864		
8.913	0.2093	8.318	0.2029		
11.22	0.2555				
13.49	0.3026				
16.98	0.3673				

from the highest metal ion concentration as $\bar{n}$ is very small and it has a very narrow range of values. The limitations were imposed by the tendency for the change in e.m.f. to diminish with successive incremental addition of titrant and by the ultimate appearance of a gadolinium fluoride precipitate. Separate experiments were always carried out in order to determine the point in a titration at which precipitation occurred and e.m.f. data near or beyond it were not subsequently used. This check was performed for each system studied throughout the present work.

The lowest gadolinium concentration gave the largest range for $\bar{n}$ (0.01 - 0.37). However, there are unlikely to be advantages in attempting to use lower $[M]_t$ since this entails addition of more dilute $[F^-]$ and already at the lowest $[M]_t$ used, the incremental addition of $[F^-]$ is near the limit of response by the electrode. For a lanthanide the metal ion concentration would of necessity have to be appreciably greater than the concentration of lanthanum ion derived from solution of membrane. The two titration curves lowest in $[M]_t$ give β_1 and β_2 only (Table 2.7) and it was concluded that no more than two steps in gadolinium complex ion formation can be investigated by this electrode method. The β_m values are recorded in Table 2.6; they are in fair agreement with those from other sources[13,14].

TABLE 2.7

Stability constant data for gadolinium fluoride system in aqueous solution at 25°C

Method	Ionic strength	$\beta_1 \times 10^{-3}$	$\beta_2 \times 10^{-6}$	Ref.
F.I.M.E.	0.500	2.46±0.05	-	p.w.
"		2.39±0.04	2.73±0.38	p.w.
"		2.29±0.05	4.16±0.48	p.w.
Dis	0.500	2.67±0.30	5.17±0.32	13
Ferri	0.500	2.34	-	14
	0.500	2.36±0.35		15
	1.00	2.06±0.13		15

F.I.M.E. = fluoride ion membrane electrode.

Dis = liquid-liquid extraction.

Ferri = potentiometric method using ferrous-ferric half-cell.

p.w. = present work.

The europium-fluoride ion system

Studies similar to those with gadolinium, but more limited in range, were made on europium(III)-fluoride system. One of the experimental runs is reported in Table 2.8 which on further analysis shows that only β_1 can be calculated. The value of β_1 is in good agreement with values obtained from partition studies[16] (Table 2.9).

The yttrium-fluoride ion system

One of the three experimental runs at 25.0°C each starting with the same concentration of yttrium is reported in Table 2.10. Only β_1 and β_2 could be calculated, the values for which are recorded in Table 2.11 with other[17] published data. The reproducibility of e.m.f. data in these runs was very good. The electrode system was used to determine β_1 and β_2 at various temperatures. Table 2.10 also shows one of the selective titration runs at 15.0 and 35.0°C. The calculated stability constants in addition to those at 25.0°C are reported in Table 2.11. Comparative data from other[17] sources are also given in the same table of results. β_2 values for yttrium fluoride is unusually a decreasing function of the increasing temperature. Such behaviour was observed by Kury et al[18] in the course of their work on the scandium-fluoride ion system (Table 2.11). In consideration with the following equilibria

TABLE 2.8

Europium(III) fluoride system

pH = 3.60;   T = 25.00 ± 0.05°C

$[Eu^{3+}]_{initial}$ = 1.008 x 10^{-3}M; V_o = 100.0 ml.

Ml. of fluoride (10^{-3}M)	e.m.f.	$[F^-] \times 10^6$	$\bar{n}$
0.0	269	-	-
0.2	199	-	-
0.6	168	1.200	0.0037
0.8	160	1.657	0.0049
1.0	156	1.992	0.0062
1.2	150	2.508	0.0074
1.5	143	3.383	0.0090
2.0	135	4.670	0.0118
2.2	132	5.362	0.0127
2.5	128	6.299	0.0142
3.0	126	6.750	0.0178
3.2	124	7.574	0.0186
3.5	122	8.115	0.0205
4.0	119	9.102	0.0236
4.5	117	-	-
5.0	115	-	-

TABLE 2.9

Stability constant data for Europium(III) fluoride system at 25°C.

Method	Ionic strength	$\beta_1 \times 10^3$	$\beta_2 \times 10^3$	Ref.
F.I.M.E.	0.500	2.54±0.05	-	p.w.
Dis	0.500	2.48	3.01	16
"	1.00	1.59±0.20	-	15

For abbreviations see footnote of Table 2.7.

TABLE 2.10

The yttrium fluoride system

pH = 3.60; μ = 0.500

$[Y^{3+}]_{initial} = 4.94 \times 10^{-4}$M; V_o = 100.0 ml.

15.00±0.05°C		25.00±0.05°C		35.00±0.05°C	
[F] x 10^5	$\bar{n}$	[F] x 10^5	$\bar{n}$	$[F^-]$ x 10^5	$\bar{n}$
0.6761	0.0513	0.5121	0.0400	0.6607	0.0555
1.047	0.0762	0.6750	0.0535	0.8318	0.0692
1.380	0.1018	0.8694	0.0664	1.349	0.1104
1.738	0.1269	1.069	0.0791	1.738	0.1369
2.089	0.1522	1.379	0.1064	2.291	0.1772
3.020	0.2141	2.287	0.1716	2.692	0.2034
3.715	0.2483	2.687	0.1970	3.090	0.2295
4.074	0.2732	3.085	0.2223	4.169	0.2931
4.677	0.3092	3.710	0.2596	5.248	0.3565
5.129	0.3321	4.162	0.2837	6.457	0.4169
6.310	0.3882	4.778	0.3211	7.244	0.4518
7.413	0.4457	5.240	0.3450	7.762	0.4751
8.710	0.4989	5.879	0.3817	9.330	0.5275
9.550	0.5239	6.446	0.4032	10.23	0.5596
10.00	0.5519	7.233	0.4368	10.72	0.6237
10.96	0.5796	9.534	0.5050		
		9.608	0.5532		
		10.70	0.5634		
		11.20	0.6024		
		12.00	0.6186		

TABLE 2.11

Stability constants for yttrium fluoride system in aqueous $NaClO_4$ (0.500M) at different temperatures.

Metal ion	Temp °C	Method	β_1	β_2	Ref.
Y^{3+}	15.00±0.05	F.I.M.E.	$(7.61\pm0.06)10^3$	$(15.5\pm0.7)10^6$	p.w.
Y^{3+}	15	Ferri	7.41×10^3	5.24×10^6	17
Sc^{3+}	15	Ferri	1.55×10^6	3.24×10^{11}	18
Y^{3+}	25.00±0.05	F.I.M.E.	$(8.22\pm0.06)10^3$	$(14.4\pm0.7)10^6$	p.w.
Y^{3+}	25	Ferri	8.51×10^3	13.49×10^6	17
Sc^{3+}	25	Ferri	1.51×10^6	2.82×10^{11}	18
Y^{3+}	35.00±0.05	F.I.M.E.	$(8.72\pm0.06)10^3$	$(14.3\pm0.7)10^6$	p.w.
Y^{3+}	35	Ferri	9.80×10^3	47.86×10^6	17
Sc^{3+}	35	Ferri	1.62×10^6	2.95×10^{11}	18

For abbreviations see the footnote to Table 3.7.

$$Y^{3+}_{(aq.)} + F^{-}_{(aq.)} \overset{K_1}{\rightleftharpoons} YF^{2+}_{(aq.)} \qquad (2.4)$$

$$YF^{2+}_{(aq.)} + F^{-}_{(aq.)} \overset{K_2}{\rightleftharpoons} YF^{+}_{2(aq.)} \qquad (2.5)$$

values for the enthalpy, ΔH_1, and entropy, ΔS_1, changes appropriate to the conditions of measurements were calculated for eq. 2.4 and ΔH_2 and ΔS_2 for eq. 2.5. ΔH_1 and ΔS_1 thus obtained are in reasonable agreement with the results obtained by Kury et al[18] (Table 2.12) from potentiometric studies using the 'Ferri' method. ΔH_1 is however considerably different from that obtained by Walker and Choppin[15] from recent calorimetric measurements (Table 2.12). This largely explains the wide discrepancy in ΔS_1 even though there is a factor of two separating the β_1 values from which the free energy changes, ΔG_1, were calculated. It is hardly conceivable that the difference in ionic strengths (0.5 - 1) of the media in which these measurements were made can account for the differences in ΔH_1 and ΔS_1. Additional work is clearly needed to resolve the discrepancy and establish reliable data. ΔH_2 and ΔS_2 values obtained in this work, though in line with those published for scandium[18] (Table 2.12), are regarded as no more than very rough estimates in view of the uncertainties in the β_1 and β_2 values.

TABLE 2.12

Free energy, enthalpy and entropy changes for YF^{2+}_{aq}, $YF^{+}_{2\,aq}$ formation from Y^{3+}_{aq} and F^{-}_{aq} at $\mu = 0.500$ ($NaClO_4$) and 25°C temperature.

Metal ion	Method	ΔH_1	ΔG_1	ΔS_1	ΔH_2	ΔG_2	ΔS_2	Ref.
Y^{3+}	F.I.M.E.	1.205	-5.34	22.0	-1.20	-4.43	11.0	p.w.
	Ferri	2.37	-5.34	26.6	-	-	-	17
	Cal(μ = 1.00)	8.32±0.08	-4.91±0.44	44.5±1.5	-	-	-	15
Sc^{3+}	Ferri(μ = 0.500)	0.40	-8.36	29.4	-1.23	-7.19	19.9	18

For abbreviations see the previous Tables in this Chapter.

The scandium-fluoride ion system

A representative set from the three titration runs carried out with scandium is given in Table 2.13. To avoid hydrolysis the measurements were performed at pH 3.00. The titration curves represented the formation of at least three fluoro complexes of scandium in the range of fluoride ion where the possibility of precipitation is almost negligible. The formation of a fourth complex could not be established because of limited data and the metal ion concentration used. β_1 and β_2 values are in fair agreement with the values obtained by other methods[18,19] (Table 2.14); β_3 is less certain.

The iron(III)-fluoride ion system

One of the three experimental runs carried out with the same iron(III) concentration is reported in Table 2.15. At least three complexes are predicted from the titration run. To avoid hydrolysis of iron(III) the titrations were performed at pH 2.00. A least squares treatment of the data at low fluoride ion concentrations gave β_1 and β_2 values in good agreement with those obtained by other workers[14,20] (Table 2.16). A β_3 value obtained by graphical analysis is also recorded in the table.

TABLE 2.13

The scandium fluoride system

pH = 3.20; T = 25.00 ± 0.05°C; μ = 0.500

$[Sc^{3+}]_{initial} = 4.91 \times 10^{-4}$M

$[F] \times 10^{6}$	$\bar{n}$	x	$\frac{x-1}{L} \times 10^{-6}$
1.319	0.8048	3.523	1.913
2.090	0.9378	5.272	2.044
2.456	1.004	6.167	2.104
3.092	1.066	7.836	2.211
3.632	1.136	9.401	2.313
5.014	1.268	15.16	1.823
6.029	1.333	19.28	3.032
7.244	1.397	23.69	3.132
8.917	1.461	31.92	3.467
10.48	1.524	40.62	3.782
12.03	1.588	50.39	4.106
14.13	1.650	65.43	4.559
16.23	1.713	82.58	5.027
19.06	1.773	109.4	5.686
22.40	1.833	146.4	6.493
25.71	1.892	189.5	7.330
28.85	1.952	236.5	8.162
33.13	2.009	311.3	9.366
37.17	2.066	393.6	10.56
41.71	2.122	501.2	11.99
47.88	2.175	674.5	14.07

x is defined in Chapter I, page 12.

TABLE 2.14

Stability constant data for scandium fluoride system at an ionic strength $\mu = 0.500$ and $25.00 \pm 0.05^{\circ}C$

Method	$\beta_1 \times 10^{-6}$	$\beta_2 \times 10^{-11}$	$\beta_3 \times 10^{-15}$	$\beta_4 \times 10^{-18}$	Ref.
F.I.M.E.	1.66 ± 0.08	2.16 ± 0.10	1.7 ± 0.2	-	p.w.
Ferri	1.51	2.82	3.31	2.34	18
Dis	1.47 ± 0.11	1.77 ± 0.07	2.91 ± 0.14	3.06 ± 0.12	19

For abbreviations see footnote of Table 3.7.

TABLE 2.15

The iron(III) fluoride system

pH = 2.00; T = 25.00 ± 0.05°C; μ = 0.500

$[Fe^{3+}]_{initial} = 5.001 \times 10^{-4}M$

$[F] \times 10^{6}$	$\bar{n}$	$\frac{\bar{n}}{(1-\bar{n})[F]} \times 10^{-5}$
1.548	0.1885	1.501
2.039	0.2423	1.568
2.689	0.2960	1.562
3.086	0.3223	1.541
3.544	0.3487	1.512
3.977	0.3752	1.510
4.360	0.4018	1.541
4.672	0.4286	1.605
5.122	0.4550	1.630
5.617	0.4814	1.653
6.018	0.5080	1.716
6.599	0.5342	1.738
7.072	0.5879	2.018
7.753	0.6413	2.306
8.699	0.6941	2.609
9.321	0.7476	3.177
9.988	0.8010	4.029
10.70	0.8543	5.477

TABLE 2.16

Stability constant data for iron(III) fluoride system at an ionic strength $\mu = 0.500$ and 25.00 ± 0.05°C

Method	$\beta_1 \times 10^5$	$\beta_2 \times 10^9$	$\beta_3 \times 10^{12}$	Ref.
F.I.M.E.	1.46 ± 0.02	1.17 ± 0.16	~1*	p.w.
Ferri	1.54	1.31	1.13	p.w.
"	1.50	1.26	1.02	14
"	1.53	1.29	0.61	20

* = estimated graphically.

For abbreviations see footnote of Table 3.7.

The magnesium and calcium fluoride ion systems

Representative titration data are reported (Tables 2.17 and 2.18) for both metal ion systems. Because of the low stability of the fluoro-complexes the metal ion concentrations used were fairly large compared to other systems already mentioned. Like the other systems the ratio of $[F^-]$ to $[M]_t$ are also restricted by precipitation. The value for β_1 for the formation of MgF^+_{aq} is in good agreement with the value reported by Connick and Tsao[11]; their approximate value for that of CaF^+_{aq} is reported for comparison (Table 2.19). As seen from recent results reported by Tanner et al[21] while this work was in progress, it appears that β_1 for magnesium and calcium is not greatly influenced by ionic strength of the medium in the 0.5 - 1.0 range although such an effect may become more evident at lower ionic strengths.

The 'Ferri' method

Iron(III) and yttrium fluoride ion systems

The method of interpretation of the results for both iron(III) and yttrium fluoride systems by this method is that due to Kury[14]. The experimental results may be systematically interpreted by considering the following equilibria only:

TABLE 2.17

The magnesium fluoride system

pH = 3.60; $\mu = 0.500$; T = 25.00 ± 0.05°C

$[Mg^{2+}]_{initial} = 0.088M$

$[F]_f \times 10^5$	$[M]_t \times 10^2$	$\bar{n} \times 10^4$	$\frac{\bar{n}}{(1-\bar{n})[F]_f}$
0.6026	8.782	1.201	19.93
0.7244	8.778	1.534	21.17
0.8710	8.774	1.838	21.10
1.023	8.769	2.136	20.87
1.175	8.765	2.434	20.72
1.230	8.780	2.843	23.11
1.445	8.756	3.068	21.23
1.622	8.751	3.337	20.58
1.778	8.748	3.629	20.41
1.950	8.743	3.904	20.02
2.042	8.739	4.269	20.91
2.239	8.734	4.515	20.16
2.291	8.730	4.925	21.50
2.344	8.722	5.805	24.77

TABLE 2.18

The calcium fluoride system

pH = 3.60; μ = 0.500; T = 25.00 ± 0.05°C

$[Ca^{2+}]_{initial}$ = 0.154M

$[F]_f \times 10^5$	$\bar{n} \times 10^4$	$\frac{\bar{n}}{(1-\bar{n})[F]}$
0.4778	0.2287	4.787
0.9533	0.2582	4.806
1.410	0.6995	4.961
1.859	0.9447	5.081
2.340	1.169	4.997
2.813	1.398	4.967
3.157	1.711	5.418
3.884	1.772	4.561
4.162	2.127	5.109
4.670	2.340	4.989
5.121	2.571	5.020
5.487	2.865	5.222

TABLE 2.19

Stability constant data for magnesium and calcium fluoride systems at 25.00 ± 0.05°C

Metal ion	Method	Ionic strength	β_1	Ref
Mg^{2+}	F.I.M.E.	0.500	20.7 ± 0.2	p.w.
	"	1.000	20.8 ± 1.0	21
	Ferri	0.500	20.0	11
Ca^{2+}	F.I.M.E.	0.500	4.97 ± 0.15	p.w.
	//	1.000	4.3 ± 0.3	21
	Ferri	0.500	$\leqslant 3$	11

For abbreviations see footnote of Table 3.7.

$$\begin{array}{lllll} Fe^{3+} + HF & \rightleftharpoons & FeF^{2+} + H^{+} & & K_1 \\ FeF^{2+} + HF & \rightleftharpoons & FeF_2^{+} + H^{+} & & K_2 \\ FeF_2^{+} + HF & \rightleftharpoons & FeF_3 + H^{+} & & K_3 \\ HF & \rightleftharpoons & H^{+} + F^{-} & & K_{HF} \\ Fe^{3+} + H_2O & \rightleftharpoons & FeOH^{2+} + H^{+} & & K_H \\ Y^{3+} + HF & \rightleftharpoons & YF^{2+} + H^{+} & & K_4 \\ YF^{2+} + HF & \rightleftharpoons & YF_2^{+} + H^{+} & & K_5 \\ YF_2^{+} + HF & \rightleftharpoons & YF_3 + H^{+} & & K_6 \end{array}$$

where the K's represent equilibrium constants for these reactions. Making the following assumptions set out below the model becomes simpler for purposes of computation.

(i) Iron(II) does not interact with fluoride ion.

(ii) HF_2^- can be neglected.

(iii) Iron(II) and iron(III) do not interact with the perchlorate ion.

(iv) Hydrolysis of iron(III) is negligible.

In calculating K_1, K_2 and K_3 one needs the e.m.f. values from titration data in the cell A-B. The e.m.f. of the concentration cell A-B is given by

$$E_{AB} = \frac{-RT}{F} \ln \frac{[Fe^{3+}]_A[Fe^{2+}]_B}{[Fe^{3+}]_B[Fe^{2+}]_A} \qquad (2.6)$$

From considerations of stoichiometry,

$$[\Sigma F^-]_A = [HF]_A + [F^-]_A + [FeF^{2+}]_A + 2[FeF_2{}^+]_A + 3[FeF_3]_A \qquad .....(2.7)$$

$$[\Sigma Fe^{3+}]_A = [Fe^{3+}]_A + [FeF^{2+}]_A + [FeF_2{}^+]_A + [FeF_3]_A + [FeOH^{2+}]_A \qquad .....(2.8)$$

and $$[\Sigma Fe^{3+}]_B = [Fe^{3+}]_B + [FeOH^{2+}]_B \qquad .....(2.9)$$

As the initial hydrogen ion concentration in both half cells A and B are the same and the change in hydrogen ion concentration is negligible on complex formation the assumption can be made that

$$1 + \frac{K_H}{[H^+]_A} = 1 + \frac{K_H}{[H^+]_B} \qquad (2.10)$$

From the assumptions already stated and the above equations it is possible to derive the expression

$$\left[1 + \frac{K_H}{[H^+]_A}\right]\left[e^{\frac{FE}{RT}} - 1\right] = K_1[\tfrac{HF}{H}]_A + K_1K_2[\tfrac{HF}{H}]_A^2 + K_1K_2K_3(\tfrac{HF}{H})_A^3 \qquad .....(2.11)$$

which by rearrangement and substitution gives

$$[\tfrac{HF}{H}]_B = \frac{1}{K_{HF} + [H^+]_A}\Big[[\Sigma F^-]_A - [\Sigma Fe^{3+}]_A + [Fe^{3+}]_A(1 + \frac{K_H}{[H^+]_A}) - K_1K_2[Fe^{3+}]_A[\tfrac{HF}{H}]_A^2 - 2K_1K_2K_3[Fe^{3+}]_A[\tfrac{HF}{H}]_A^3\Big] \qquad .....(2.12)$$

Using these equations, K_1, K_2 and K_3 can be calculated by an iteration procedure as reported by Kury[14]. From the two titration curves (Fig. 2.5) representing the e.m.f.'s of cells A-B and B-C plotted as a function of total fluoride concentration, we define

$$\Delta[\Sigma F^-] = [\Sigma F^-]_{E_{AC}} - [\Sigma F^-]_{E_{BC}} \qquad (2.13)$$

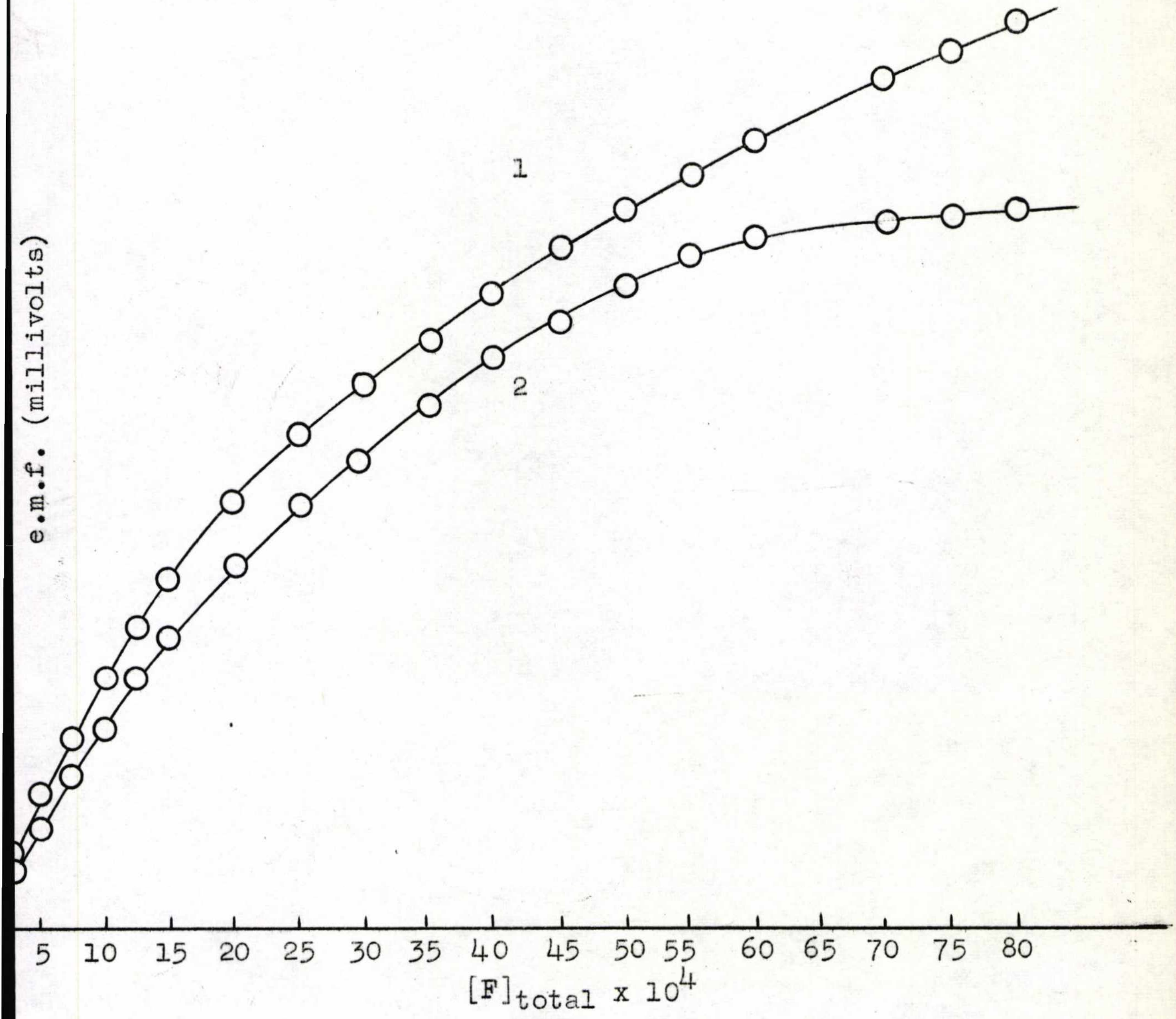
where $E_{AC} = E_{BC}$ because the cell AB and CB have the same $[\Sigma H_i^+]$, $[\Sigma Fe_i^{3+}]$ and $[\Sigma Fe_i^{2+}]$.

$\Delta[\Sigma F^-]$ is a measure of the fluoride ion complexing yttrium. Knowing $\Delta[\Sigma F^-]$, $[Y^{3+}]_C$ and defining $\bar{n}$, the average ligand number as reported earlier (Chapter I), the equilibrium constants K_4, K_5 and K_6 can be calculated.

$$\bar{n} = \frac{K_4[\frac{HF}{H}] + 2K_4K_5[\frac{HF}{H}]^2 + 3K_4K_5K_6[\frac{HF}{H}]^3}{1 + K_4[\frac{HF}{H}] + K_4K_5[\frac{HF}{H}]^2 + K_4K_5K_6[\frac{HF}{H}]^3} \qquad (2.14)$$

$[\frac{HF}{H}]$ values are calculated from the known K_1, K_2 and K_3 values got from equation (2.11) with the help of an electronic digital computer. Knowing the values of K_{HF}, the β_m values can be calculated by a least squares method. All the calculations in the present work and those reported elsewhere in the thesis were performed with the help of the ICL-1430 computer of the University.

Typical sets of potentiometric titration data are presented in Tables 2.20 and 2.21. Three concentrations (1.98×10^{-4}, 4.98×10^{-4} and 1.98×10^{-3} Ml^{-1} of yttrium)



. 2.5. Titration curves for Ferrous-Ferric half cell, curves 1 and 2 represent change in e.m.f. in Cell A-B and C-B respectively.

TABLE 2.20

The iron(III) fluoride system measured by the 'Ferri' method at an ionic strength $\mu = 0.500$ and 25.00+0.05°C

Initial volume, $V_o = 100$ ml.

$[Fe^{2+}] = 4.50 \times 10^{-4}M$; $[Fe^{3+}] = 4.75 \times 10^{-4}M$;

$[H^+] = 3.26 \times 10^{-2}M$; $K_H = 1.9 \times 10^{-3}$;

$K_{HF} = 1.23 \times 10^{-3}$

Ml. of 0.5M NaOH	E_{AB}	$[\frac{HF}{H}] \times 10^2$	Q	S
0.05	9.00	0.2433	0.4584	188.4
0.10	19.68	0.6276	1.227	195.5
0.15	29.75	1.129	2.318	205.3
0.20	38.50	1.707	3.685	215.9
0.25	46.35	2.366	5.408	228.6
0.30	53.50	3.063	7.413	242.1
0.35	59.75	3.821	9.819	257.0
0.40	65.55	4.589	12.50	272.4
0.45	70.00	5.294	15.17	286.6
0.50	74.70	6.072	18.37	302.5
0.60	82.45	7.550	25.16	333.2
0.70	89.55	9.147	33.64	367.8
0.80	97.20	11.13	45.78	411.3
0.90	103.5	12.92	58.48	452.6

$$Q = (1 + \frac{K_H}{H^+})(e^{\frac{EF}{RT}} - 1)$$

$$S = Q.(\frac{H}{HF})$$

TABLE 2.21

The yttrium fluoride system measured by the 'Ferri' method at an ionic strength μ=0.500 and 25.00 ± 0.05°C

$[Fe^{2+}] = 4.50 \times 10^{-4}M$; $[Y^{3+}] = 4.945 \times 10^{-4}M$;

$[Fe^{3+}] = 4.75 \times 10^{-4}M$; $[H^{+}] = 3.26 \times 10^{-4}M$.

$\Delta[\Sigma F] \times 10^4$	$[F]_f \times 10^5$	$\bar{n}$	$\frac{\bar{n}}{(1-\bar{n})[F]} \times 10^{-3}$
0.30	0.7719	0.0607	8.371
0.53	1.400	0.1074	8.592
0.77	2.100	0.1560	8.800
1.03	2.910	0.2088	9.068
1.30	3.767	0.2636	9.500
1.56	4.699	0.3166	9.857
1.82	5.644	0.3695	10.38
2.11	6.511	0.4286	11.52
2.40	7.469	0.4878	12.75
2.65	8.370	0.5389	13.96
2.90	9.286	0.5900	15.50
3.16	10.12	0.6432	17.81
3.55	11.25	0.7229	23.81
6.80	12.47	1.385	-

were used in these runs. Owing to the insolubility of YF_3, only a few aliquot parts of sodium fluoride solution could be added to half-cell C before precipitation interfered. The precipitation could be observed easily since upon its occurance, the e.m.f. of cells having half-cell C in them would drift rapidly to lower values. Checks for precipitation were also separately performed under identical conditions to those of the experimental run. The values of K_1, K_2 and K_3 for the iron(III) fluoride system used in the calculation of $[\frac{HF}{H}]$ and therefore $[F^-]$ were those obtained by Kury[14] and in the course of the present work. β_1, β_2 and β_3 values for the iron-fluoride system determined from three different runs give good agreement with those of others[14,20] (Table 2.16).

The calculated β_1, β_2 and β_3 for the yttrium fluoride system are reported in Table 2.22 with relevant published[15,17,19] data for comparison. Fair agreement with the values obtained by Paul et al[17] and in this laboratory using solvent extraction method was obtained. The error limits represent the standard errors of the mean.

TABLE 2.22

Stability constant data for yttrium fluoride system by 'Ferri' method at 25.00 ± 0.05°C

Method	Ionic strength	β_1 x 10^3	β_2 x 10^6	β_3 x 10^9	β_4 x 10^4	Ref.
Ferri	0.500	8.20±0.21	13.8±0.6	19.5±0.8	-	p.w.
"	0.500	8.51	13.49	21.3	~176	17
"	1.00	4.02±0.36	-	-	-	15
F.I.M.E.	0.500	8.22±0.06	14.4±0.7	-	-	p.w.
Dis	0.500	7.70±0.21	12.8±0.3	20.0	-	19

For abbreviations see footnote of previous Tables in this Chapter.

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CHAPTER III

Study of Metal Fluoro Complexes in Aqueous Solution by Liquid-Liquid Extraction and Ion-Exchange Methods

INTRODUCTION

Since the determination of the first stability constants for some rare earth mononuclear fluoro complexes by Kury[1], there has not been any further advance in methods available for the study of interaction of this ligand with trivalent rare earths and actinides. Walker and Choppin[2], during the progress of the work described here, reported the stability constants in addition to thermodynamic parameters for the formation of first mononuclear fluoro complexes of all the trivalent rare earths. There has not been any such work done on the fluoro complexes of trivalent actinides as far as is known to the writer.

The present study using a liquid-liquid extraction method was undertaken in order to try to obtain equilibrium constants for the formation of higher fluoro complexes of trivalent rare earths and actinides in aqueous solution. Yttrium, scandium and indium metal ions in their interaction with fluoride ion, for which reliable stability constant data are available[3-5], were also studied in order to provide checks on the validity and reliability of the methods to be applied to the lanthanides and actinides.

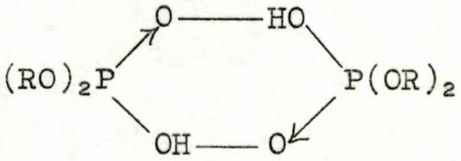
Limited use was made of the cation exchanger to study the distribution of partially complexe positively charged fluoro complexes of trivalent rare earths and actinides as the ion exchange distribution results[6] could not be used directly in the determination of equilibrium constants. Di-2-ethylhexyl phosphoric acid (HDEHP) diluted with toluene was used as the extractant; such a system had of course been used earlier[6] in this laboratory for such sort of measurements.

The extractant

In studying the extraction chemistry of a given class of reagents, it is important to examine separately, insofar as possible, each of the many variables such as solvent, reagent structure, and the size, charge and bonding properties of the extracted species. In many cases this task has proven specially difficult because the extractant (and the extraction products) are often extensively associated, they may distribute appreciably to the aqueous phase, and besides extracting the metallic species of interest they may extract acids, water and other aqueous solutes. The dialkylphosphoric acids, $(RO)_2$ P(O)OH, in solvent extraction are relatively free of these complications[7-11]. At low loading they extract cations by a simple hydrogen ion exchange (often free of water, acid and anion extraction) and the extraction products are usually mononuclear. For these extractants it was noted[7-9] that the extraction coefficient for various cations varied as -Zth power of acidity (where Z is the cation charge) and the +Zth power of the reagent concentration, and that often the saturation mole ratio of metal ion to extractant corresponded to the formula MD_Z ($D = (RO)_2PO_2^-$). This of course suggested the general extraction reaction to be

$$M^{Z+}_{aq} + Z\,HD \rightleftharpoons MD_{Z_{aq}} + Z\,H^{+}_{aq} \tag{3.1}$$

It was subsequently found[7-9], however, that in non-polar solvents, e.g. toluene (in which the distribution ratios were the highest) these extractants were present as stable hydrogen bonded dimers

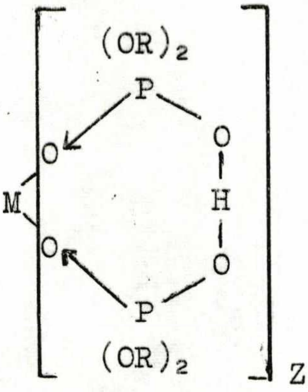


(3.2)

Thus it was concluded that the general extraction reaction is instead

$$M^{Z+}_{aq} + Z(H_2D_2)_{aq} \rightleftharpoons M(HD_2)_Z + ZH^{+}_{aq} \tag{3.3}$$

at low loading. While additional extraction complexes are usually formed as loading is increased (complexes which are often polynuclear and which can contain water and anions). At low loading the reaction (3.3) leading to the formation of $M(HD_2)_Z$ in which only half the acidic hydrogen of the extractant is replaced, has been found to be quite common[7-11]. The chelate structure for the extracted complex can be written as



(3.4)

which may be abbreviated to $M(HD_2)_Z$. The extraction chemistry of di-2-ethylhexyl phosphoric acid has been developed and is very well known in this laboratory[6] and also that of Peppard and co-workers[7-9] at Oak Ridge.

Suppose metal ion M^{3+} with its successive fluoro complexes MF^{2+}, MF_2^{+}, MF_3, ... are present in the aqueous phase at a constant ionic strength. On the basis of the extraction (eq. 3.3) and the following assumptions

(i) HDEHP is insoluble in the aqueous phase,

(ii) $M(HD_2)_3$ or any other metal chelate species if formed has negligible solubility in the aqueous phase,

(iii) the partially complexed metal ions MF^{2+}, MF_2^+, ..., do not partition into the organic phase.

It can be shown that

$$\phi_L = \frac{[M(HD_2)_3]}{[M^{3+}]+[MF^{+2}]+[MF_2^+]+ \; ....} \qquad (3.5)$$

Equation (3.5), on further substitution and rearrangement as set out in Chapter I, gives

$$\phi_{1L} = 1 + \beta_1[F^-] + \beta_2[F^-]^2 + \beta_3[F^-]^3 + \; ... \qquad (3.6)$$

(The notation is the same as that in Chapter I). $[F^-]$ is the free fluoride ion concentration. As very low concentrations of metal ions were used in all the partition measurements the total fluoride ion concentration after making an allowance for proton association products is considered equal to the free fluoride[11] concentration.

<u>Partition of partially complexed metal ion into a cation exchanger</u>

The partition of a metal ion in the presence of fluoride ion into a cation-exchange resin is given by the relation

$$\phi_{1R} = \frac{(\beta_1 - l_1') + (\beta_2 - l_2')[F^-] + \; .....}{1 + l_1'[F^-] + l_2'[F^-]^2 + \; ......} \qquad (3.7)$$

In combination with suitable HDEHP distribution data, equations 3.6 and 3.7 can be used to calculate partition ratios for the partially complexed fluoro metal species. Combining equations 3.6 and 3.7 and on rearrangement we get

$$\frac{\phi_{1L} - \phi_{1R}}{1 + \phi_{1R}[F^-]} = l_1' + l_2'[F^-] + l_3'[F^-]^2 + \ldots\ldots \quad (3.8)$$

From a plot of the L.H.S. of equation 3.8 against $[F^-]$ one can, at least in principle, compute the values of l_1', l_2', l_3' ..... l_m' and therefore l_m values for the partition of MF_m^{3-m} into the cation exchange resin.

EXPERIMENTAL

Chemicals and Reagents

All the chemicals used were of analytical reagent grade unless otherwise specified. The stock solution of sodium perchlorate and sodium fluoride (10^{-2}M in fluoride) were prepared as reported in Chapter II. The appropriate ionic strength of fluoride solution was adjusted with sodium perchlorate.

Di-2-ethylhexylphosphoric acid (HDEHP)

HDEHP supplied by Messrs. Kodak Ltd., Kirby, Lancashire was used after its purification by the method described by Peppard[7] et al. The essential steps in this method are (i) the removal of metal impurities like iron by stripping the HDEHP with hydrochloric acid, (ii) removal of neutral impurities such as alcohols and trialkylphosphates with petrolium ether from the sodium salt of HDEHP, and (iii) separation of monoester by extraction into ethylene glycol and petroleum ether. The purity of the HDEHP thus treated was checked by determing its molecular weight. HDEHP appearing to be of 99.9% purity was obtained by this method.

A stock solution of HDEHP, 0.5% (w/v) in toluene, was prepared and stored in an air-tight Pyrex glass flask. Before each series of distribution measurements the stock solution diluted to the required strength, was pre-equilibrated with an equal volume of aqueous sodium perchlorate solution at the ionic strength and pH required in the experiment to be performed.

Ion-exchange Resin

The cation exchange resin, Zec Karb-225 (SRC-15) "chromatographic grade", 100-200 mesh having a nominal 8% cross-linking was used. The resin is a polystyrene cross-linked type polymer prepared by mixing the required amount of divinylbenzene with the monomer styrene. The sulphonate groups are attached to the benzene rings by a substitution reaction after polymerization. The resin was conditioned before use as it is likely to contain metal contaminants if taken directly from the bottle as purchased. The resin was first washed free of 'fines' by decanting several times from 2M hydrochloric acid. It was then treated in a column with more 2M HCl until free of iron. The resin is washed with doubly-distilled water until free from acid. To change the resin into the sodium from the column was washed with 5-6 column volumes of 2M sodium chloride and washed again with doubly-distilled water until the washings were free from chloride. The resin was dried in an oven at 80°C until the particles no longer adhere to each other (12-24 hours). Resin was stored in a glass air-tight bottle after cooling to room temperature.

Radioactive Metal Ions

All the radioactive isotopes used in the present study were supplied by the Radiochemical Centre, Amersham, England unless otherwise mentioned.

Lanthanum-140: Lanthanum-140 was separated in a carrier free form from Ba-140 essentially by the method described by Kiba et al.[12]

To 3 or 4 drops of barium-140 and lanthanum-140 mixture are added 5 ml of distilled water, 1.6 ml of 9M ammonia solution, 10.4 ml of 0.9M ammonium acetate and 2 ml of 5% cupferron solution. Shake the mixture for 10-15 minutes and add 5 ml of chloroform, shake for a further 10 minutes and separate the chloroform phase. Add in all three different portions of chloroform containing cupferron in 5:3 by volume ratio to extract the lanthanum-140. The chloroform containing lanthanum-140 was then stripped with 2N HNO_3 to transfer lanthanum-140 into the aqueous phase. This lanthanum-140 containing solution was evaporated and eventually ignited to remove traces of organic matter from cupferron decomposition. The residue was dissolved in perchloric acid and diluted to the required ionic strength and pH with sodium perchlorate solution and the minimum possible addition of perchloric acid and sodium hydroxide. To check the purity of the tracer the γ-spectrum of a portion was obtained using a multi channel analyser and another portion was used for a half-life determination.

Europium-152 and 154 mixture, gadolinium-153 and cerium-144/praesodymium-144 supplied in hydrochloric acid were converted into the perchlorate form by evaporation to dryness with perchloric acid 3 to 4 times. The solutions were made up to a required ionic strength by sodium perchlorate and the pH adjusted by the addition of very small portions of dilute sodium hydroxide while shaking in order to avoid precipitation of these metal ions as hydroxide.

Actinium-228: Actinium-228 was separated in carrier free form from radium-228 by an ion exchange method reported by Bhatki and Adloff[13]. A column (20 mm x 3 mm) of Zeo Karb-225 (100-200 mesh) was conditioned with 2.0N nitric acid. Two to three drops of the radium sample taken into 2N HNO_3 was placed on the column and then eluted with 5 ml of 2N HNO_3. Thorium-228 is retained in the resin whereas radium-228 and actinium-228 collect in the eluate. Keep the solution for a month so that the daughter radium-224 and subsequent granddaughters are removed by radioactive decay processes. The γ-spectra taken using a multichannel analyser and a 3" x 3" NaI(Tl) crystal scintillator as detector was noted after the initial stages of separation and at the end of the 30th day. The absence after 30 days of a photo-peak at 240 keV due to lead and bismuth indicated that the next stage of the separation could be carried out. The solution was dried and the residue taken into 2N HNO_3 and placed on a cation exchange column (similar to the first column) pre-conditioned with the same acid. Radium-228 comes out of the column after eluting with about 20 ml of 2N HNO_3 and actinium-228 remains in the column. Further elution was made with 3N HNO_3 where actinium comes out of the column with 5-6 ml of the acid. The actinium solution in the nitric acid was evaporated to dryness, converted to the perchlorate form and made up to the required ionic strength and pH as already described for other elements. The purity of actinium-228 was checked by its γ-spectra and half-life. Each batch of actinium-228 separated by this method was further checked by its distribution into HDEHP under standardised conditions.

Americium-241 and Curium-244 were used in these measurements. Curium-244 was obtained from A.E.R.E., Harwell in dilute nitric acid solution. The isotopes were checked for daughter activity before use. The requisite perchlorate solutions of these metal ions were made as noted earlier for other elements. Care was always taken in the adjustment of pH to avoid hydrolysis.

Yttrium-91, scandium-46 and indium-114_m isotopes of high specific activity were used as sources of these metal ions. The requisite perchlorate solutions were made with the help of $HClO_4$ and $NaClO_4$. The indium content in the solution was determined spectrophotometrically using a 8-hydroxyquinoline/chloroform method[14].

The stock solutions of each isotope were kept in air-tight polythene bottles.

Counting: Lanthanum-140, cerium-144, actinium-228, yttrium-91 and indium-114_m were counted (10 ml of the aqueous solution) in an annular type Geiger-Müller liquid counter. Gadolinium-153, europium-152 and 154 mixture, americium-241 and scandium-46 were counted (5 ml in a polythene capsule) in a well-type NaI(Tl) crystal scintillation counter. Curium-244 and americium-241 were counted in a liquid scintillation counter described in the next part of this chapter.

Apparatus and Instruments

Geiger-Müller Counter

A Twentieth Century Electronics annular tube type-M6H liquid Geiger-Müller counter was used for the assay of all energetic β-emitters. The counter consists of a halogen quenched thin-walled counter tube of borosilicate glass. An annular space around the counting tube takes 10 ml of the solution to be counted. The tube was used with a special lead castle designed and made in this laboratory. The electronic accessories used were those developed at A.E.R.E., Harwell with a modification in probe unit for use with halogen quenched type tubes. The counting rate of the tube was checked 2 to 3 times a day with a standard source of cesium-137.

Crystal scintillation counting

A well type NaI(Tl) crystal scintillator 8/1A - F/8 ($1\frac{1}{2}$" diameter, 1" height) mounted on a photomultiplier tube supplied by Nuclear Enterprises (G.B.) Ltd., Edinburgh, was used for the measurement of γ-emitters. The electronic equipment used was the Harwell 2000 series made by Dynatron Ltd., England. An assembly (in block diagram form) for scintillation counting is shown in Fig. 3.1. A snap-top polythene capsule which can sit in the well and with a capacity of 6 ml was used for counting. A multi-channel analyser, Laben - Mod. A-51-Cise, was used with the crystal scintillator whenever the γ-spectrum analysis of a particular radioactive sample was required.

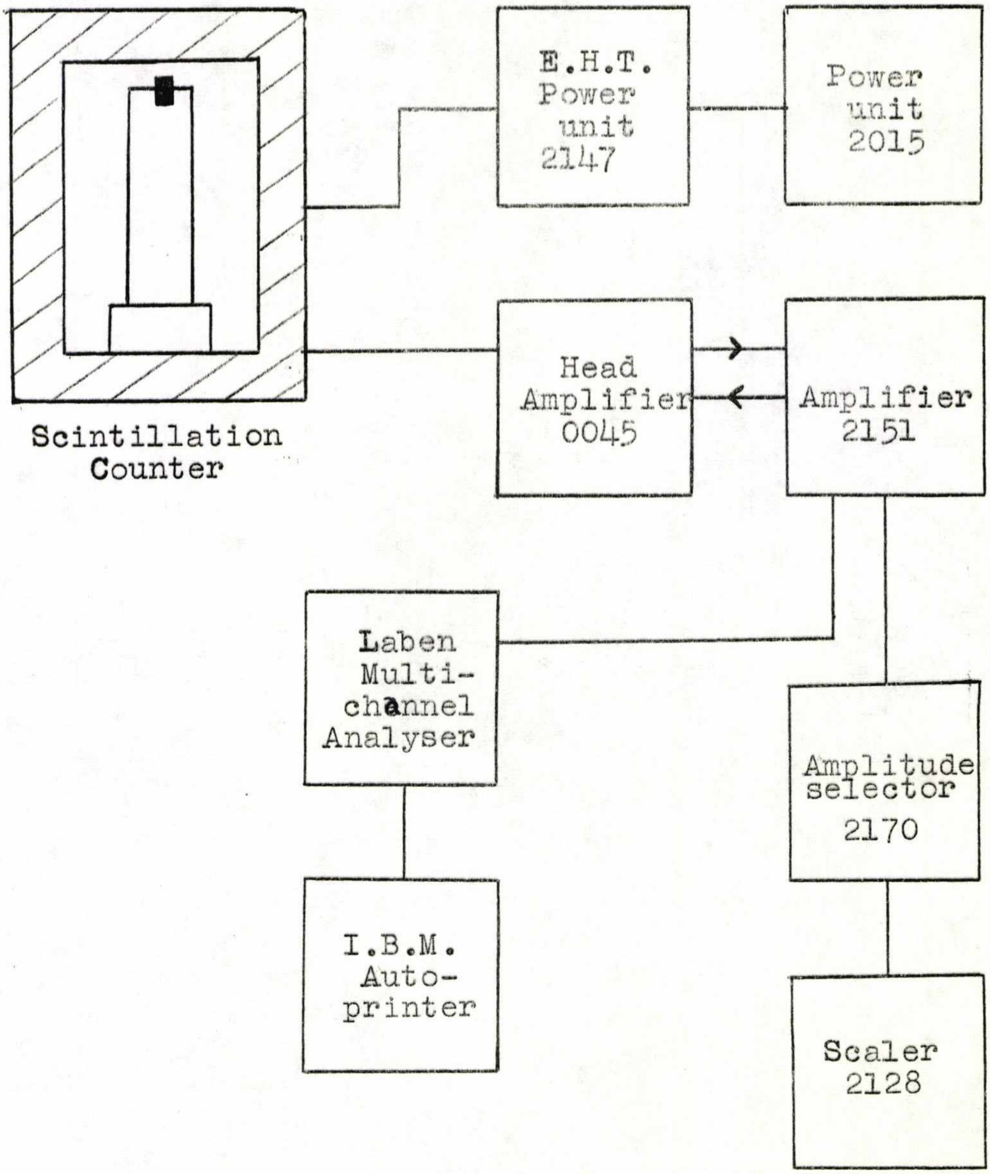


Fig. 3.1. Block diagram of typical accembly for Scintillation Counting.

Liquid scintillation counting

Liquid scintillation counting methods have been widely[15-24] used for the radioactive assay of soft β-emitters like carbon-14 and tritium. Comprehensive reviews[16-20] on the subject have appeared over the last ten years. 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. The high energy of α-particles which results in the production of larger light pulses comparedto β-particles is advantageous in this case[15-20]. In part this allows the operator to eliminate the phosphorescence effect and the interference from electrical noise in the electronics associated with the counting. The main difficulty encountered with the counting of α-emitting cations relates to their solubility and dispersion in the scintillation media. It is also desirable to use chemical substances that do not result in the formation of colour or other light quenching agents, hence α-emitters of high specific activity are most convenient to use. The liquid scintillation mixtures are usually organic based and do not readily assimilate water or aqueous solutions containing inorganic salts. Water frequently exerts a large quenching effect[15]. Much work, reviewed by Rapkin[16], has been done towards the development of scintillator solutions capable of absorbing aqueous samples without detrimental effects to performance. For example, Horrocks and Studier[21] and Glendenin[22], by using various complexing and extracting agents in the scintillator mixture, were able to count α-particles from plutonium-239 and 240 and thorium-232 respectively. In general alcohols, such as methanol and ethanol, ethers such as dioxan and cellosolve and naphthalene are among the substances being used in dealing with aqueous mixtures[15,16,23]

In the present work use was made of a dioxane-cellosolve based mixture originally proposed by Bruno and Christian[24] for carbon-14 counting. The scintillation mixture consists of 10 gm of 2,5-diphenyloxazole (PPO) [B.D.H. Laboratory reagent grade], 0.5 gm of 1,4-bis-2-(5-phenyloxazolyl)-benzene (POPOP) [supplied by Nuclear Enterprises (G.B.) Ltd.], 5 gm of naphthalene [Micro Analytical Reagent grade] and 170 ml of 2-ethoxyethanol [Hopkin and Williams Ltd., "General Purpose Reagent") made up to one litre with 1,4-dioxan [B.D.H., "Laboratory Reagent Grade"].

The solubility of aqueous solution in the above mixture was at least 15% (v/v). The counting apparatus consisted of a single photomultiplier tube (E.M.I. 6097S type) having a high signal to noise response, used in conjunction with pre and main amplifiers (NE 5202) and suitable discriminating equipment (single channel pulse height selector (NE 51027) all supplied by Nuclear Enterprises (G.B.) Ltd. In some later measurements the above electronic accessories except the photomultiplier tube were replaced by Harwell 2000 series modules. In all measurements 2 ml of aqueous solution were mixed with 10 ml of scintillation mixture in a glass container (2.5 cm diameter, 4.5 cm in height) ground flat on the bottom. Good optical contact with the photomultiplier window (made of quartz) was obtained through the use of a few drops of viscous silicone oil (Hopkin and Williams, "silicon fluid", MS200/1000CS). The sample container was covered with a brass cap (4.7 cm diameter, 5 cm in height) the interior surface of which was painted white; the cover was of such a fit as to exclude external light from the phototube. The whole of the assembly inside a lead castle was covered with a black cloth for complete removal of light. Prior to actual measurements, several tests on the sensitivity of the above scintillation mixture with the aqueous solution were carried out in the presence of all the ligands anticipated to be used in the present measurements. The count rate of a curium-244 sample containing high salt content, incorporated to control ionic strength, was found constant over a month. This sample was used as a standard to check the counter from time to time. The check on the variation in activity or the quenching due to the presence of sodium perchlorate in addition to fluoride, sulphate and oxalate was studied in detail. The results are reported in Table 3.1. It is found that about

Table 3.1 - Quenching effect of fluoride, sulphate and oxalate on the liquid scintillation counting of curium-244

Ligand	Concentration	Activity (c.p.m.) without ligand	Activity (c.p.m.) with ligand	Remarks
Fluoride	6.64×10^{-4}M	1230 1182*	1235 1168*	Clear mixture and no quenching.
	16.61×10^{-4}M	1230 1178*	1186 1162*	
Sulphate	5.38×10^{-2}M	1410 1398*	1400 1365*	No quenching precipitate formed on addition of SO_4.
Oxalate	4×10^{-5}M	1182 1219*	1201 1189*	No quenching, clear mixture.
	2.5×10^{-3}M	1387 1338*	1353 1318*	

*Activity measured after 24 hours whereas the others were measured 5 minutes after the addition of scintillator.

The amount of the aqueous solution containing curium-244 activity was the same (2 ml) in the absence or presence of ligand. The pH and ionic strength of the aqueous solution added was 3.60 and 0.500 M ($NaClO_4$) respectively.

30 minutes are required in order to obtain reproducible counting rates after mixing the aqueous radioactive solution and the scintillator. Quenching due to the presence of perchlorate and fluoride ion is almost absent, while in sulphate and oxalate solutions it is not marked, e.g. an aqueous solution 5.38×10^{-2}M in sulphate is about 4% and for oxalate even at the highest concentration 2.5×10^{-3}M it is not more than 2%. On mixing the aqueous sulphate solution with scintillator a precipitate results, whereas a clear solution is obtained in the presence of perchlorate, fluoride and oxalate ligands. As counting ratios are used in this work there is no adverse effect due to inhomogeneity of sulphate mixture. The reduction in the counting efficiency noted above includes a possible contribution from this source. In all cases the precipitate of well-defined crystalline form is allowed to settle down before the mixture then counted. The reliability of liquid scintillation counting can be checked by counting americium-241 both by crystal and liquid scintillator. In a limited study it was found that ϕ_{1L} at certain fluoride concentrations has the same value determined by both methods. A detailed study of this sort was made in the presence of sulphate ion. The results reported in chapter IV show that the method is highly reliable for counting α-emitters even in the presence of precipitate in the liquid scintillation mixture.

Equilibration Method

The distribution ratio K_d of a metal ion between an aqueous phase in the presence or in the absence of ligand and HDEHP/toluene solution or ion-exchange resin was obtained by measuring the counting rate of the aqueous phase before (B) and after (A) equilibration. K_d is then defined as

$$K_d = \frac{(B-A)v}{Am} \qquad (3.9)$$

where m is the mass of the resin (~ 0.1 gm) or the volume of the HDEHP solution (15 ml) and v is the volume of the aqueous phase (15 ml). When the distribution ratio is very high the HDEHP/toluene solution is further diluted with toluene. In the systems containing resin a correction, δ, the swelling factor, is normally applied to v to account for the uptake of water from the aqueous phase by the dry resin. δ was determined by the method described by Sonesson[25] and for the system described above found negligible (0.1 - 0.3 gm of resin in 15 ml of aqueous solution). The equilibrations in the liquid-liquid extraction systems at 25.0 ± 0.5°C were carried out in polythene bottles (50 ml capacity) shaken in air by means of a mechanical shaker to ensure adequate mixing. The equilibrations involving ion-exchange resin were carried out in polythene capsules (20 ml capacity) which could be heated sealed; the capsules were attached to a rotating disc immersed in a thermostat at 25.0 ± 0.1°C. The time of equilibration sufficient for the attainment of equilibrium was checked independently in this laboratory in the course of the present work and before[26]; it is usually 1-4 hours for HDEHP extraction systems and about 18-20 hours for ion-exchange resin systems.

The pH of the aqueous phase was checked after counting and if it changed by more than 0.03 units that particular run was discarded. Care was taken to keep the counter tube and other necessary apparatus covered in order to protect the solutions from the laboratory atmosphere. Measurements of pH were carried out by means of a Doran Universal pH meter (Derritron Instrument Co. Ltd., Stroud, Glos., England) fitted with a glass/calomel electrode assembly, the latter electrode having a saturated sodium chloride rather than the more usual potassium chloride bridge. The meter was "standardized" against 0.05M potassium hydrogen phthalate. After equilibration the phases were carefully separated by centrifugation. In separating the aqueous phase from the resin or HDEHP/toluene phase, care was taken to avoid pipetting the resin particles or organic phase. A material balance check was made in the liquid-liquid extraction system both in the presence and absence of ligand (like fluoride, sulphate and oxalate) by measuring the activity in both phases.

In order to make correction on the fluoride due to the presence of HF and acid fluoride HF_2^- at the experimental pH, the dissociation constant and thereby the pK was measured appropriate to our electrode system at 25°C and an ionic strength of 0.5 and 1.0 over the ligand range covered in the distribution studies. Table 3.2 represents the results.

Table 3.2

pK values for hydrogen fluoride (HF).

Ionic strength	pK
0.5	2.91
1.0	2.93

The contribution of HF_2^- is negligible at the experimental pH (3.6) as found by the constancy of K_{HF} over the range of pH studied (see Chapter II).

EXPERIMENTAL DATA AND ITS TREATMENT

The dependence of k_0, the distribution ratio of metal ion into the HDEHP/toluene phase and an aqueous phase of sodium perchlorate at constant ionic strength on the pH of the aqueous phase and the extractant (HDEHP) concentration was carried out and representative results are shown in Tables 3.3 and 3.4. It is seen that k_0 is

Table 3.3 - The Distribution of Gadolinium between di(2-ethylhexyl)phosphoric acid (H_2D_2) in toluene (2.5×10^{-2}% (w/v)) and an aqueous phase $\mu = 0.500$ ($NaClO_4$) at different pH values

Experiment No.	pH	k^0	k^{0*}
1	3.42	4.36	4.29
2	3.54	9.29	9.83
3	3.62	17.1	-
4	3.65	20.0	19.6
5	3.78	52.2	51.6
6	3.85	82.3	83.7

*On the basis of data from experiment 4 assuming k^0 is proportional to $[H^+]^{-3}$.

Table 3.4 - The distribution ratio, k^0, for americium(III) between an aqueous phase of $NaClO_4$ (0.500 M) at pH 3.60 and a toluene solution of variable HDEHP.

Experiment No.	HDEHP % w/v x 10^2	k^0	k^{0*}
1	2.50	0.4850	0.4840
2	5.00	3.830	3.869
3	7.50	13.06	-
4	12.5	61.16	60.46

*On the basis of data from experiment 3 assuming k^0 is proportional to $[HDEHP]^3$.

directly and inversely dependent on the cubic power of HDEHP and hydrogen ion concentration respectively for all the trivalent metal ions studied. Furthermore, the distribution ratio in the presence of ligand, ϕ_L, for all the metal ions studied is found cubic dependent on the HDEHP concentration in the organic phase. Representative results are shown in Tables 3.5 and 3.6.

The distribution parameters,

$$\phi_{1L},\ \phi_{1R} \text{ and } \frac{\phi_{1L} - \phi_{1R}}{1 + \phi_{1R}[F^-]}$$

at constant ionic strength and pH for lanthanum, cerium(III), gadolinium, europium(III), actinium, americium(III), curium(III), yttrium, indium and scandium over a range of fluoride ion concentration are reported in Tables 3.7 - 3.16.

It is seen from the results that ϕ_{1L} is an increasing function of fluoride for indium and scandium systems at constant pH (2.8 - 3.60) and ionic strength over the whole range of fluoride studied. After attaining a broad maximum value at certain fluoride concentrations, ϕ_{1L} becomes a decreasing function with increasing fluoride concentration for all the other systems studied, namely trivalent lanthanides, actinides and yttrium.

It is assumed according to the model previously used[6] that if only $M(HD_2)_3$ extracts into the toluene phase ϕ_{1L} should be a steadily increasing function of fluoride, $[F^-]$, as observed for indium and scandium. The behaviour of other

Table 3.5 - Distribution ratio, ϕ_L, for indium(III) between HDEHP in toluene and an aqueous phase pH 3.20, μ = 1.000 ($NaClO_4$) containing 10.4 x 10^{-4}M fluoride

Experiment No.	HDEHP %(w/v) x 10^3	ϕ_L	ϕ_L^*
1	1.25	1.09	1.10
2	2.50	8.83	8.83
3	3.100	15.2	15.2
4	5.00	70.6	-

*On the basis of the experimental data for experiment 4 assuming ϕ_L is proportional to $[HDEHP]^3$.

Table 3.6 - Distribution ratio, ϕ_L, for yttrium and americium(III) between HDEHP in toluene and an aqueous phase pH 3.60, $\mu = 0.500$ ($NaClO_4$) containing 33.22×10^{-4}M fluoride

Metal ion	Experiment No.	HDEHP % w/v	ϕ_L	ϕ_L^*
Y^{3+}	1	0.0075	0.648	0.651
	2	0.0100	1.544	-
	3	0.0250	24.04	24.13
	4	0.0400	97.94	98.82
Am^{3+}	1	0.050	0.642	0.630
	2	0.0750	2.127	-
	3	0.1000	5.113	5.042
	4	0.125	9.788	9.847

*On the basis of data from experiment 2 for both yttrium and americium(III), assuming ϕ_L is proportional to $[HDEHP]^3$.

Table 3.7 - HDEHP and cation-exchange partition data for the lanthanum-fluoride system at $\mu = 0.500$ ($NaClO_4$), pH = 3.60 and 25.0 ± 0.5°C

$[F] \times 10^4$	$\phi_{1L} \times 10^{-2}$	$\phi_{1R} \times 10^{-2}$
0.1661	-	4.421
0.3322	-	4.404
0.6644	-	4.490
0.9966	-	4.532
1.329	-	4.558
1.661	5.356	4.639
2.658	5.370	-
3.322	5.490	4.820
4.982	6.063	4.930
6.644	6.233	4.850
8.305	6.453	4.880
9.966	6.776	4.750
11.62	7.501	4.720
13.29	7.112	4.830
16.60	6.746	4.700
19.93	6.175	4.700
21.59	5.828	-
23.25	5.445	4.650
24.92	4.767	-
26.58	4.326	4.580
29.90	3.299	4.520
33.22	2.619	4.550
36.54	1.250	-

ϕ_{1L} were obtained using 0.25% w/v HDEHP with $k_0 = 30.41 \pm 0.98$ (6 values) and ϕ_{1R} using 0.100 gm of exchange resin with $l_0 = 6783 \pm 62$ (10 values).

Table 3.8 - HDEHP and cation exchange partition data for the cerium(III)-fluoride system at $\mu = 0.500$ ($NaClO_4$), pH = 3.60 and 25.0 ± 0.5°C

$[F] \times 10^4$	$\phi_{1L} \times 10^{-3}$	$\phi_{1R} \times 10^{-3}$	$\frac{\phi_{1L}-\phi_{1R}}{1+\phi_{1R}[F]} \times 10^{-2}$
1.661	1.912	-	-
2.658	1.715	0.806	7.49
3.322	1.827	0.946	6.70
4.983	2.096	0.790	9.39
5.979	2.245	0.880	8.94
6.644	2.301	0.806	9.74
7.641	2.542	0.880	9.85
8.305	2.587	0.774	11.04
9.966	2.788	0.948	9.46
10.96	3.043	0.932	10.44
12.62	3.158	0.951	10.03
13.29	2.951	0.849	
16.61	2.857	0.887	
19.93	2.745	0.868	

ϕ_{1L} were obtained using 0.075% w/v HDEHP with $k_0 = 21.83 \pm 1.07$ (8 values) and ϕ_{1R} using 0.1000 gm of exchange resin for which $l_0 = 6262 \pm 68$ (8 values).

Table 3.9 - HDEHP and cation exchange partition data for the Europium(III) fluoride system at μ = 0.5000 ($NaClO_4$), pH = 3.60 and 25.0 ± 0.5°C

$[F] \times 10^4$	$\phi_{1L} \times 10^{-3}$	$\phi_{1R} \times 10^{-3}$	$\frac{\phi_{1L}-\phi_{1R}}{1+\phi_{1R}[F]}$
1.661	2.783	2.211	418.4
3.322	3.511	2.434	595.4
4.319	3.863	2.528	638.2
4.983	3.924	2.517	624.1
6.644	4.621	2.596	743.1
8.305	5.409	2.671	850.7
9.966	5.793	2.732	822.1
10.63	6.213	2.801	857.8
13.29	7.106	2.807	-
16.61	7.047	2.808	-

ϕ_{1L} were obtained using 0.05% w/v HDEHP with $k_0 = 70.70 \pm 2.71$ (8 values) and ϕ_{1R} using 0.100 gm of exchange resin for which $l_0 = 5625 \pm 65$ (6 values).

Table 3.10 - HDEHP and cation exchange partition data for the gadolinium-fluoride system at $\mu = 0.5000$ ($NaClO_4$), pH = 3.60 and 25.0 ± 0.5°C

$[F] \times 10^4$	$\phi_{1L} \times 10^{-3}$	$\phi_{1R} \times 10^{-3}$	$\frac{\phi_{1L}-\phi_{1R}}{1 + \phi_{1R}[F]} \times 10^{-3}$
2.584	4.334	2.245	1.322
3.190	4.790	2.311	1.427
4.173	5.170	2.258	1.499
5.310	6.463	2.487	1.713
7.050	7.942	2.744	1.771
9.690	10.10	2.609	2.123
11.13	10.35	2.689	1.919
12.84	12.24	2.692	2.142
15.93	12.05	2.685	-
17.60	11.83	2.621	-
19.14	9.610	2.582	-
22.33	4.240	2.504	-

ϕ_{1L} were obtained using 0.025% w/v HDEHP with k_0 = (16.00 ± 0.89) (6 values) and ϕ_{1R} using 0.1000 gm of exchange resin for which l_0 = 5145 ± 54 (12 values).

Table 3.11 - HDEHP partition data for actinium fluoride system at μ = 0.500 ($NaClO_4$) and 25.0 ± 0.5°C

$[F] \times 10^4$	ϕ_L	$\phi_{1L} \times 10^2$
1.661	2.282	5.513
3.322	2.089	5.792
4.982	1.910	6.106
5.980*	1.899	6.299
6.644	1.748	6.397
8.305	1.591	6.803
9.966	1.457	7.120
11.62*	1.402	7.450
13.29	1.239	7.603
16.61	1.079	7.878
19.93	0.9453	8.204
21.59*	0.9513	8.096
23.25	0.8781	7.900
24.92*	0.8947	7.715
26.58	0.8264	7.577
29.90	0.8928	5.986
33.22	0.9354	5.006
36.54	0.9803	4.217
39.86*	1.149	3.201

ϕ_{1L} were obtained with 0.25% w/v HDEHP with k_o = 2.491 ± 0.072 (6 values).

*k_o = 2.615 ± 0.101 (4 values).

Table 3.12 - HDEHP and cation exchange partition data for the americium(III) fluoride system at $\mu = 0.500$ ($NaClO_4$), pH = 3.60 and 25.0 ± 0.5°C

$[F] \times 10^4$	$\phi_{1L} \times 10^{-3}$	$\phi_{1R} \times 10^{-3}$
0.1661	-	1.581
0.3322	-	1.862
0.4983	-	2.016
0.6644	-	1.987
0.8305	-	2.091
0.9966	-	1.794
1.163	-	2.122
1.329	-	2.146
1.661	2.563	2.156
2.658	2.787	2.188
3.322	2.889	2.214
4.982	3.107	2.213
6.644	3.428	2.218
8.305	3.579	2.358
9.966	3.734	2.360
11.63	4.038	2.409
13.29	4.204	2.400
16.61	4.203	2.415
19.93	3.414	2.250
21.59	2.956	2.202
23.25	2.628	2.130
24.92	2.410	2.100
26.58	2.044	2.200
29.90	1.709	2.188
33.22	1.302	2.189
36.54	1.194	-

ϕ_{1L} were obtained using 0.075% w/v HDEHP with $k_0 = 11.33 \pm 0.53$ (8 values) and ϕ_{1R} using 0.100 gm of exchange resin with $l_0 = 5272 \pm 65$ (9 values).

Table 3.13 - HDEHP and cation-exchange partition data for the curium(III) fluoride system at $\mu = 0.500$ ($NaClO_4$), pH = 3.60 and 25.0 ± 0.5°C

$[F] \times 10^4$	$\phi_{1L} \times 10^{-3}$	$\phi_{1R} \times 10^{-3}$
1.661	-	1.970
2.658	2.494	2.027
3.322	2.854	2.106
4.982	2.970	2.108
5.980	3.015	2.124
6.644	3.269	2.207
8.305	3.422	2.261
9.966	3.733	2.107
10.63	3.807	2.000
11.63	3.949	2.043
13.29	4.106	1.961
16.61	3.742	1.850
19.93	2.994	1.798
26.58	1.786	1.678
29.90	1.492	1.652
33.22	1.230	-
36.54	1.050	-

ϕ_{1L} were obtained using 0.075% w/v HDEHP with $k_0 = 10.16 \pm 0.28$ (9 values) and ϕ_{1R} using 0.100 gm of exchange resin with $l_0 = 3245 \pm 64$ (6 values).

Table 3.14 - HDEHP and cation exchange partition data for the yttrium-fluoride system at μ = 0.500 ($NaClO_4$), pH = 3.60 and 25.0 ± 0.5°C

$[F] \times 10^4$	$\phi_{1L} \times 10^{-3}$	$\phi_{1R} \times 10^{-3}$
0.1661	8.135	7.132
0.3322	8.022	7.304
0.6644	8.398	7.499
0.9966	8.873	7.614
1.329	-	7.722
1.661	9.860	7.657
2.658	-	7.773
3.322	11.25	7.664
4.983	13.31	7.872
6.644	15.58	7.884
8.305	18.15	7.963
9.966	19.92	7.939
10.63	-	8.071
11.63	21.65	-
13.29	22.25	8.282
14.95	25.59	-
16.61	21.81	8.113
19.93	17.44	8.075
23.25	13.71	8.011
26.58	12.02	7.897
29.90	-	7.932
33.22	8.937	7.807
39.86	7.041	7.776
49.83	5.202	-
59.80	4.191	-
66.44	3.564	-

ϕ_{1L} were obtained using 0.01% w/v HDEHP with $k_0 = 47.38 \pm 1.23$ (8 values) and ϕ_{1R} using 0.100 gm exchange resin with $l_0 = 3271 \pm 42$ (8 values).

Table 3.15 - HDEHP and cation exchange partition data for the indium-fluoride system at $\mu = 1.000$ ($NaClO_4$) and 25.0 ± 0.5°C

$[F] \times 10^4$	$\phi_{1L} \times 10^{-3}$	$\phi_{1R} \times 10^{-3}$	$\frac{\phi_{1L}-\phi_{1R}}{1+\phi_{1R}[F]}$
2.602	-	4.901	-
3.406*	5.662	4.921	-
3.904	5.019	-	-
5.204*	5.930	5.120	-
6.505	5.647	-	-
7.806	7.475	5.397	399
8.515*	7.031	5.318	-
10.41	7.350	5.410	293
11.71	7.196	5.360	252
11.92*	7.839	5.353	-
13.01	8.218	5.312	368
15.33*	8.765	-	-
15.61	9.093	5.147	437
18.21	9.250	5.516	338
19.52	9.322	5.280	357
20.82*	9.840	5.047	416
23.42	10.87	4.87	483
25.55*	10.98	-	-
26.02	11.02	4.524	509
27.25	-	4.877	
28.62	12.55	-	
30.65*	-	5.325	
31.22	13.86	-	
36.43	17.31	4.794	
41.63	19.23	-	
46.84	21.66	-	
49.44	23.27	-	

*Measurements were made at pH 2.80 while the rest of the experiments were performed at pH 3.20.

ϕ_{1L} were obtained using 0.0025% w/v HDEHP with k_o 76.41 ± 1.23 (8 values) at pH 3.20 and 15.59 ± 0.87 (6 values) at pH 2.80 and ϕ_{1R} using 0.100 gm of resin for which $l_o = 364.7 \pm 0.3$ (6 values).

Table 3.16 - HDEHP and cation exchange partition data for the scandium-fluoride system at μ = 0.500 ($NaClO_4$), pH = 2.50 and 25.0 ± 0.5°C

$[F] \times 10^{4}$	$\phi_{1L} \times 10^{-8}$	$\phi_{1R} \times 10^{-6}$	$\frac{\phi_{1L}-\phi_{1R}}{1+\phi_{1R}[F]} \times 10^{-5}$
0.022	0.0218	-	-
0.045	0.0270	-	-
0.056	0.0310	1.701	1.329
0.067	0.0350	-	-
0.089	0.0401	2.000	1.064
0.112	0.0461	2.214	0.929
0.168	0.0615	2.207	1.035
0.224	0.0768	2.870	0.736
0.280	(0.9400)	2.588	0.928
0.336	0.1084	3.089	0.740
0.392	(0.1300)	2.810	0.917
0.448	(0.1680)	3.163	0.956
0.560	0.2737	3.544	1.192
0.670	(0.3600)	4.010	1.183
0.784	0.4519	4.259	1.222
1.120	0.7580	-	-
1.680	1.396	-	-
2.240	2.163	-	-
3.360	3.169	-	-
5.60	9.480	-	-
7.84	19.80	-	-
11.20	59.13	-	-
13.44	94.18	-	-
16.80	173.1	-	-
20.16	292.1	-	-
22.40	402.4	-	-

ϕ_{1L} were obtained using (0.00125 - 0.125)% w/v HDEHP with k_0 = 136.3 ± 2.7 at 0.00125% w/v HDEHP (mean of 8). k_0 at other HDEHP concentrations were obtained measuring $k_0 \alpha [HDEHP]^3$.

ϕ_{1R} were obtained using 0.100 gm of exchange resin for which l_0 = 2729 ± 16 (6 values).

Interpolated data are given in parentheses.

metal ions in their extraction into HDEHP therefore awaits detailed study. The results are explained under the heading "Treatment of liquid-liquid extraction results". The cation-exchange results show that in all the systems ϕ_{1R} is almost independent of fluoride concentration. The ion-exchange results are limited to a few systems and they are subsequently explained under the heading "Treatment of ion-exchange results".

Treatment of liquid-liquid extraction results

The solvent extraction results represented here are classified on the basis of extraction behaviour. In the earlier studies on the unusual distribution behaviour of lanthanide and actinide fluoride systems, several tests were carried cut. Whether the decrease in ϕ_{1L} with fluoride after a certain concentration is reached is due to the extraction or exchange of fluoride with HDEHP was independently checked. This was done by shaking different amounts of fluoride with HDEHP in the absence of metal ion. The fluoride content in the aqueous phase was measured before and after shaking with HDEHP by a fluoride ion membrane electrode. There was no exchange or partition of fluoride into the HDEHP phase.

The distribution of americium(III) and yttrium into variable concentrations of HDEHP in toluene was measured in the presence of aqueous solutions containing a high concentration of fluoride. The results (Table 3.6) show the cubic dependence of ϕ_L on HDEHP exist in the presence of high fluoride concentration even though the distribution behaviour is unusual over this ligand range. Independent potentiometric studies (Chapter II) have provided reliable data for overall stability constants, β_m, for yttrium in its interaction with fluoride. Accordingly, the yttrium system, the behaviour of which is similar to the lanthanides and actinides, was used in an attempt to find a suitable model whereby this unusual extraction behaviour can be explained in addition to the determination of stability constants for higher fluoro metal complexes. From the extraction data one can calculate β_1 and β_2 from the straight line part of the ϕ_{1L} vs. $[F^-]$ plot (Fig. 3.2) whereas the value of β_3 cannot be computed directly for these systems (c.f. indium and scandium systems). This approach to find β_3 from the HDEHP partition data may be justified on the grounds (i) that existing potentiometric methods are not applicable to a study of actinium, americium(III) and curium(III), (ii) that it should provide information concerning the nature of the extraction process.

Yttrium-fluoride system

β_1 and β_2 values calculated from the measurements over the limited and sufficiently low fluoride concentration range are in good agreement with the values got in the course of the present work by independent methods of

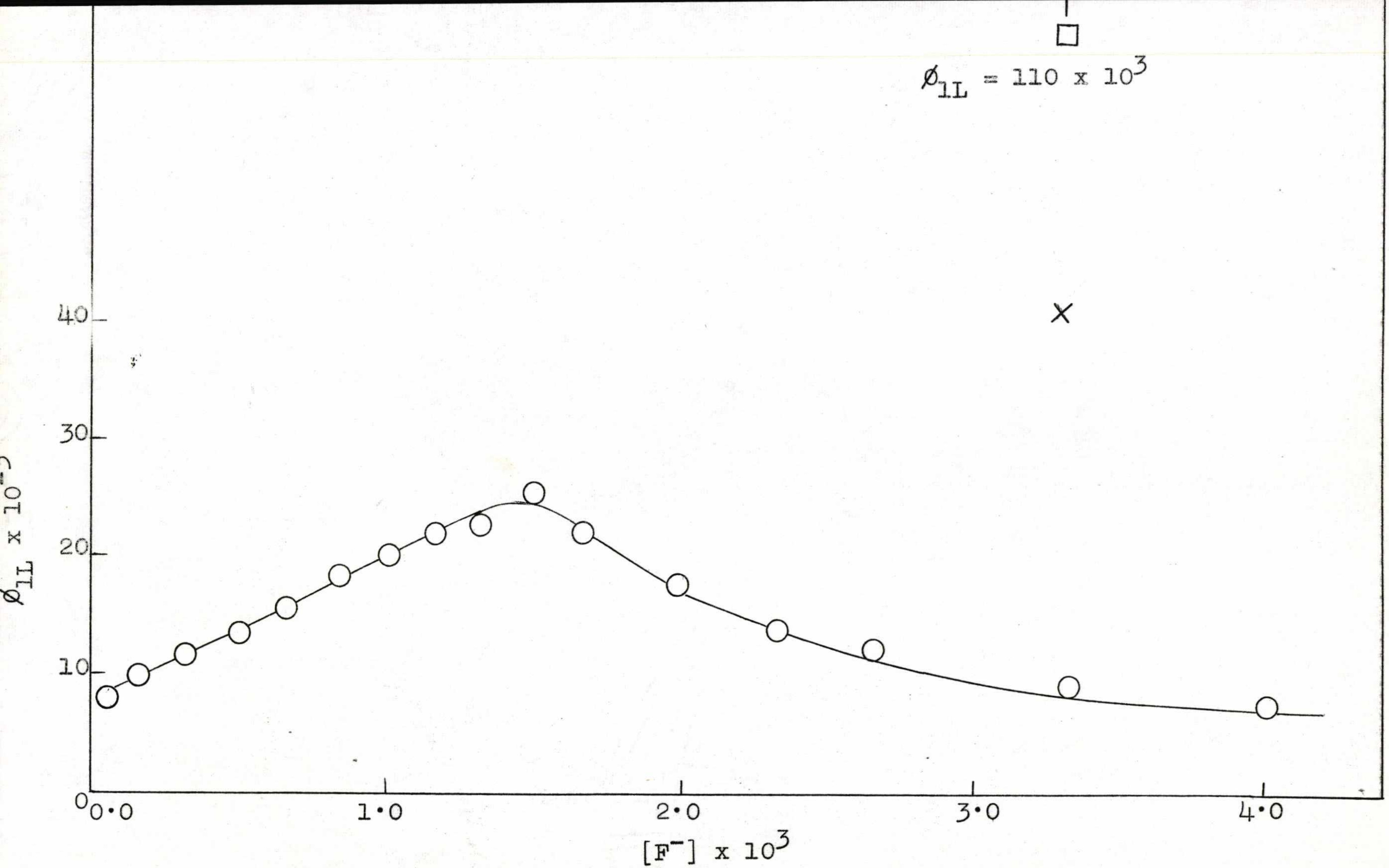


Fig. 3.2 ϕ_{1L} plotted ○ as a function of $[F^-]$ for yttrium distribution from aqueous $[F^-]$ at $\mu = 0{\cdot}500$ ($NaClO_4$), and pH 3·60 into 0·01% w/v HDEHP in toluene. X and ☐ represent ϕ_{1L} from similar solutions at $[F^-] = 3{\cdot}32 \times 10^{-3} Ml^{-1}$ and pH 3·83 and 3·97 respectively. The full curve represents ϕ_{1L} calculated from eqs. 3·23 or 3·24 taking K = 1·92 (see text). The temperature was 25°C.

measurement in addition to other published results[3] (Table 3.17). The decrease in ϕ_{1L} over the high fluoride concentration range could conceivably be explained as being due to (i) metal fluoride precipitated or adsorbed on the surface of containers, or (ii) the presence of more than one extractable species in the aqueous phase.

The enhanced change in ϕ_{1L} could not be explained on the basis of first possibility since a careful material balance check on both phases ruled this out. It may therefore be concluded that fluoride interaction with the metal ion gives rise to a fluoro metal complex which is readily solvated by and thus extracted into HDEHP. In view of the ϕ_{1L} - [F] curve (fig. 3.2) at low fluoride and the suspected low degree of solvation of MF_3 by water, it seems reasonable to conclude that YF_3 is solvated by the HDEHP.

To ascertain quantitatively whether one or more species were undergoing phase transfer an experiment devised by Martin and Gillies[27] was performed. If a series of equilibrations are carried out wherein all the conditions are kept constant except for the organic to aqueous volume ratios and if the yttrium concentration in the organic phase is plotted as ordinate against the yttrium concentration in the aqueous phase as absissa, a straight line should result if only one species is being extracted. For a solution containing an extractable species in equilibrium together with one (or more) inextractable

Table 3.17 - Stability constant data for yttrium, lanthanum, actinium, americium(III) and curium(III) fluoride systems at an ionic strength of 0.500

Metal ion	Method	$\beta_1 \times 10^3$	$\beta_2 \times 10^6$	$\beta_3 \times 10^9$	Ref.
Y^{3+}	dis	7.70 ± 0.21	12.8 ± 0.3	20	p.w.
	Ferri	8.51	13.6	21.8	3
	Ferri	8.20 ± 0.21	13.8 ± 0.6	19.5 ± 0.8	p.w.
La^{3+}	dis*	0.486 ± 0.021	0.151 ± 0.026	0.06	p.w.
	Ferri	0.470 ± 0.030	-	-	2
	Ferri	0.479	-	-	1
Ac^{3+}	dis	0.529 ± 0.010	0.167 ± 0.010	~0.08	p.w.
Am^{3+}	dis	2.46 ± 0.07	1.28 ± 0.09	1.0	p.w.
Cm^{3+}	dis	2.21 ± 0.07	1.50 ± 0.09	1.0	p.w.

*Values calculated from the distribution data at pH = 6.0.

dis = liquid-liquid extraction;

Ferri = potentiometric method using ferrous-ferric half cell;

p.w. = present work.

species not in rapid equilibrium, a straight line cutting the absissa at some positive value is obtained, the intercept giving the properties of inextractable species and slope of the line the extraction coefficient of the extractable species at equal volumes. A curve instead of a straight line cutting the absissa provides evidence for several extractable and inextractable species in the aqueous phase. Yttrium distribution into HDEHP/toluene solution gave (Fig. 3.3) a straight line (curve I) passing through the origin, a straight line (curve II) cutting the absissa and a curve (curve III) cutting the absissa when the aqueous phase contains none, 9.966×10^{-4}M and 3.322×10^{-3}M fluoride in that order. The distribution results show conclusively the existance of at least one other extractable species at the highest fluoride concentration in the aqueous phase in addition to M^{3+} as proposed earlier[6] or elsewhere[8,9].

Distribution studies with equal volumes of phases for which the HDEHP concentration in toluene is varied showed that ϕ_L retains a cubic dependence on HDEHP even at high $[F^-]$ (Table 3.6). It was also observed that constant HDEHP in the toluene phase and at a constant and large (3.322×10^{-3}M) concentration of fluoride at which the second partitioning species might be expected to swamp any contribution from $Y(HD_2)_3$, ϕ_L is independent of hydrogen ion over the pH range 3.4 - 4.0 (Table 3.18).

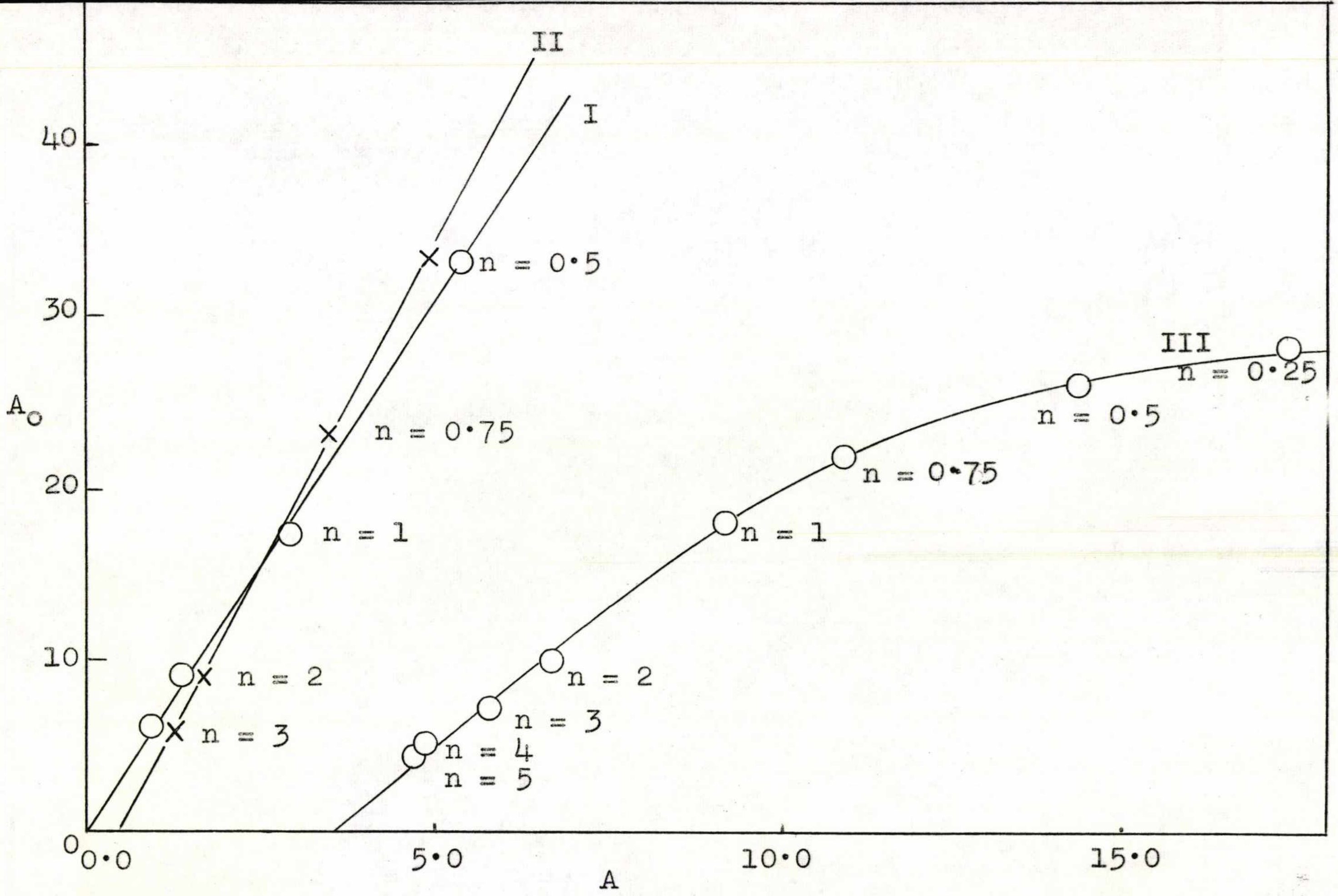


Fig.3.3. The effect of changing organic:aqueous phase ratio, n, on the distribution of yttrium from aqueous solutions of three different compositions into 0·01% w/v HDEHP in toluene. Curve I, $[F^-]$ absent; curve II, $[F^-] = 9{\cdot}97 \times 10^{-4} Ml^{-1}$ and for curve III, $[F^-] = 3{\cdot}32 \times 10^{-3} Ml^{-1}$. $\mu = 0{\cdot}500$ ($NaClO_4$) at 25°C. A_o and A represent the relative concentrations of yttrium in the organic phase to that in the aqueous phase.

Table 3.18 - pH dependence for yttrium distributing between 0.01% w/v HDEHP in toluene and an aqueous phase containing $[F^-] = 3.32 \times 10^{-3}$M at $\mu = 0.500$ and 25°C

Experiment No.	pH	ϕ_L	$\phi_{1L} \times 10^3$	$\phi^*_{1L} \times 10^3$
1	3.42	1.383	-	-
2	3.60	1.544	8.94	270.9
3	3.83	1.692	40.9	-
4	3.95	1.637	97.5	-
5	3.97	1.670	109.0	-

ϕ^*_{1L} is calculated on the basis of β values in Table 3.17. k_0 for experiments 1, 3, 4 and 5 were obtained from experiment 2 assuming k_0 is proportional to $[H^+]^{-3}$.

On the basis of these observations it is proposed that YF_3 (or in general MF_3) solvated by HDEHP and $Y(HD_2)_3$ or in general $M(HD_2)_3$ extract into the toluene at and beyond the fluoride concentration at which ϕ_{1L} attains a maxima (Fig. 3.2). The distribution equilibria can be explained in accordance with the following model

$$M^{3+} + 3H_2D_2 \overset{k'}{\rightleftharpoons} M(HD_2)_3 + 3H^+ \qquad (3.10)$$

$$MF_3 + 3H_xD_x \overset{k''}{\rightleftharpoons} MF_3.3H_xD_x \qquad (3.11)$$

where x is an unknown integer (probably 1 or 2), k', k" are the equilibrium constants for reaction (3.10) and (3.11) respectively and M^{3+} the metal ion, e.g. yttrium, americium(III), etc. If it is assumed that $M(HD_2)_3$ and $MF_3.3H_xD_x$ concentrations are negligible in the aqueous phase or that their distribution coefficients are very large, the overall distribution ratio ϕ_L for the metal ion is given by

$$\phi_L = \frac{[M(HD_2)_3]_{org} + [MF_3.3H_xD_x]_{org}}{[M^{3+}] + [MF^{2+}] + [MF_2{}^+] + [MF_3] + \ldots.} \qquad (3.12)$$

The aqueous phase concentrations are distinguished by the absence of a subscript. By limiting the discussion to only three fluoro complexes in the aqueous phase

$$\phi_L = \frac{k'[H_2D_2]^3_{org}[M^{3+}][H^+]^{-3} + k''\beta_3[H_xD_x]^3_{org}[M^{3+}][F^-]^3}{M^{3+} + \beta_1[M^{3+}][F^-] + \beta_2[M^{3+}][F^-]^2 + \beta_3[M^{3+}][F^-]^3} \qquad (3.13)$$

where $$k' = \frac{[M(HD_2)_3]_{org}[H^+]^3}{[M^{3+}][H_2D_2]^3_{org}} \qquad (3.14)$$

and $$k'' = \frac{[MF_3.3H_xD_x]_{org}}{[MF_3][H_xD_x]^3} \qquad (3.15)$$

β_m is the overall stability constant for the mth fluoro complex from M^{3+} and m$[F^-]$ as defined earlier. At limiting conditions when $[F^-] \longrightarrow o$

$$\phi_L^o = k_o = k'[H_2D_2]^3_{org}[H^+]^{-3} \qquad (3.16)$$

so that equation (3.13) becomes

$$\phi_L = \frac{k_o + k'\beta_3[H_xD_x]^3[F^-]^3}{1 + \beta_1[F^-] + \beta_2[F^-]^2 + \beta_3[F^-]^3} \qquad (3.17)$$

since the H_2D_2 concentration is kept constant in all the measurements we put

$$k''[H_xD_x]^3 = \text{constant} = k \qquad (3.18)$$

Then on rearrangement

$$\left(\frac{k^o}{\phi_L} - 1\right)/[F^-] = \phi_{1L} = \beta_1 + \beta_2[F^-] + \beta_3[F^-]^2 - \frac{k\beta_3}{\phi_L}[F^-]^2 \qquad (3.19$$

or $$\phi_{1L} = \phi_{1L}^* - \frac{k\beta_3}{\phi_L}[F^-]^2 \qquad (3.20)$$

where $$\phi^*_{1L} = \beta_1 + \beta_2[F^-] + \beta_3[F^-]^2 + \ldots.. \qquad (3.21)$$

It should be noted that the ϕ_{1L} previously employed[6] is here ϕ^*_{1L} which is the value of this distribution function when only $M(HD_2)_3$ partitions into the organic phase over the whole range of fluoride. Rearranging equation (3.20) we get

$$\frac{\phi^*_{1L} - \phi_{1L}}{[F^-]^2} = K\beta_3 \qquad (3.22)$$

On substituting values for ϕ^*_{1L} (calculated from the known values of β_1, β_2 and β_3) and, the experimentally observed ϕ_{1L}, the left-hand side of equation (3.22) can be evaluated numerically; $K\beta_3$ and therefore K values over the fluoride range of $(2\text{-}4)10^{-3}$M are set out in Table 3.19. It should be noted from Table 3.19 that K is not strictly constant, but appears to increase slightly with increasing fluoride concentration. Application of equation (3.19) to calculate ϕ_{1L} from the mean value of K and accepted values for β_m thus do not lead to satisfactory agreement with experimental ϕ_{1L} values at fluoride greater than 1.0×10^{-3}M. The large discrepancies arise because the third and fourth terms on the R.H.S. of equation (3.19) numerically dominate and small changes in K have a considerable effect on the resultant ϕ_{1L} value. The assumptions, therefore, applied here are not strictly valid, but they appear close enough

Table 3.19 - Test of equation (3.22) using yttrium distribution data

$[F^-] \times 10^3$	1.993	2.325	2.658	3.322	3.986
$K\beta_3 \times 10^{-10}$*	3.20	3.54	3.50	3.68	3.86
K	1.60	1.77	1.75	1.84	1.93

*Calculated from equation (3.22) taking (see Chapter II) $\beta_1 = 8.00 \times 10^3$, $\beta_2 = 13.0 \times 10^6$ and $\beta_3 = 2.0 \times 10^{10}$.

to permit calculation of reasonable (having regard to the present stage of development) stability constants.

Yttrium over the ligand rang $(2\text{-}4)10^{-3}$M $[F^-]$ obeys the above model, but due to non-availability of equilibrium data for higher fluoro complexes of trivalent actinides and lanthanides, the behaviour of which are similar to yttrium, the model needs modification so as to use the partition data alone in the direct measurement of equilibrium constants for such metal ions.

Equation (3.17) on rearrangement becomes

$$\frac{1}{\phi_L} = \left(\frac{1 + \beta_1[F^-] + \beta_2[F^-]^2}{[F^-]^3}\right)\frac{1}{K\beta_3 + \dfrac{k^o}{[F^-]^3}} + \frac{1}{K + \dfrac{k^o}{\beta_3[F^-]^3}} \qquad (3.23)$$

Under conditions where $K\beta_3 >> k_0/[F^-]^3$, i.e. where the extraction of $M(HD_2)_3$ is negligible compared with $MF_3.3H_xD_x$, equation (3.23) reduces to

$$\frac{1}{\phi_L} = \left(\frac{1 + \beta_1[F^-] + \beta_2[F^-]^2}{[F^-]^3}\right)\frac{1}{K\beta_3} + \frac{1}{K} \qquad (3.24)$$

A plot of $\frac{1}{\phi_L}$ against $\frac{1 + \beta_1[F^-] + \beta_2[F^-]^2}{[F^-]^3}$ gave a straight line for yttrium over the fluoride range $(2.5 - 4.9)10^{-3}$M (Fig. 3.4). [$\beta_1 = 7.7 \times 10^3$ and $\beta_2 = 12.8 \times 10^6$ are taken from Fig. 3.2 at sufficiently low fluoride concentrations.] The ratio of the intercept with the vertical axis to the

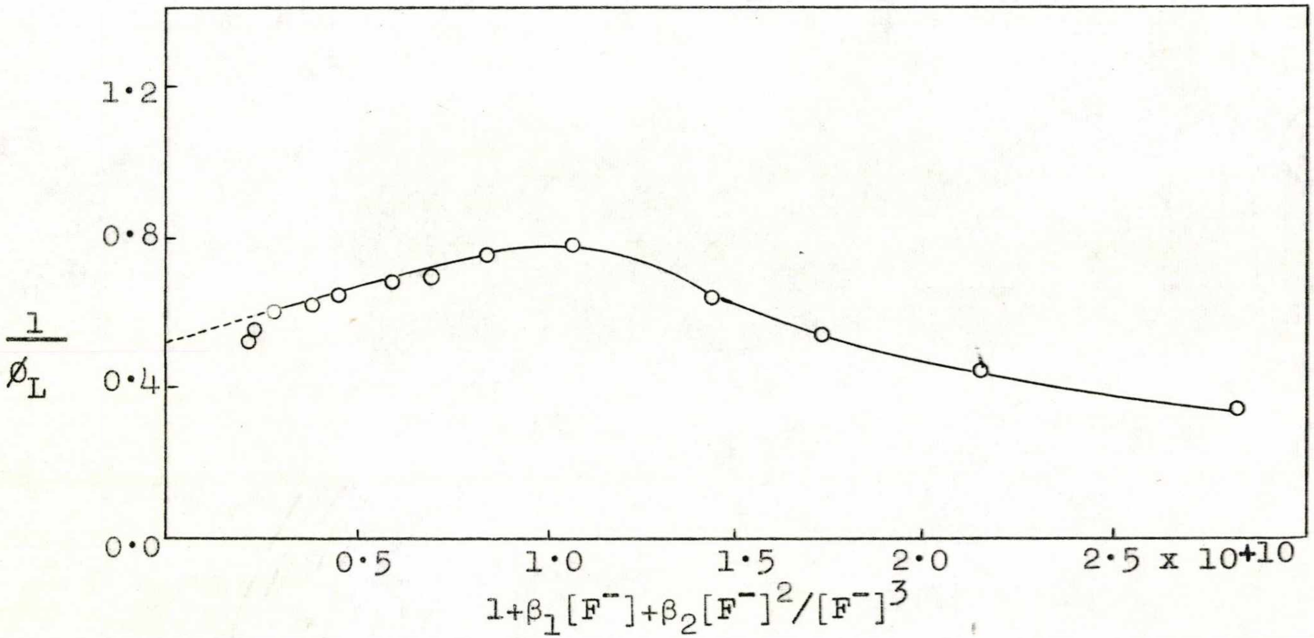


Fig. 3.4. Experimentally based points, o plotted for yttrium from the same data as that used in Fig. 1. The full line corresponds to $1/\phi_L$ calculated from eq. 3·23 or 3·24.

slope of the curve gave $\beta_3 = 2.0 \times 10^{10}$ in good agreement with the values from other sources[3] (Table 3.17).

In Fig. 3.4, a departure was observed for points corresponding to $[F^-]$ greater than 5×10^{-3}M. This could be explained by the formation of additional extractable fluorocomplexes. It should be noted that the function $1 + \beta_1[F^-] + \beta_2[F^-]^2/[F^-]^3$ converges with increasing fluoride so that the two points falling below the extrapolated (broken) line in Fig. 3.4 represent values at widely different $[F^-]$ from each other and the nearest point on the curve. At fluoride concentration lower than 2×10^{-3}M the distribution of $Y(HD_2)_3$ becomes significant and equation (3.24) is no longer adequate (see Fig. 3.2). K obtained from Fig. 3.4 enables ϕ_L to be calculated from the β values using equation (3.23) over the range $(0.5 - 2.0)10^{-3}$M $[F^-]$ where $\frac{k_0}{[F^-]^3}$ cannot be ignored. Values for ϕ_L thus calculated fit the curve in Fig. 3.4 confirming the method of treatment at low and moderately high $[F^-]$ up to 4×10^{-3}M. ϕ_L thus obtained from equations (3.23) and (3.24) give ϕ_{1L} values in good agreement with those obtained experimentally (Fig. 3.2). It may be concluded that by means of a careful analysis, the partition data of the form obtained for yttrium can yield satisfactory values for the first three overall stability constants without recourse to results from other experimental methods. It is desirable, however, to apply a number of tests of the assumptions involved as far as possible for each metal ion-fluoride system studied (see below).

Lanthanum, actinium, americium(III) and curium(III) fluoride systems

Measurements were made on the interaction of lanthanum, actinium, americium(III) and curium(III), with fluoride ion in aqueous solution by the HDEHP partition method over a fluoride range of $(1 - 40)10^{-4}$M. The treatment of the results was similar to that outlined for yttrium. Equilibrium constants obtained are recorded in Table 3.17. β_1 and β_2 were calculated by the least squares method from HDEHP distribution results at low fluoride concentrations. Results suitable for comparison have to the best of our knowledge not been published. The values of β_1 for lanthanum are in good agreement with those reported by Kury[1] and Walker and Choppin[2] (Table 3.17). The β values for lanthanum are the same as those for actinium. Americium(III) and curium(III) have similar β values when compared with each other and with those of europium(III) and gadolinium at an ionic strength of 0.500. The values for β_3 reported here were obtained by the graphical method except where otherwise mentioned.

Cerium(III), gadolinium and europium(III) fluoride systems

The partition data for these systems are reported earlier in Tables 3.8 - 3.10. Though the distribution behaviour is similar to the systems mentioned in earlier paragraphs, a less detailed study of these metal ion fluoride systems was carried out. Due to non-availability of enough results only β_1 and β_2 are calculated over the range of fluoride where ϕ_{1L} vs $[F^-]$ plot is roughly a straight line. The calculated β values are reported in Table 3.20 in addition to published results. Fair agreement is obtained with those reported by Naqvi and Lyle[6] for cerium(III), europium(III) and gadolinium.

Indium and scandium fluoride systems

The partition data for indium and scandium are reported in Tables 3.15 and 3.16. ϕ_{1L} is an increasing function of fluoride over the whole range of ligand studied in both the systems. On the basis of this HDEHP distribution behaviour, β_m values can be calculated assuming

$$\phi_{1L} = \beta_1 + \beta_2[F^-] + \beta_3[F^-]^2 + \beta_4[F^-]^3 + \cdots\cdots \qquad (3.25)$$

From the shape of the ϕ_{1L} - $[F^-]$ curve for indium and scandium it appears that three or more complexes are present. Best fitting parameters β_1, β_2, β_3, ... are in fact obtained by assuming three complexes for indium and

Table 3.20 - Stability constant data for cerium(III), europium(III) and gadolinium fluoride systems at 25°C

Metal ion	Method	Ionic strength	$\beta_1 \times 10^3$	$\beta_2 \times 10^6$	Ref
Ce^{3+}	dis	0.5	1.32 ± 0.04	1.51 ± 0.05	p.w.
	dis	0.5	1.41 ± 0.08	0.91 ± 0.08	6
	Ferri	0.5	1.29	-	1
	Ferri	0.5	1.30 ± 0.20	-	2
Gd^{3+}	dis	0.5	2.32 ± 0.17	5.56 ± 0.23	p.w.
	dis	0.5	2.67 ± 0.27	5.17 ± 0.32	6
	Ferri	0.5	2.34	-	1
	Ferri	0.5	2.36 ± 0.35	-	2
Eu^{3+}	dis	0.5	2.25 ± 0.09	3.58 ± 0.11	p.w.
	dis	0.5	2.48	3.01	6
	dis	1.0	1.59 ± 0.20	-	2
	Ferri	1.0	1.54 ± 0.05	-	2

For abbreviations see the footnote of Table 3.17.

four for scandium; the β values with their standard errors are given in Table 3.21. Agreement with the constants obtained by Sundén[5] for the indium-fluoride system is good (Table 3.21) showing that the assumptions concerning the extraction of indium from aqueous fluoride solutions are valid. The extent of the agreement is further shown in Fig. 3.5 by the experimentally obtained ϕ_{1L} in relation to the full line constructed from equation (3.25) using the stability constant data of Sundén[5].

The equilibrium constants for the first four fluoroscandium complexes are in good agreement with those of Kury and coworkers[4] (Table 3.21). ϕ_{1L} calculated from equation (3.25) using the β values of Kury et al[4] fall very close to experimental ϕ_{1L} values over the whole range of fluoride studied.

Extraction of various metal ions by HDEHP

In the measurements described, the distribution ratio ϕ_L at the higher end of the $[F^-]$ range, is the sum of contributions from $M(HD_2)_3$ and HDEHP solvated fluorometal complexes, mainly MF_3. The first is dependent on the inverse of the third power where as the second is independent of $[H^+]$. Table 3.22 represents the collected data for all the metals studied. It is seen that scandium and indium have by far the largest k_0 values at the pH common to all the ions of the elements listed; the fraction

Table 3.21 - Stability constant data for indium and scandium fluoride systems at 25°C

Metal ion	Ionic strength	Method	β_1	β_2	β_3	β_4	Ref.
In^{3+}	1.0	dis	$(4.7 \pm 0.3)10^3$	$(1.8 \pm 0.3)10^6$	$(4.1 \pm 0.6)10^8$	-	p.w.
	1.0	Pot	$(5.0 \pm 0.3)10^3$	$(1.8 \pm 0.4)10^6$	$(4 \pm 1)10^8$	$(5 \pm 3)10^8$	5
	1.0	i.ex.	1.0×10^3	0.6×10^6	4×10^8	-	28
	0.5	Ferri	6.0×10^3	2.6×10^6	-	-	29
Sc^{3+}	0.5	dis	$(1.47 \pm 0.07)10^6$	$(2.77 \pm 0.07)10^{11}$	$(2.91 \pm 0.14)10^{15}$	$(3.06 \pm 0.12)\times 10^{18}$	p.w.
	0.5	Ferri	1.51×10^6	2.82×10^{11}	3.31×10^{15}	2.34×10^{18}	4

Pot = potentiometric.

i.ex = ion-exchange.

For other abbreviations see footnote of Table 3.17.

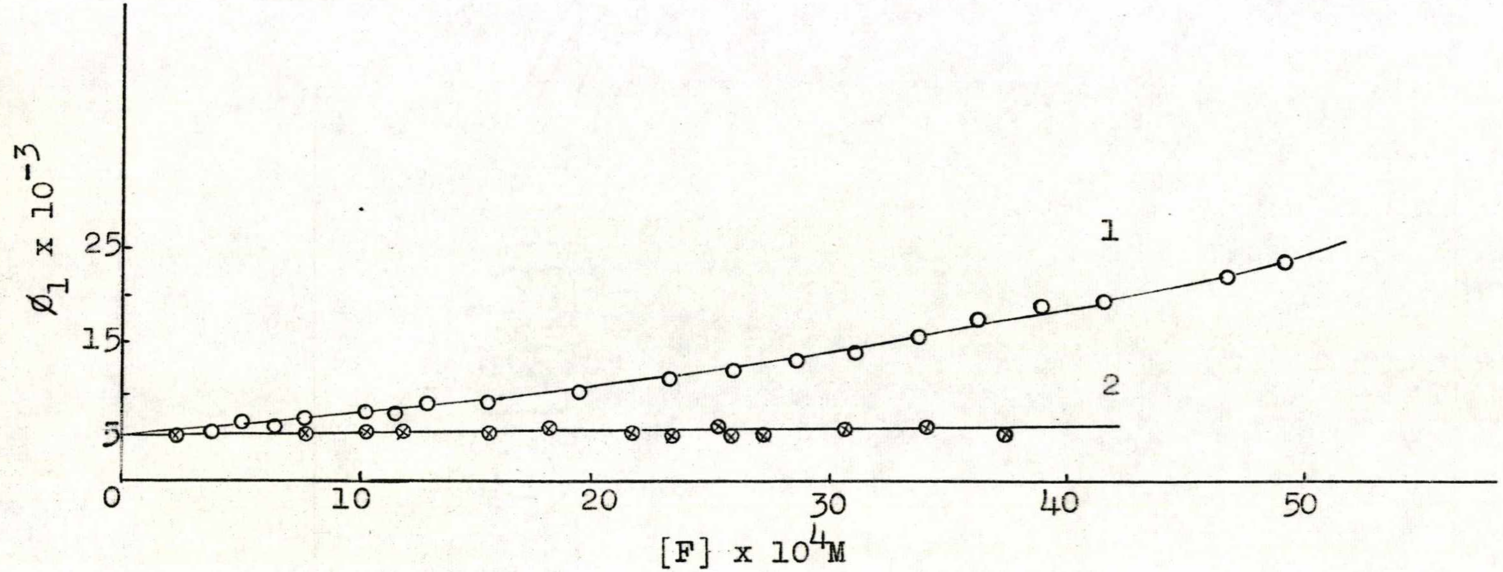


Fig. 3.5 ϕ_1 as a function of fluoride concentration at $\mu = 1{\cdot}000$ $(NaClO_4)$. Curve 1 and 2 refer to 0·0025% w/v HDEHP in toluene and ion-exchange distribution respectively. The circles in 1 represent experimental points but the solid line drawn on the basis of the equilibrium contants of sundén.

Table 3.22 - Distribution ratios,* k_o, for trivalent metal ions between 0.075% w/v HDEHP and 0.50M $NaClO_4$ at pH 3.60 and 25°C

Metal ion	Sc^{3+}	In^{3+}	Y^{3+}	Gd^{3+}	Eu^{3+}	Am^{3+}	Cm^{3+}
k_o	$6x10^{10}$	$3x10^{7}$	$2x10^{4}$	$4x10^{2}$	$2x10^{2}$	11	10

Metal ion	La^{3+}	Ac^{3+}
k_o	$9x10^{-1}$	$7x10^{-2}$

*'normalised' to the common HDEHP concentration quoted and rounded up to one significant figure (except for Am^{3+}).

of each of these metals extracted as $MF_3.3H_xD_x$ is negligible compared to that extracted as $M(HD_2)_3$, although M^{3+}_{aq} diminishes rapidly in concentration as $[F^-]$ increases. Evidently under the conditions of measurement the contributions from the former source are considerable in the extraction of yttrium, americium(III), curium(III), actinium, lanthanum and other trivalent lanthanides. However, from equations (3.12) and (3.13) an increase in pH should result in an increase in ϕ_{1L} for a given high $[F^-]$; ϕ_{1L} should tend to a limiting value, ϕ^*_{1L}. This has been demonstrated for yttrium (Table 3.18), lanthanum (Fig. 3.6) and americium(III) (Table 3.23). It may be noted that k_0 values were computed from the relatively much smaller k_0 at pH = 3.60; the lower than expected ϕ_{1L} at pH 4.58 (Table 3.23) is thereby readily accounted for from the expected error in k_0. A detailed study of the lanthanum fluoride system has been carried out at different pH values. Experiments were carried out at pH 4.0, 5.6 and 6.0; k_0 was determined experimentally for each set. It is seen (Fig. 3.6) that ϕ_{1L} increases at higher fluoride concentrations as the pH is increased. The ϕ_{1L} values at pH 5.6 and 6.0 are the same over the fluoride range studied $(1 - 30)10^{-4}$M $[F^-]$. The fall in ϕ_{1L} values at fluoride concentrations > 3 x 10^{-3}M follows the trend observed at lower pH values, but at higher fluoride concentrations. This means that as the pH is increased

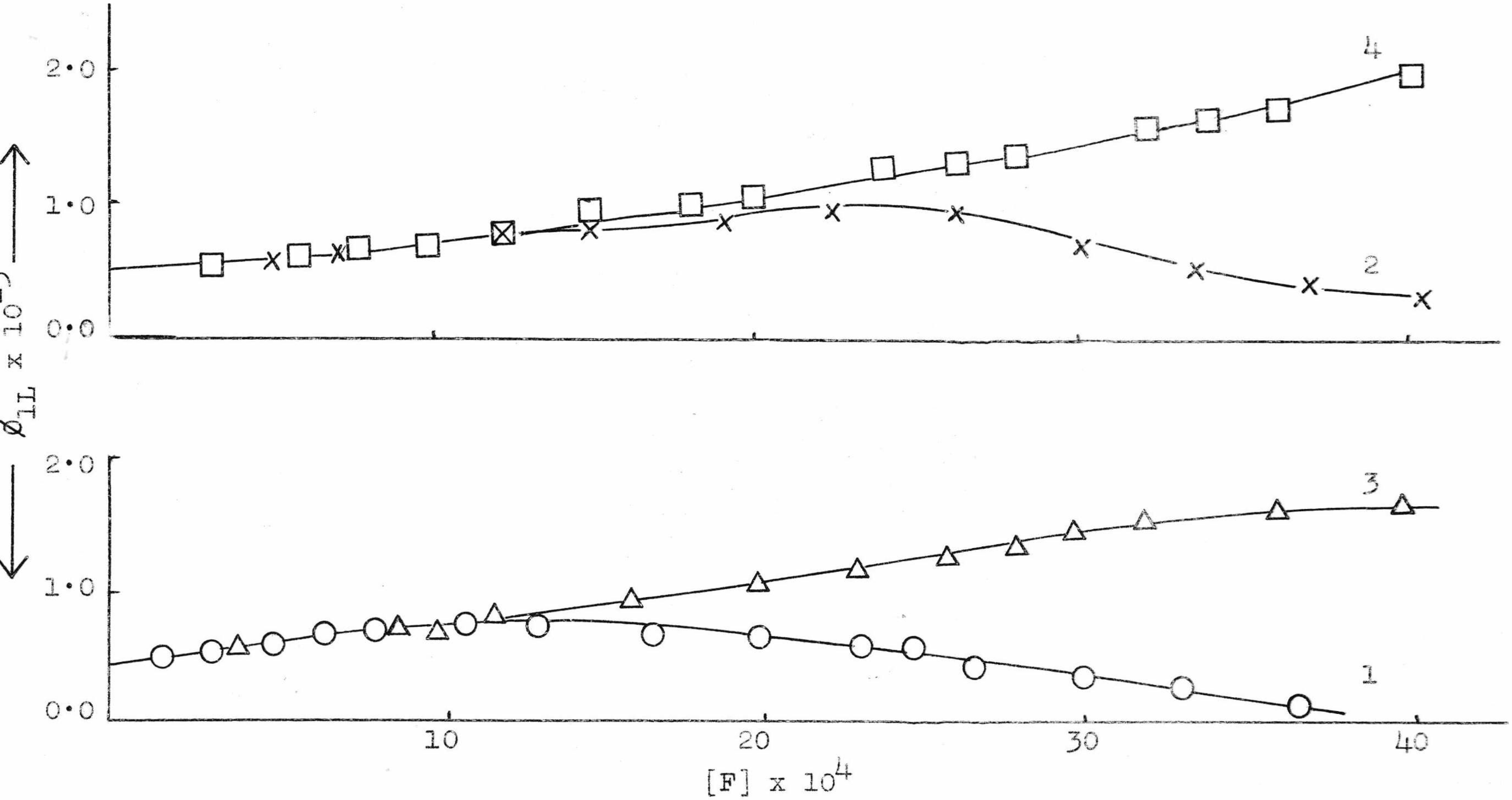


Fig. 3.6. Distribution of lanthanum into HDEHP toluene solution at $\mu = 0{\cdot}500$. Curves 1,2,3 and 4 represent distributions made at pH3·60, 4·00, 5·60 and 6·00 in that order.

Table 3.23 - pH dependence of americium(III) distributing between 0.075% w/v HDEHP in toluene and an aqueous phase containing $[F^-] = 3.32 \times 10^{-3}$M at $\mu = 0.500$ and 25°C

pH	k_o	ϕ_L	$\phi_{1L} \times 10^{-3}$	$\phi^*_{1L} \times 10^{-3}$
3.60	11.33	2.13	1.302	18.07
3.86	68.33	2.50	7.920	
4.02	179.0	3.07	16.30	
4.50	5661	96.46	17.37	
4.58	9872	190.4	15.31	

ϕ^*_{1L} is calculated on the basis of the β values in Table 3.17.

the contribution of $LaF_3.3H_xD_x$ to the total lanthanum extraction decreases until at a certain limit the behaviour of extraction resembles that of indium and scandium systems. A test of the effect of pH on ϕ_{1L} at low fluoride was also carried out for yttrium, americium(III) and lanthanum. It is observed (Table 3.24) that ϕ_{1L} for yttrium increases with increase in pH for a constant fluoride concentration as low as 6.644×10^{-4}M. The value of ϕ_{1L} approaches ϕ^*_{1L} at pH $\geqslant 4.0$. Though there is a fairly large contribution from $YF_3.3H_xD_x$ even in the presence of a low fluoride concentration ($\sim 6 \times 10^{-4}$M) there is unlikely to be any serious error in obtaining β_1 and β_2 from the plot ϕ_{1L} against $[F^-]$ at very low fluoride concentration where ϕ^*_{1L} and ϕ_{1L} lie on the same straight line. At $[F^-] > 3 \times 10^{-4}$M; ϕ_{1L} measured at pH 3.60 is colinear with ϕ_{1L} at lower fluoride, $[F^-]$, but of course not with ϕ^*_{1L}. Thus it is fortuitous that the plot of ϕ_{1L} against $[F^-]$ is a straight line at fluoride concentration $(3 - 8)10^{-4}$M and a working pH of 3.60.

The results in Tables 3.25, 3.26 and Fig. 3.6 on the other hand for americium(III) and lanthanum confirm that $MF_3.3H_xD_x$ contributes to a negligible extent to ϕ_L at fluoride $\leqslant 8 \times 10^{-4}$M. The constancy of ϕ_{1L} is consistent with the model from which β_3 is calculated and the text provides a useful check on the data from which β_1 and β_2 are obtained.

Table 3.24 - pH dependence for yttrium distributing between HDEHP in toluene and an aqueous phase containing $[F^-] = 6.644 \times 10^{-4}M$ at $\mu = 0.500$ and 25°C

Experiment No.	pH	ϕ_{1L}	ϕ^*_{1L}
1	3.60	15.58	25.10
2	3.82	19.91	
3	3.99	24.90	
4	4.22	25.86	

Distributions were made using 0.01, 0.005, 0.0025 and 0.00025% w/v HDEHP in toluene for experiments 1, 2, 3 and 4 respectively.

ϕ^*_{1L} is calculated on the basis of the β values in Table 3.17.

Table 3.25 - pH dependence of americium(III) distributing between 0.075% w/v HDEHP in toluene and an aqueous phase containing $[F^-] = 8.305 \times 10^{-4}$M at $\mu = 0.500$ and 25°C

pH	k_o	ϕ_L	$\phi_{1L} \times 10^{-3}$
3.60	11.33	2.852	3.579
3.86	68.33	17.20	3.560
4.12	410.0	102.6	3.610
4.48*	182.4	48.34	3.340

*Distributions were measured for 0.025% w/v HDEHP and the appropriate k_o calculated to obtain ϕ_{1L}.

Table 3.26 - HDEHP extraction data for the lanthanum fluoride system at μ = 0.500 ($NaClO_4$), 25.0 ± 0.5°C at different pH values.

RUN I		**RUN II**		**RUN III**	
pH = 4.0		pH = 5.60		pH = 6.00	
$[F] \times 10^4$	$\phi_{1L} \times 10^2$	$[F] \times 10^4$	$\phi_{1L} \times 10^{-2}$	$[F] \times 10^4$	$\phi_{1L} \times 10^2$
7.398	6.200	3.991	5.484	3.996	5.521
14.80	7.800	7.982	6.640	7.992	6.235
18.50	8.997	11.97	7.623	11.99	7.124
22.19	9.060	15.96	8.820	15.98	8.577
25.89	9.020	17.95	9.522	19.98	10.61
		19.96	10.57	27.97	13.98
27.74	7.906	23.95	12.12		
33.29	4.595	27.94	13.83	31.97	16.02
		31.93	15.51		
36.99	3.670	35.92	16.56	35.96	17.48
40.69	2.680	39.91	16.82	39.96	20.00

ϕ_{1L} were obtained using 0.125%, 0.0025% and 0.001% w/v HDEHP with k_o = 57.50 ± 1.02 (4 values), 30.62 ± 0.79 (5 values) and 31.15 ± 0.93 (5 values) for Runs I, II and III respectively in that order.

It should, however, be noted (Table 3.17) that the value of β_3 for lanthanum at pH 6.00 and 5.60 calculated by assuming

$$\phi_{1L} = \beta_1 + \beta_2[F^-] + \beta_3[F^-]^2$$

is smaller than those calculated from all the data presented in Table 3.27 for pH 3.60 and 4.00 in accord with the present proposed extraction model. (β_3 was found graphically to be 1.4×10^8 and 1.0×10^8 for measurements at pH 3.60 and 4.00 respectively.) The higher of these two values for β_3 arrived at on the basis of the present extraction model is less reliable because of all too few points at sufficiently high fluoride concentration and the inclusion of those points on the straight line plot of $1/\phi_L$ against $1 + \beta_1[F^-] + \beta_2[F^-]^2/[F^-]^3$ where the contribution of M^{3+} to the overall metal extraction is not negligible. However, for both sets of data if due care is taken concerning this point and values thus rejected from the graphical plots β_3 becomes 0.7×10^8. This entails rejection of two pairs of values from data at pH 3.60 and one at pH 4.00 (Table 3.27). The first set thereby gives a rather uncertain value for β_3 if considered in isolation from the other sets of data. Results for actinium are as sparse as in the data for lanthanum at pH 3.60 so that β_3 is probably none-too-certain. Similar analyses performed on yttrium, americium(III) and curium(III) results give what should be fairly reliable values for β_3 (Table 3.17).

Table 3.27 - HDEHP distribution data for the lanthanum fluoride system at μ = 0.500 ($NaClO_4$)

RUN I pH = 3.60			RUN II pH = 4.00		
x 10^4	$\frac{1 + \beta_1[F] + \beta_2[F]^2}{[F]^3}$ x 10^{-9}	$1/\phi_L$	[F] x 10^4	$\frac{1 + \beta_1[F] + \beta_2[F]^2}{[F]^3}$ x 10^{-9}	$1/\phi_L$
4.92	0.214	0.078	25.89	0.201	0.058
6.58	0.189	0.071	27.74	0.178	0.055
9.90	0.150	0.066	29.59	0.150	0.050
3.22	0.124	0.058	33.29	0.124	0.044
6.58	0.105	0.053	36.99	0.106	0.041
			40.69	0.090	0.036

= 501 and β_2 = 1.71 x 10^5 were used in calculating $1 + \beta_1[F] + \beta_2[F]^2/[F]^3$.

Treatment of ion-exchange results

Partition of lanthanum, cerium(III), gadolinium, europium(III), americium(III), curium(III), yttrium, indium and scandium between aqueous solutions containing fluoride ion and a solid cation-exchanger was studied. The results are represented in Tables 3.7 - 3.16. The range of fluoride employed was the same as that for the liquid-liquid extraction except for scandium. From the ion-exchange and liquid-liquid extraction data information concerning the ion-exchange of fluoro-metal cations may be deduced. [In the discussion to follow l_0 and ϕ_{1R} are quantities applicable to ion-exchange behaviour corresponding to k_0 and ϕ_{1L} respectively for HDEHP extraction; $l'_m = \frac{\beta_m l_m}{l_0}$ where l_m represents the distribution of $MF_m^{(3-m)+}$ in the ion-exchange system.] For this purpose the relation (applied here specifically to $[F^-]$ system)

$$\frac{\phi^*_{1L} - \phi_{1R}}{1 + \phi_{1R}[F^-]} = X = l'_1 + l'_2[F^-] + l'_3[F^-]^2 + \cdots \qquad (3.26)$$

was derived on the assumption that only $M(HD_2)_3$ extracted into HDEHP in toluene. ϕ^*_{1L} was formerly referred to as ϕ_{1L}. In the succeeding discussion ϕ^*_{1L} used in the calculation of L.H.S. of equation (3.26) was calculated from the β values obtained from liquid-liquid extraction results. Depending upon the quantity of experimental data for a specific system the complete analysis of the results were made to limited systems. The analysis of this type reported earlier[6] was only confined to the liquid-liquid extraction data over which β_1 and β_2 were calculated, e.g. the cerium(III), europium(III), gadolinium, indium and scandium systems were also discussed in the light of this limited analysis in the present study. A more detailed experimental study and analysis of the liquid-liquid extraction and ion-exchange data was made for the lanthanum, yttrium, americium(III) and curium(III) fluoride systems.

Lanthanum, yttrium, americium(III) and curium(III) systems

ϕ_{1R} in all these systems is nearly independent of fluoride concentration. At low fluoride concentrations, however, it is found that ϕ_{1R} is a decreasing function of fluoride. The variation in $\dfrac{\phi^*_{1L} - \phi_{1R}}{1 + \phi_{1R}[F^-]}$ (= X) with $[F^-]$ is similar for all these systems (Table 3.28 and Fig. 3.7). The value of l_1' was calculated from the region of the curve at low fluoride concentration having zero slope whereas l_2' was got from the slope of the straight line part of the plot. In all these systems it seems that only MF^{2+} and MF_2^+ partition appreciably into the cation-exchanger under the conditions employed. ϕ^*_{1L} for lanthanum was calculated from the β values at pH 6.0 whereas for other systems it was calculated from β_1, β_2 and β_3 values obtained according to the liquid-liquid extraction model presented earlier in this chapter. The values of l_1 and l_2 and

Table 3.28 - Ion-exchange data for lanthanum, yttrium, americium(III) and curium(III) at $\mu = 0.500$ ($NaClO_4$), pH = 3.60 and 25.0 ± 0.5°C

Lanthanum

$[F] \times 10^{4}$	0.1661	0.3322	0.6644	0.9966	1.329
X	45.2	50.6	46.6	45.0	45.0
$[F] \times 10^{4}$	1.661	3.322	4.982	6.644	8.305
X	46.2	53.6	56.0	96.0	116
$[F] \times 10^{4}$	9.966	11.62	13.29	16.61	19.93
X	150	174	188	243	286
$[F] \times 10^{4}$	23.25	26.58	29.90	33.22	
X	334	385	434	476	

Yttrium

$[F] \times 10^{4}$	0.1661	0.3322	0.6644	0.9966	1.329	
$X \times 10^{-2}$	6.640	6.788	7.600	8.869	10.03	
$[F] \times 10^{4}$	1.661	2.658	3.322	4.982	6.644	8.305
$X \times 10^{-2}$	14.81	15.45	18.32	22.69	27.48	31.73
$[F] \times 10^{4}$	9.966	10.63	13.29	16.61	19.93	23.25
$X \times 10^{-3}$	3.632	3.740	4.309	5.251	6.118	7.009
$[F] \times 10^{4}$	26.58	29.90	33.22			
$X \times 10^{-3}$	7.963	8.770	9.768			

Americium(III)

$[F] \times 10^{4}$	0.1661	0.3322	0.4983	0.6644	.8305
$X \times 10^{-2}$	-	6.020	4.580	4.972	4.089
$[F] \times 10^{4}$	0.9966	1.163	1.661	2.658	3.322
$X \times 10^{-2}$	6.751	3.944	4.006	4.332	4.522
$[F] \times 10^{4}$	4.982	6.644	8.305	9.966	11.63
$X \times 10^{-2}$	5.427	6.197	6.339	7.071	7.715
$[F] \times 10^{4}$	13.29	16.61	19.93	23.25	16.58
$X \times 10^{-2}$	8.426	9.848	12.27	14.65	15.66
$[F] \times 10^{4}$	29.90	33.22			
$X \times 10^{-3}$	1.729	1.880			

Curium(III)

$[F] \times 10^{4}$	1.661	2.658	3.322	4.982	5.980	
$X \times 10^{-2}$	3.901	4.242	4.185	5.350	5.901	
$[F] \times 10^{4}$	6.644	8.305	9.966	10.62	11.63	13.29
$X \times 10^{-2}$	5.861	6.552	8.364	9.358	9.664	11.11
$[F] \times 10^{4}$	16.61	19.93	26.58	29.90	33.22	
$X \times 10^{-3}$	1.377	1.609	2.121	2.354	-	

$$X = \frac{\phi^{*}_{1L} - \phi_{1R}}{1 + \phi_{1R}[F]}$$

ϕ^{*}_{1L} were calculated from the corresponding β values (Table 3.17) using equation (3.21). ϕ_{1R} were those experimentally obtained and reported in Tables 3.7, 3.12-3.14.

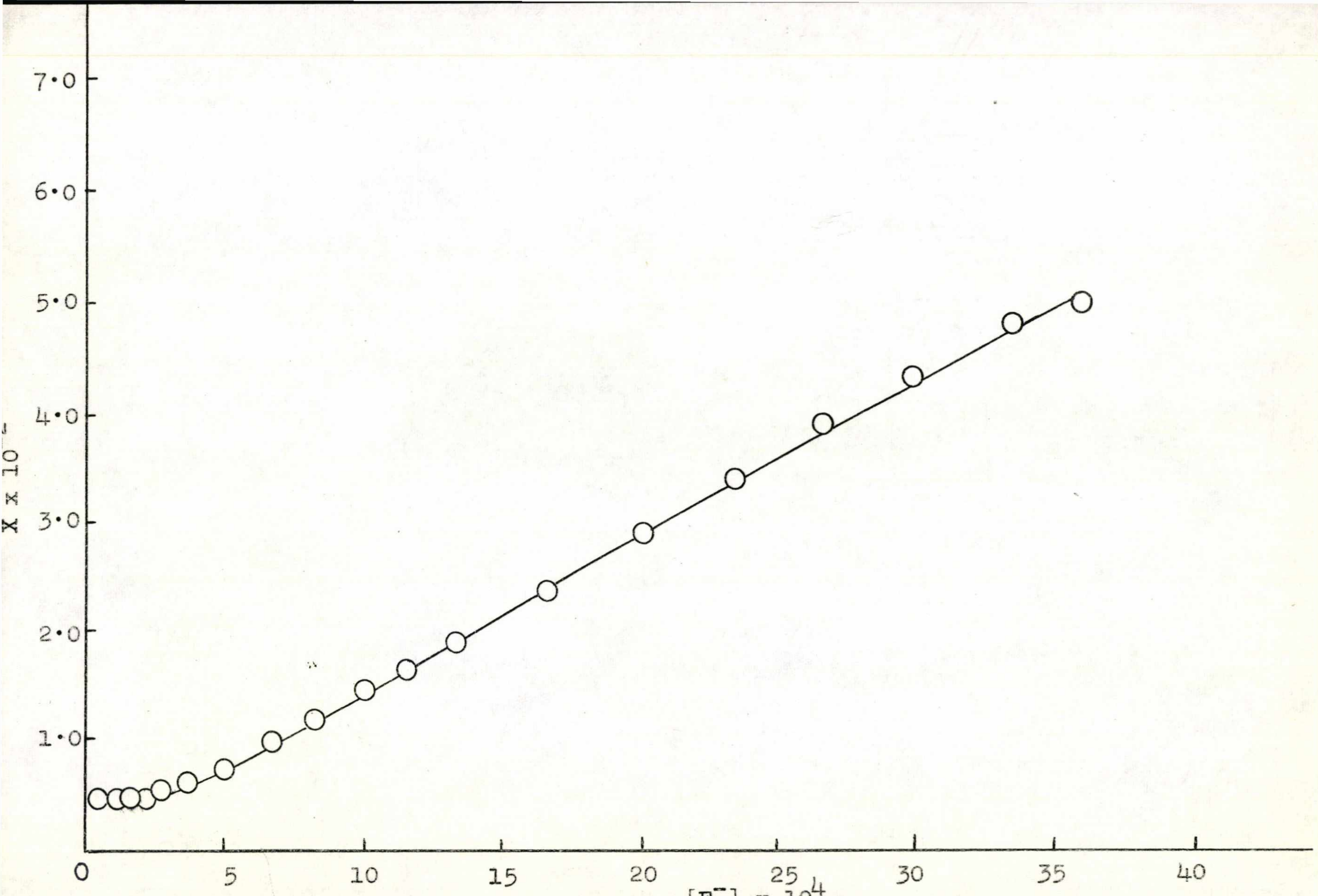


Fig. 3.7. Distribution data for positively charged lanthanum fluoro complexes into a cation-exchange resin at an ionic strenght $\mu = 0{\cdot}500(NaClO_4)$ and 25·0 ± 0·1°C.

therefore l_0/l_1 and l_0/l_2 for all of these systems are reported in Table 3.29. It is seen that with the use of ϕ_{1L} values instead of ϕ_{1L}^* at low fluoride concentrations for lanthanum, americium and curium one gets the same values for l_1' as are recorded above in Table 3.29. The large contribution of MF_3 and MF_2 at quite low fluoride concentration for the yttrium system relative to lanthanum, americium, etc., shows a larger departure in ϕ_{1L}^* and ϕ_{1L} at these low ligand concentrations and therefore in the ion-exchange parameters l_2' and l_2. A value of $l_2' = 8 \times 10^5$ and $l_2 = 200$ is found on the basis of ϕ_{1L}. The value of l_1 is the same when calculated on the basis of parameters ϕ_{1L}^* or ϕ_{1L}. The departure of X from the straight line at low $[F^-]$ may well arise from experimental uncertainty in the ϕ_{1L} and ϕ_{1R} values which are tending to converge as $[F^-] \longrightarrow 0$. Part of this uncertainty may arise in a systematic way from the presence of foreign cations competing for $[F^-]$.

Cerium(III), gadolinium and europium(III) fluoride systems

A limited study has been carried out on the behaviour of these metals on partition into a cation-exchanger. The results are reported in Tables 3.8 - 3.10. $\dfrac{\phi_{1L} - \phi_{1R}}{1 + \phi_{1R}[F^-]}$ first shows an increasing trend followed by a slight decrease with increase in fluoride concentration in all these systems. In treating this data it was assumed[*]

[*] Note: This work was done before the more detailed studies described in the previous section.

Table 3.29 - Cation-exchange ratios for free and partially complexed trivalent metal ions

Metal ion	l_0	l_1'	l_2'	l_1	l_2	l_0/l_1	l_0/l_2	Ref.
Y^{3+}	3270	700	2.8×10^6	297	715	11	5	p.w.
La^{3+}	6783	45	1.4×10^5	622	6300	11	1	p.w.
Am^{3+}	5270	420	5.6×10^5	900	2306	6	2	p.w.
Cm^{3+}	3245	420	7.5×10^5	617	1622	5	2	p.w.
Ce^{3+}	6262	600	-	2846	-	2	-	p.w.
	6017	-	-	3380	-	2	-	6
Eu^{3+}	5626	400	-	1000	-	6	-	p.w.
	4154	-	-	828	-	5	-	6
Gd^{3+}	5145	1000	-	2217	-	2	-	p.w.
	4269	-	-	1950	-	2	-	6
Sc^{3+}	2729	1×10^5	-	186	-	15	-	p.w.
In^{3+}	365	399	-	31	-	12	-	p.w.

l_m were calculated on the basis of β values in Tables 3.17, 3.20 and 3.21;

p.w. = present work.

when the measurements were made that only M^{3+}_{aq} extracted into HDEHP. On this basis the results for the function above were best fitted by assuming that only one species of cation other than M^{3+}_{aq} partitioned into the ion-exchange resin. The results are reported in Table 3.29 in addition to other[6] published results. The previous[6] presentation of values of l_2' and l_2 for these systems is not considered to be justified having regard to the refined extraction model since introduced. l_1', l_1 and l_0/l_1 should only be regarded as being very approximate, since it is not certain that ϕ_{1L} and ϕ_{1R} were measured down to sufficiently low $[F^-]$ or at what point in the ϕ_{1L} versus $[F^-]$ system the extraction of MF_3 becomes significant.

Indium and scandium fluoride systems

The ion-exchange partition results for indium and scandium fluoride systems are reported in Tables 3.15 and 3.16. Similar to the systems previously mentioned ϕ_{1R} is roughly independent of $[F^-]$ concentration for indium (Fig. 3.5) whereas it is a slightly increasing function of fluoride $[F^-]$ for scandium. The behaviour of scandium in cation-exchange in the presence of fluoride is similar to that of yttrium, americium(III) and lanthanum, etc., at low concentration. As ϕ_{1R} was only readily measured over a $[F^-]$ range $(0.05 - 0.70)10^{-4}$M for scandium because of very low affinity of its 'free' ions for the resin, only l_1' and l_1 were obtained.

The values of $\frac{\phi_{1L} - \phi_{1R}}{1 + \phi_{1R}[F^-]}$ for indium have a considerable scatter although the [F^-] range is appreciable and only calculation of l_1' and l_1 seems justified. The results are represented in Table 3.29. If it is assumed that MF_2^+ also partitions into the resin in addition to M^{3+} and MF^{2+} the least square analysis of results for scandium and indium systems thus obtained show a larger error on l_1' than when only MF^{2+} and M^{3+} are considered to be partitioning into the resin.

The constancy in the values of X for scandium and indium shows that only MF^{2+} partitions significantly into the resin because the stability of MF_2^+ is one tenth that of MF^{2+}.

For the indium system the results obtained by Schufle and Eiland[28] make ϕ_{1R} an increasing function of concentration in the fluoride range 0.88×10^{-3} to 4.4×10^{-3}M; the stability constants calculated from these data have been criticised[30] on the grounds that the pH (3.8) used would give rise to indium(III) hydrolysis. While hydroxyl ion may be competing for metal ion at this pH it has been noted in the course of present work that l_0 increases rapidly with increasing pH above about 3.2 (Fig. 3.8) (also see Chapter V). The initial stages of hydrolysis, provided colloid formation was not involved, might be expected to decrease rather than increase uptake of indium by the exchanger. Similar behaviour has been observed[31,32] for lanthanide (III) ions under a variety of conditions in aqueous solution and with a

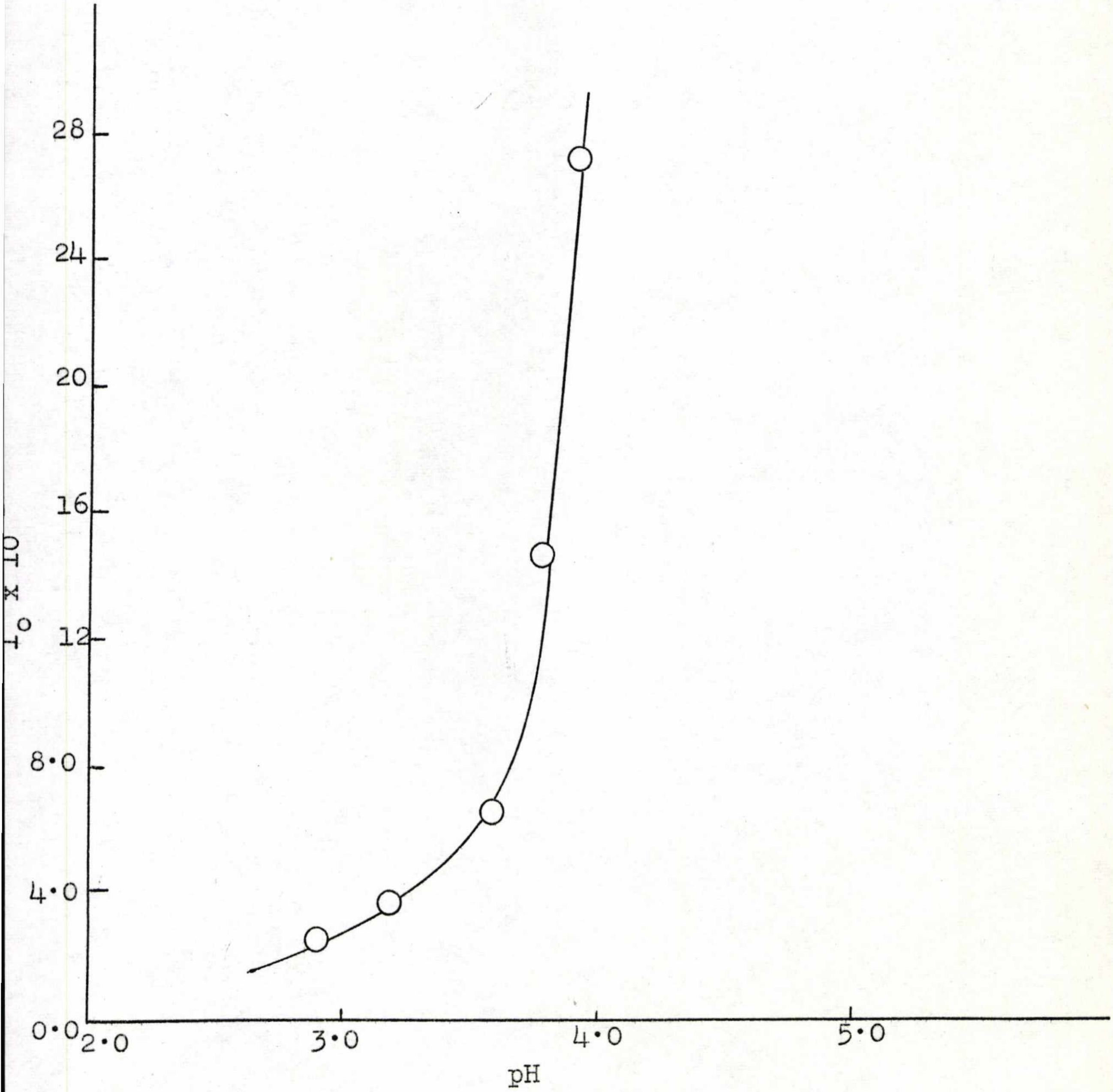


Fig. 3.8. Distribution ratios, l_o for indium (III) between an aqueous phase, $\mu = 1\cdot000$ ($NaClO_4$) and the cation-exchanger as a function of pH.

range of ion-exchange resins; l_0 increases rapidly above about pH 4 suggesting that some additional exchange property of the resin may come into play since hydrolysis of such metal ions is not expected below pH 6. The very steep pH dependence of l_0 around pH 3.8 (Fig. 3.8) whether due to hydrolysis, some additional exchange property of the resin or both, would nevertheless be expected to make reliable ϕ_R measurement difficult particularly in the absence of a buffering action of a ligand. Thus a l_0 value around 500 rather than 110 applied to the ϕ_R values of Schufle and Eiland[29] give β_1 for indium-chloride, -bromide and -fluoride complex ion formation in better accord with the results of other workers. It is then found that the recalculated ϕ_{1R} are nearly constant for three of the five measurements in fluoride.

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CHAPTER IV

Sulphate and Oxalate Complexes of some Trivalent Metal Ions

Introduction

The behaviour of rare earth sulphates in solution has been studied by many workers[1]. Since sulphuric acid is commonly used to attack rare earth ore bodies, the separation of these elements often starts from a sulphate solution. The solubility of the sulphates and the formation of double sulphates with alkali metals have been very extensively studied mainly from the point of view of effecting separations. Many methods[2-8] have given indications of complex formation by the trivalent lanthanide and actinide ions in solutions containing sulphate. The compilation of Sillén and Martell[9] lists several studies of sulphate complexes of rare earths and actinides. More recently De Carvalho and Choppin[10] used partition methods to determine stability constants for rare earth and actinide sulphate complexes formed at an ionic strength of 2.

Many studies of oxalates have also been carried out because of their application to separations of rare earths, yttrium and thorium from other metal ions by precipitation reactions. A summary of the chemistry of oxalate complexes has been published by Krishnamurthy and Harris[11]. Sekine[12] and Grenthe and co-workers[13] measured stability constants of oxalate complexes of trivalent rare earth and actinide ions by partition methods.

In the present work partition of europium(III), americium(III), curium(III), actinium and lanthanum between aqueous sulphate or oxalate solutions at constant ionic strength ($\mu = 0.500$) and a cation exchanger or toluene solution of HDEHP has been examined. In particular the study of actinium sulphate and oxalate complexes for comparison with those of lanthanum was carried out as very little is known about the chemistry of actinium in solutions containing sulphate and oxalate.

Measurements were also made on the indium(III) sulphate system at an ionic strength of 1.000 in order to compare its behaviour on ion-exchange and partition into a HDEHP/toluene solution with that of trivalent rare earths and actinides. The indium system was also examined by Sundén[14,15] who obtained rather different β_2 values from two independent measurements.

EXPERIMENTAL

All the reagents and chemicals used were of analytical reagent grade and they are discussed in Chapter III. Sodium sulphate - sodium perchlorate solution of ionic strength 0.500 was made by the neutralization of standard sulphuric acid, perchloric acid and sodium hydroxide solutions. The oxalate solution was made by dissolving sodium oxalate in doubly distilled water and the ionic strength was adjusted with sodium perchlorate solution.

pK values for the sulphate-acid sulphate system were measured at an ionic strength of 0.500 and 1.00 using a glass-calomel electrode pair (the latter having a saturated sodium chloride bridge) and different acid-salt mixtures. The pK of monoacid oxalate at $\mu = 0.500$ was similarly determined for the electrode system employed. The results are reported in Table 4.1.

TABLE 4.1

Dissociation constants for the acid sulphate and acid oxalate systems at 25.0 ± 0.5°C.

Acid	Ionic strength	pK
mono-hydrogen sulphate	0.500	1.08
"	1.000	1.05
mono-hydrogen oxalate	0.500	3.51

The methods of equilibration, measurements and other experimental conditions were similar to those reported in Chapter III. The initial experiments on counting curium-244 by the liquid scintillation method in the presence of sulphate and oxalate are reported in Chapter III under the heading 'Liquid Scintillation Counting'. Since counting ratios are required in this work the small quenching effect due to sulphate and oxalate is unimportant for the present purpose.

RESULTS AND DISCUSSION

Sulphate system

To test the liquid scintillation counting method for curium-244 and americium-241 (α-emitters) in the presence of inhomogeneity arising from sodium sulphate precipitation in the scintillation mixture (see Chapter III) the distribution ratios ϕ_R were measured for americium-241 both by the crystal (Na(Tl)I) and liquid scintillation counting methods. Representative results are presented in Table 4.2. The results show fair agreement in ϕ_R values determined by both methods and hence it may be concluded that the liquid scintillation assay will be reliable for the pure α-emitter curium-244.

Preliminary experiments on the dependence of ϕ_L on the HDEHP concentration were carried out by measuring the distribution of metal ions studied into HDEHP at various concentrations in toluene and a common aqueous phase containing sulphate ion. The present results (Table 4.3) in addition to earlier findings by Lyle and Naqvi[16], show that over the range of ligand studied only $M(HD_2)_3$ is extracted into HDEHP (H_2D_2).

TABLE 4.2

Distribution ratios for Americium-241 between Zeo-Karb-225 cation exchanger and aqueous phases containing sulphate.

$[SO_4^{=}] \times 10^2$ mole/l	Distribution ratio x 10^{-3} Liquid scintillator	Distribution ratio x 10^{-3} Crystal scintillator
1.595	2.437	2.420
3.190	1.454	1.437
4.786	0.9905	0.9685
6.381	0.7252	0.7090
7.976	0.5488	0.5539
9.571	0.4508	0.4385

The ionic strength was 0.500, the pH 3.60 and the temperature 25.0 ± 0.5°C. Portions of aqueous phase were counted.

TABLE 4.3

Distribution ratios, ϕ_L for indium(III) between HDEHP in toluene and an aqueous phase pH 3.20, $\mu = 1.000(NaClO_4)$ containing $8.35 \times 10^{-2} Ml^{-1}$ of sulphate ion.

Expt. No.	HDEHP (% w/v) x 10^3	ϕ_L	ϕ_L*
1	1.25	1.05	1.03
2	2.50	8.30	8.26
3	5.00	66.6	66.1
4	7.50	223.1	-

*On the basis of the experimental data for experiment 4 assuming ϕ_L is proportional to $(HDEHP)^3$.

Europium(III), Americium(III) and Curium(III) Sulphate Systems

The results of the partition of europium(III), americium(III) and curium(III) into the cation exchanger (Zeokarb-225, 8% cross-linked D.V.B. 100-200 mesh) or a toluene solution of HDEHP and an aqueous phase containing sulphate at an ionic strength $\mu = 0.500$ are reported in Tables 4.4, 4.5 and 4.6. It is seen that ϕ_{1L} is an increasing function of $[SO_4^{=}]$ and the plot ϕ_{1L} against $[SO_4^{=}]$ suggests the presence of only two complexes in each of the three systems over the range of ligand concentration studied. The values of β_1 and β_2 calculated by a least squares method are reported in Table 4.7; other relevant published data are recorded for comparison and discussion. Published stability constants for lanthanide and actinide sulphate systems have been reported over a wide range of ionic strengths. A direct comparison is however not possible. However, it may be noted that irrespective of whether it is a lanthanide or actinide, β_1 and β_2 remain sensibly constant from metal ion to metal ion; this was also found in the more extensive measurements at very low[20] and at very high ionic[10] strengths.

The ion exchange results show that ϕ_{1R} is an increasing function of $[SO_4^{=}]$ unlike the fluoride systems (Chapter III). As was found previously[16] for a given sulphate concentration $\phi_{1L} > \phi_{1R}$ suggesting that some partitioning of ion associated

TABLE 4.4

Liquid-liquid extraction and cation exchange partition data for Europium(III) sulphate system at an ionic strength μ = 0.500 and 25.0 ± 0.5°C

$[SO_4^{=}] \times 10^2$ (moles/1)	$\phi_{1L} \times 10^{-2}$ (1/mole)	$\phi_{1R} \times 10^{-2}$ (1/mole)	$\frac{\phi_{1L}-\phi_{1R}}{1+\phi_{1R}[SO_4^{=}]}$ (1/mole)
0.4810	0.8191	0.7817	-
0.9610	0.8231	0.8124	0.601
1.922	0.8912	0.8631	1.056
2.884	0.9298	0.8977	0.894
3.845	0.9787	0.9092	1.540
4.806	1.051	0.9941	0.986
5.767	1.144	1.059	1.196
7.689	1.229	1.181	0.475
9.612	1.357	1.274	0.629
11.53	1.480	1.371	0.649

ϕ_{1L} was obtained using 0.05% w/v HDEHP with $k_0 = 71.10 \pm 2.03$ (mean of six) and ϕ_{1R} using 0.100 gm of ion exchange resin for which $l_0 = 5625 \pm 65$ (mean of six values).

TABLE 4.5

Liquid-liquid extraction and cation exchange partition data for the americium(III) sulphate system at $\mu = 0.500$ and $25.0 \pm 0.5^{\circ}C$

$[SO_4^{=}] \times 10^2$ (moles/l)	$\phi_{1L} \times 10^{-2}$ (l/mole)	$\phi_{1R} \times 10^{-2}$ (l/mole)	$\frac{\phi_{1L}-\phi_{1R}}{1+\phi_{1R}[SO_4^{=}]}$ (l/mole)
0.7976	0.7123	-	-
1.595	0.8004	0.7891	0.5003
2.393	0.8821	0.8350	1.571
3.190	0.9376	0.8792	1.535
3.988	0.9998	0.9250	1.595
4.786	1.010	0.9702	0.7053
6.381	1.161	1.051	1.428
7.976	1.258	1.112	1.479
8.774	1.320	1.156	1.472
9.571	1.341	1.198	1.330
10.37	1.360	1.230	-

ϕ_{1L} was obtained using 0.075% w/v HDEHP with $k_0 = 14.26 \pm 0.19$ (mean of six values) and ϕ_{1R} using 0.100 gm of ion exchange resin for which $l_0 = 5480 \pm 43$ (mean of six values).

TABLE 4.6

Liquid-liquid extraction and cation-exchange partition data for the Curium(III) sulphate system at μ = 0.500 and 25.0 ± 0.5°C

$[SO_4^{=}] \times 10^2$ (moles/l)	$\phi_{1L} \times 10^{-2}$ (l/mole)	$\phi_{1R} \times 10^{-2}$ (l/mole)	$\frac{\phi_{1L}-\phi_{1R}}{1+\phi_{1R}[SO_4^{=}]}$ (l/mole)
0.7976	0.7533	-	-
1.595	0.8372	0.7659	3.212
2.393	0.8799	0.7782	3.552
3.190	0.9208	0.7799	4.039
3.988	0.9602	0.8276	3.083
4.786	1.001	0.8194	3.689
5.583	1.056	0.8448	3.694
6.381	1.090	0.8534	3.670
7.178	1.138	0.9129	2.850
7.976	1.186	0.8834	3.760
8.774	1.229	0.9411	3.110

ϕ_{1L} was obtained using 0.05% w/v HDEHP with k_0 = 2.637 ± 0.032 (mean of six values) and ϕ_{1R} using 0.100 gm of resin for which l_0 = 3246 ± 11 (mean of six values).

TABLE 4.7

Stability constant data for Americium(III), Curium(III) and Europium(III) sulphate systems

Metal ion	Method	Temp. (°C)	μ	β_1 (l/mole)	β_2 ($l^2/mole^2$)	Ref.
Am^{3+}	dis	25	0.5	70.1 ± 1.8	$(6.82 \pm 0.31)10^2$	p.w.
	i.ex.	25	0.5	72.8 ± 2.5	$(6.25 \pm 0.42)10^2$	p.w.
	dis	25	2.0	27 ± 4	71 ± 19	10
	i.ex.	25	1.0	30.62 ± 0.62	227.9 ± 2.6	17
	dis	25	1.0	37 ± 8	457 ± 85	8
Cm^{3+}	dis*	25	0.5	68.0 ± 2.0	4.28 ± 0.32	18
	dis	25	0.5	73.3 ± 0.8	5.69 ± 0.15	p.w.
	i.ex.	25	0.5	71.9 ± 1.3	2.34 ± 0.24	p.w.
Eu^{3+}	dis	25	0.5	76.7 ± 0.9	$(6.12 \pm 0.15)10^2$	p.w.
	i.ex.	25	0.5	74.6 ± 1.1	$(5.42 \pm 0.18)10^2$	p.w.
	dis	25	1.0	35 ± 5	490 ± 55	8
	i.ex.	25	1.0	37 ± 2	250 ± 30	19

*The HDEHP/toluene phase or the aqueous phase back-extracted into such a medium was counted. dis = liquid-liquid extraction; i.ex. = ion exchange; p.w. = present work.

species takes place into the resin. The β_1 and β_2 values given in Table 4.7 for ion exchange do not of course take account of this; β_2 values are affected more than β_1. The differences in ϕ_{1L} and ϕ_{1R} have been used as previously to calculate ion-exchange distribution ratios (l_1) for monosulphato cations for comparison with the appropriate quantities for the free metal ions (l_0). The function

$$\frac{\phi_{1L} - \phi_{1R}}{1 + \phi_{1R}[SO_4^{=}]}$$

in Tables 4.4, 4.5 and 4.6 is constant over the range of $[SO_4^{=}]$ studied, suggesting that only one complex species is exchanging in the resin phase. A value of l_1' 0.89 ± 0.11, 1.29 ± 0.13 and 3.46 ± 0.12 for europium(III), americium(III) and curium(III) respectively were obtained taking the mean of all the values of this function. As before[16], because of possible variation in the water content of the resin samples used, a comparison of the l_0/l_1 ratio is most appropriate. The results are recorded in Table 4.8.

Actinium and lanthanum systems

The distribution results for actinium and lanthanum into HDEHP are recorded in Table 4.9. Like the other lanthanide and actinide ϕ_{1L} in this case also suggests the formation of at least two complexes over the range

TABLE 4.8

Cation exchange distribution ratios for "free" aquated metal ions, l_0, and for the mono-sulphate cations, l_1, at 25°C

Metal ion	μ	l_0	l_1	l_0/l_1	Ref.
Eu^{3+}	0.5	5625 ± 65	65 ± 8	87 ± 11	p.w.
Am^{3+}	0.5	5480 ± 43	101 ± 11	54 ± 6	p.w.
Cm^{3+}	0.5	3246 ± 11	153 ± 6	21 ± 1	p.w.
			76 ± 27*	43 ± 15	
In^{3+}	1.0	364.7 ± 0.3	12.4 ± 0.5	29 ± 1	p.w.

*Calculated using the liquid-liquid distribution data obtained by counting HDEHP/toluene phase or the aqueous phase back-extracted into such a medium.

TABLE 4.9

Liquid-liquid extraction data for Lanthanum and Actinium sulphate systems at μ = 0.500 and 25.0±0.5°C

$[SO_4^{=}] \times 10^2$ (mole/l)	$\phi_{1L} \times 10^{-2}$ (l/mole) Lanthanum	Actinium
0.5981	0.6196	0.5911
1.196	0.6403	0.6099
1.794	0.6695	0.6498
2.392	0.7195	0.6599
2.991	0.7297	0.6700
3.589	0.7398	0.7198
4.217	0.7799	0.7400
4.785	0.8201	0.7690
5.383	0.8600	0.8003
5.981	0.8800	0.8096
7.177	0.9402	0.8901
8.433	0.9800	0.9191
9.570	1.060	0.9692
10.77	1.099	1.010
11.96	1.119	1.091

ϕ_{1L} was obtained using 0.25% (w/v) HDEHP with k_0 = 32.14 ± 0.82 and 2.615 ± 0.028 for lanthanum and actinium respectively.

of $[SO_4^{=}]$ studied. A least squares treatment by electronic digital computer gave the values of β_1 and β_2 which are recorded with other necessary published data in Table 4.10. There is very close agreement in β values for both lanthanum and actinium sulphate systems suggesting greater similarity between these two metal ions than is found for europium(III) and the corresponding actinide, americium(III) (Table 4.7).

Indium system

A series of ϕ_{1L} (Table 4.11) obtained from the distribution of indium between HDEHP in toluene and a range of aqueous sulphate concentrations at two different pH values (2.80 and 3.20) are adequately represented by a single curve (Fig. 4.1) when plotted against sulphate as would be expected in the absence of indium hydrolysis. A limited study of the dependence of k_0 on pH at a constant HDEHP concentration for indium was carried out. A suitable plot of the results (Table 4.12) confirms the absence of appreciable hydrolysis at or below pH 3.5 (measured with our electrode system) by the adherence of k_0 to an inverse third power dependence on hydrogen ion (Chapter V).

The stability constants β_1 and β_2, which are recorded in Table 4.13 with other necessary published results for comparison, can be calculated from the straight line plot (Fig. 4.1). The β_2 value for indium-sulphate is in fair

TABLE 4.10

Stability constant data for Lanthanum and Actinium sulphate systems

Metal ion	Method	μ	Temp. °C	β_1	β_2	Ref.
La^{3+}	dis	0.5	25	59.44 ± 0.74	458.3 ± 11.0	p.w.
	dis	1.0	25	28.18	288.4	8
	Pot	1.0	25			12
	sp	1.0	25	25.12	-	21
Ac^{3+}	dis	0.5	25	56.05±0.54	431.8±8.4	p.w.
	dis	1.0	25	15.9 ±1.3	71.4 ±7.3	22

dis = liquid-liquid extraction; p.w. = present work;

Pot = Potentiometric; sp = spectrophotometric.

TABLE 4.11

Liquid-liquid extraction and cation exchange partition data for the Indium sulphate system at $\mu = 1.000$ and $25.0 \pm 0.5^\circ C$

$[SO_4^=] \times 10^2$ (mole/l)	$\phi_{1L} \times 10^{-2}$ (l/mole)	$\phi_{1R} \times 10^{-2}$ (l/mole)	$\frac{\phi_{1L}-\phi_{1R}}{1 + \phi_{1R}[SO_4]}$ (l/mole)
1.193	6.388	6.189	1.145
2.385	6.785	6.544	0.941
3.537	7.291*	-	-
3.575	7.373	6.617	2.246
4.771	7.682	6.749	2.211
5.895	7.864*	-	-
5.964	7.855	6.988	1.678
7.150	8.394	6.977	2.366
8.253	8.595*	-	-
8.349	8.588	7.391	1.669
9.542	9.247	7.452	2.213
10.61	9.383*	-	-
10.74	9.506	7.605	2.080
11.93	9.909	7.737	2.123

*ϕ_{1L} obtained at pH 2.80; all others were obtained at pH 3.20. ϕ_{1L} was obtained using $2.5 \times 10^{-3}\%$ (w/v) HDEHP with $k_0 = 68.4 \pm 0.9$ at pH 3.20 and ϕ_{1R} using 0.100 gm of resin for which $l_0 = 364.7 \pm 0.3$.

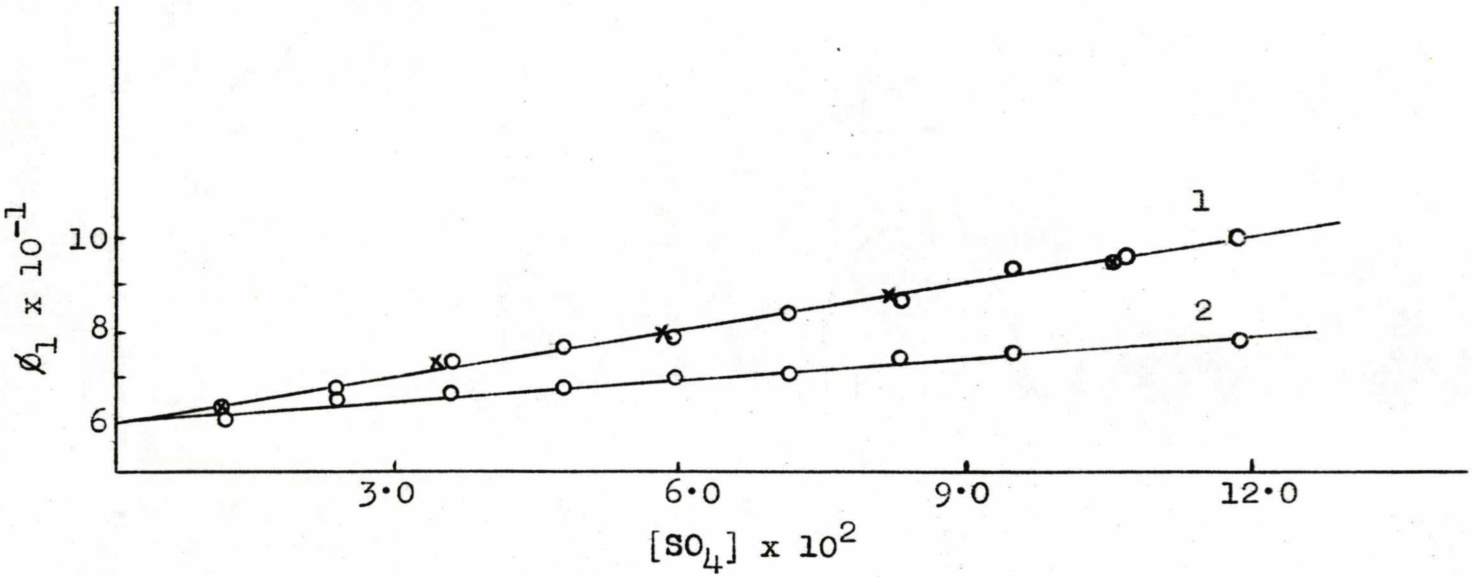

Fig 4.1. ϕ_1 as a function of sulphate concentration at $\mu = 1{\cdot}000$ ($NaClo_4$) Curve 1 and 2 represent distribution into HDEHP and ion-exchanger respectively. Circles on curve 1 refer to distributions at pH 3·20 into 0·0025% w/v HDEHP in toluene, crosses to pH 2·80 and 0·005% w/v HDEHP.

TABLE 4.12

Distribution ratios, k_0, for Indium(III) as a function of pH at an ionic strength μ = 1.000 in aqueous sodium perchlorate

Expt. No.	pH	$\log_{10}k_0$
1	2.50	-0.263
2	2.70	0.336
3	3.00	1.223
4	3.20	1.835
5	3.50	2.736
6	3.80	3.503

1-4 were obtained with 0.0025% w/v HDEHP and 5-6 using 0.0005% w/v HDEHP in toluene. k_0 for 5 and 6 were "normalised" to the values expected for 0.0025% HDEHP assuming k_0 follows a third power dependence on HDEHP.

TABLE 4.13

Stability constant data for Indium sulphate complexes in aqueous solution, $\mu = 1.000$

Method	Temp (°C)	β_1(1/mole)	β_2(1^2/mole^2)	β_3(1^3/mole^3)	Ref.
dis	25	61 ± 1	320 ± 10	-	p.w.
Pot*	20	60 ± 5	75 ± 15	$(2.8 \pm 0.5)10^3$	14
dis	20	70 ± 10	400 ± 50	$(1.0 \pm 0.2)10^2$	15
i.ex.	20	55 ± 10	-	-	23

dis = liquid-liquid extraction; Pot = potentiometric;

i.ex. = ion-exchange; p.w. = present work.

* $\mu = 2.000$

agreement with that of Sundén[15] who obtained from distribution studies using 1-hydroxy-2-naphthoic acid in di-isopropylether as the second phase. The β_2 value, Sundén[14], obtained from potentiometric measurements at $\mu = 2$ would appear to be excessively low in relation to β_1 and β_3. Since the β_1 at $\mu = 1$ and 2 are all in reasonable agreement a β_2 value of $(3\text{-}4)10^2$ would probably be more acceptable for indium than $\beta_1 \approx \beta_2$ at $\mu = 2$. The stability constants for the indium-sulphate system would appear to be less sensitive to changes in ionic strength than those of the lanthanides.

The ion-exchange results for indium show a similar trend as those of trivalent lanthanides where $\phi_{1R} < \phi_{1L}$ and an increasing function of $[SO_4^{=}]$ (Table 4.11). It is found that only $InSO_4{}^{+}_{aq}$ and In^{3+}_{aq} contribute significantly to indium uptake by exchanger from the aqueous solutions. A suitable analysis of the data gives a value of $l_1' = 2.07 \pm 0.09$; other parameters of distribution are recorded in Table 4.8. The ratio l_0/l_1 appears to have a value roughly comparable to that for curium(III) and half that for europium(III) and americium(III) although the partition ratio of $In^{3+}_{aq}(l_0)$ is very much smaller than either of those for Ln^{3+}_{aq} and Ac^{3+}_{aq}.

Oxalate systems

Actinium and lanthanum

The power dependence of the extraction ratio of M_{aq}^{3+} was examined as a function of the HDEHP concentration in the toluene phase; the aqueous phase contained a constant and representative concentration of oxalate ligand at pH 3.60. The expected third power dependence was observed as is deduced from the results given in Table 4.14 for lanthanum. The solvent extraction results for these metal ions in the presence of oxalate in the aqueous phase at $\mu = 0.500$ are reported in Table 4.15. The treatment of the data as outlined earlier shows the formation of only two complexes $M(C_2O_4)^+$ and $M(C_2O_4)_2^-$ and they yield directly β_1 and β_2 values (Table 4.16). Like fluoride and sulphate systems the similarity in stability constant data for actinium and lanthanum oxalate complexes provide further proof of similarity in the solution chemistry of lanthanum and actinium.

Americium(III) and curium(III)

As reported earlier[16] it is seen that there is very little difference in ϕ_{1L} and ϕ_{1R} in the oxalate systems of the trivalent rare earth metal ions over the ligand concentration studied. This suggests that the exchange of partially complexed species into the resin is negligible.

TABLE 4.14

Distribution ratios, ϕ_L, for Lanthanum(III) between HDEHP in toluene and an aqueous phase pH = 3.60, μ = 0.500 ($NaClO_4$) containing 1.985 x $10^{-4}Ml^{-1}$ of oxalate ion.

Expt. No.	HDEHP %(w/v)	ϕ_L	ϕ_L^*
1	0.125	0.368	0.363
2	0.25	2.905	-
3	0.50	23.29	23.24
4	0.40	11.81	11.90

*On the basis of the experimental data for experiment 2 assuming ϕ_L is proportional to $[HDEHP]^3$.

TABLE 4.15

Liquid-liquid extraction data for Lanthanum and Actinium oxalate systems at $\mu = 0.500$ and $25.0 \pm 0.5^\circ C$.

[oxalate] x 10^5 (moles/l)	$\phi_{1L} \times 10^{-4}$ (l/mole) Lanthanum	Actinium
2.206	2.978	3.088
4.412	3.474	3.413
6.618	3.700	3.819
8.824	3.768	3.715
11.03	4.084	4.095
13.24	4.311	4.395
15.44	4.355	4.338
17.65	4.711	4.707
19.85	4.908	4.993
22.06	5.029	5.504
24.27	5.442	5.733
26.47	6.027	6.233

ϕ_{1L} was obtained using the same batch of HDEHP as mentioned in Table 4.9.

TABLE 4.16

Stability constant data for Lanthanum and Actinium oxalate systems

Metal ion	Method	μ	Temp (°C)	β_1	β_2	β_3	Ref.
La^{3+}	dis	0.5	25	$(2.92 \pm 0.07)10^4$	$(10.02 \pm 0.44)10^7$	-	p.w.
	dis	1.0	25	1.82×10^4	7.08×10^7	1.86×10^{10}	12
Ac^{3+}	dis	0.5	25	$(2.96 \pm 0.09)10^4$	$(9.99 \pm 0.72)10^7$	-	p.w.

dis = liquid-liquid extraction; p.w.= present work.

Under these circumstances the ion exchange results like liquid-liquid extraction for americium(III) and curium(III) could be used directly to calculate equilibrium constants. The ion exchange results for these metal ions are reported in Table 4.17. A least squares treatment of the straight line plot ϕ_{1R} against $[C_2O_4^{=}]$ gives the values of β_1 and β_2 recorded in Table 4.18. Other stability data for these systems are also reported in Table 4.18. The β values for americium and curium are similar and in fair agreement with those reported by Sekine[12] at $\mu = 1$ and with those for europium(III) and gadolinium[16]. Further discussion of the results in relation to other metal ion and ligand systems is reserved for the main discussion (Chapter VII).

TABLE 4.17

Ion exchange data for Americium(III) and Curium(III) oxalate systems at $\mu = 0.500$ and 25.0 ± 0.5°C

[oxalate] x 10^5 (mole/l)	$\phi_{1R} \times 10^{-4}$ (l/mole) Americium(III)	Curium(III)
2.206	7.123	7.015
4.412	8.184	8.172
6.618	8.945	8.947
8.824	9.831	9.824
11.03	10.97	10.92
13.24	11.72	11.70
17.65	13.59	13.61
19.85	14.68	14.62
22.06	15.05	15.03

ϕ_{1R} values were obtained using 0.100 gm of resin for which $l_0 = 5480 \pm 43$ and 3246 ± 11 for Americium(III) and Curium(III) respectively.

TABLE 4.18

Stability constant data for Americium and Curium oxalate systems

Metal ion	Method	μ	Temp	$\beta_1 \times 10^{-4}$ (l/mole)	$\beta_2 \times 10^{-8}$ (l^2/mole^2)	Ref.
Am^{3+}	i.ex.	0.5	25	6.58 ± 0.23	4.00 ± 0.15	p.w.
	dis	1.0	25	4.26	2.23	12
	i.ex.	0.2	20-25	98	140	24
	elec	0.1	25	140	350	25
Cm^{3+}	i.ex.	0.5	25	6.25 ± 0.11	4.11 ± 0.08	p.w.
	i.ex.	0.2	20-25	91	140	25

elec = electromigration; other abbreviations are given in the footnote to Table 4.13.

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CHAPTER V

Hydrolysis of Indium and Lanthanum by Partition Methods

INTRODUCTION

The interaction of many metal ions with the hydroxyl ligand in aqueous solution has been studied potentiometrically and reported in a series of papers by Biedermann[1]. Although it is undoubtedly the most accurate method, it is sometimes only satisfactory at concentrations of metal ion which give rise to ambiguity in the calculation of equilibrium constants because of uncertainty concerning the degree of polymerisation of the products of hydrolysis. Partition methods can be used at very low metal ion concentrations (using radioactive tracers) thus offering the possibility of studying hydrolysis constants for mononuclear complexes. Sekine[2] described two methods for the study of metal hydrolysis by a solvent extraction method. In the first method, the metal ion in the aqueous phase is extracted with a chelating acid in the organic phase and the hydrolysis is determined from the decrease in metal extraction which corresponds to the decrease in the concentration of 'free' metal ion as a consequence of hydrolysis. This method has been applied to the hydrolysis of indium(III) by Rossotti and Rossotti[5].

The second method which he used in the study of the hydrolysis of tellurium(IV) is based on the principle that only the neutral species among the various hydrolysed species in an aqueous solution are extracted with a neutral ligand in the organic phase and the changes in distribution ratio are a function of the changes in the concentration of the neutral species in the aqueous phase.

The first method offers the possibility of studying the hydrolysis of most metal ions, but one of the difficulties encountered in such work concerns the choice of a suitable extractant; this should not form chelate complexes appreciably soluble in the aqueous phase since a knowledge of the principle species and their behaviour in the system is required. Schweitzer and Winkley[3] in their study on the hydrolysis of scandium summarised the suitability of a chelating agent after applying tests on a number of different chelating ligands (extractants) in varying solvents. They concluded that none of those examined were suitable because of erratic distribution behaviour, difficulties in obtaining sufficiently pure extractant, adduct formation and slow attainment of equilibrium. Their findings for the hydrolysis of scandium using 3,5-dinitrobenzoic acid as extractant in

4-methyl-2-pentanone indicated large discrepancies with previously published results.

In the present work, di-(2-ethylhexyl)phosphoric acid in toluene is used in the study of the hydrolysis of indium and lanthanum in aqueous sodium perchlorate. The ionic strength of 3.000 is used for the sake of comparison because under such conditions studies have been made potentiometrically by Biedermann[4,5]. The study of the hydrolysis of indium by solvent extraction using 2-thenoyltrifluoroacetone (TTA) in benzene, has also been carried out by Rossotti and Rossotti[6] at the same ionic strength. They found it necessary to make an allowance for the formation of TTA complexes in the aqueous phase in order to get agreement with Biedermann and Ciavatta[5] for the equilibrium constants associated with the formation of $InOH^{2+}$ and $In(OH)_2^+$. The use of HDEHP in such work was critically studied in order to offer a background in choosing a suitable extractant.

The hydroxyl ligand, like fluoride because of its small size, is also of interest in our studies[7] of the relative ability of partially complexed trivalent metal ions to participate in partition into a cation exchanger from aqueous solution. An attempt has therefore been made to extend the measurements to include the indium-hydroxyl system.

EXPERIMENTAL

The reagents and apparatus with the general method of equilibration for both HDEHP and ion exchange distributions have previously been described[8] (Chapter III). All measurements were performed in a sodium perchlorate medium at an ionic strength of 3.000 and a temperature of 25°C. Indium-114m and lanthanum-140 were obtained and treated as described earlier. The solutions equilibrated were 6 x 10^{-7}M in indium and carrier-free lanthanum-140. The HDEHP toluene solutions were pre-equilibrated with 3M $NaClO_4$ at the proper pH.

To compare the results obtained here with the published data, -logH (where H is the hydrogen ion concentration) is required rather than the measure of hydrogen ion activity as given by the pH. These measurements were made using the cell

$$Hg, Hg_2Cl_2, NaCl_{(sat)} | HMHClO_4, (3-H)MNaClO_4 | glass \qquad (5.1)$$

previously employed in measuring pH. For this cell the relationship between the measured potential, E (in millivolts, mV), and the concentration of free hydrogen ions is given by[9]

$$E = E_0 + 16.5H + 59.16 \log H \qquad (5.2)$$

where the term E_0 includes the standard potentials of the electrodes and the asymmetry potential of the glass electrode. The term 16.5H represents the liquid junction potential[9] for the above noted type cell (5.1) at ionic strength of 3.0. Before each measurement, the glass electrode was immersed in different standard solutions of perchloric acid (10^{-1} - 10^{-4}M); the value of E_0 was calculated from eq. (5.2). As the measurements were carried out at low acidities, where $E_0 >>> 16.5H$, the plot of mV against $-\log_{10}H$ gave a straight line the intercept of which gives the value of E_0. Knowing E_0 and E, $\log_{10}H$ is obtained directly from the expression

$$\log_{10}H = \frac{E - E_0}{59.16} \qquad (5.3)$$

or it may be got otherwise using the calibration data.

RESULTS AND DISCUSSION

Liquid-liquid extraction method

Indium system:

The distribution ratio for indium was measured at variable HDEHP concentrations. It was observed that the distribution ratio at a certain -logH (= 4.26) for the aqueous phase is directly proportional to the third power of the HDEHP concentration in the toluene (Table

5.1). The results show that only $In(HD_2)_3$ is extracted into HDEHP even in the event of hydrolysis of indium metal ion.

Dependence of ϕ_L on $-\log_{10}H$

Fig. 5.1 gives the plot of $\log\phi_L$ against -logH for indium partition into HDEHP. Below -logH = 3.90 the curve is linear with a slope of 3 as expected for an inverse cubic dependence of ϕ_L on hydrogen ion concentration. Above -logH = 3.90 the slope decreases as expected in the event of hydrolysis of indium ions. The value of k_0 (distribution ratio in the absence of hydrolysis) appropriate to each -logH was found from a linear extrapolation (broken line) of the portion of the curve obtained experimentally below -logH = 3.90. ϕ_{1L} (table 5.2) was calculated from the relation

$$\phi_{1L} = \left(\frac{k_0}{\phi_L} - 1\right) / [OH^-] \qquad (5.4)$$

at various hydroxyl ion concentrations. $[OH^-]$ was calculated from the known H using the relation[5]

$$H.[OH^-] = 10^{-14.22} = K_W \qquad (5.5)$$

The value of $K_W = 10^{-14.22}$ in a 3M $NaClO_4$ medium was that used by Frydman and co-workers[10].

A plot of ϕ_{1L} as a function of $[OH^-]$ was linear suggesting the presence of two complexes. A least squares treatment gave the β_1 and β_2 values recorded in table 5.5

TABLE 5.1

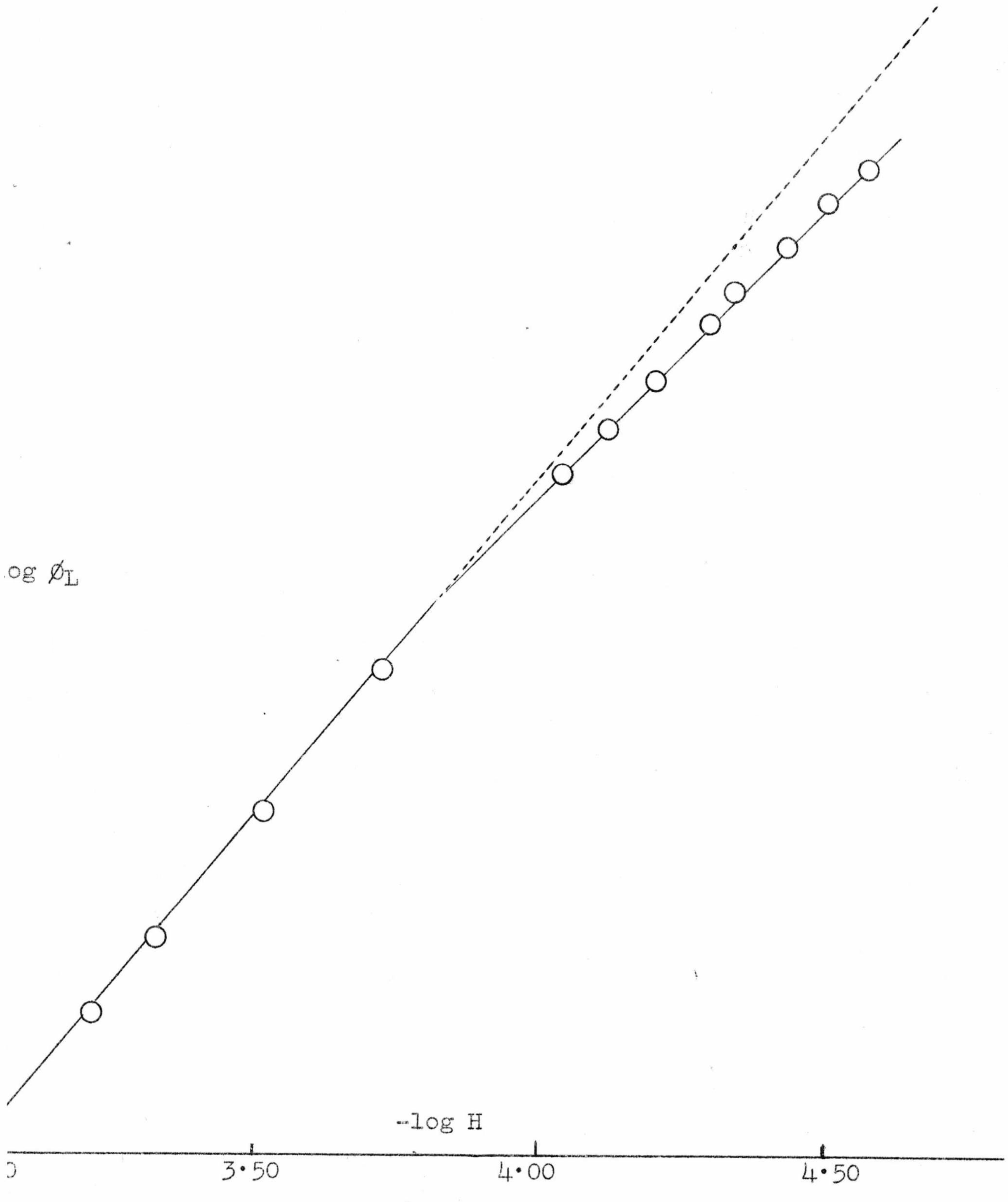
Dependence of ϕ_L, the distribution ratio for indium, on the HDEHP concentration at constant hydrogen ion concentration.

$\mu = 3.000$; $T = 25.0 \pm 0.5^{\circ}C$

$-\log_{10}H = 4.26$

Expt. No.	HDEHP (% w/v) x 10^4	ϕ_L	ϕ_L^*
1	2.50	4.88	4.97
2	3.00	9.12	8.59
3	4.00	20.35	–
4	5.00	41.0	39.75

*Calculated from the data for experiment 3 and assuming ϕ_L is proportional to $[HDEHP]^3$.



. 5.1. The distribution ($\emptyset_L = [In]_{org}/[In]_{aq}$) of indium (Full line) between HDEHP in toluene and aqueous $NaClO_4$ at various hydrogen ion concentrations, total ionic strenght 3·000.

TABLE 5.2

Distribution of indium between the HDEHP phase and aqueous phases having various hydrogen ion concentrations and an ionic strength μ = 3.000M($NaClO_4$). The temperature was 25°C.

pH	-logH	[OH^-] x 10^{10}	ϕ_L^*	k°	ϕ_{1L} x 10^{-9}
2.50	-		0.6270	-	-
2.70	-		2.221	-	-
2.80	-		5.097	-	-
3.00	-		17.67	-	-
3.20	-		69.29	-	-
3.52	3.90	0.4786	514.6	646.0	5.314
3.60	3.99	0.5888	847.2	1122.0	5.461
3.67	4.06	0.6918	1.294x10^3	1.820x10^3	5.870
3.76	4.12	0.7943	2.255x10^3	3.350x10^3	6.114
3.82	4.19	0.9333	3.162x10^3	5.012x10^3	6.269
3.90	4.26	1.096	5.125x10^3	8.913x10^3	6.744
3.97	4.33	1.288	7.413x10^3	14.13x10^3	7.035
4.04	4.38	1.445	11.182x10^3	24.55x10^3	8.273

*ϕ_L values corrected to HDEHP 2.5 x 10^{-2}%(w/v) assuming $\phi_L \alpha [\mathrm{HDEHP}]^3$. The HDEHP concentration was variable from 2.5 x 10^{-2} to 5.0 x 10^{-4}% (w/v).

Where

$$\beta_1 = \frac{[InOH^{2+}]}{[In^{3+}][OH^-]} \tag{5.6}$$

and

$$\beta_2 = \frac{[In(OH)_2^+]}{[In^{3+}][OH^-]^2} \tag{5.7}$$

The assumption was made that only mononuclear complexes are formed at such low metal ion concentration as pointed out by Rossotti and Rossotti[6]. The equilibrium constants are in reasonable agreement with those previously published (table 5.5). The small variations are only the experimental errors. It may be concluded from these results that aqueous indium-HDEHP complexes do not play a significant part in the distribution of the metal ion in the -logH range investigated.

Because of uncertainties in the HDEHP concentrations which have of necessity to be kept very low in the toluene phase difficulty was experienced in making reliable distribution measurements for indium at -logH numerically greater than 4.4.

Lanthanum system

The distribution data for lanthanum is reported in table 5.3. As pointed out earlier a difficulty similar to that arising with the indium system was encountered in applying the distribution data to the study of hydrolysis of lanthanum at high -logH. According

TABLE 5.3

Lanthanum-hydroxyl system by liquid-liquid extraction at μ = 3.000 and 25.0 ± 0.5°C.

Expt. No.	pH	-logH	ϕ_L*	logϕ_L
1	3.0	3.40	0.038	-1.421
2	3.68	4.08	4.037	0.606
3	4.27	4.60	2.786×10^{2}	2.445
4	5.12	5.40	9.867×10^{4}	4.994
5	5.84	6.05	1.271×10^{7}	7.104
6	6.23	6.35	1.586×10^{8}	8.200
7	6.61	6.80	2.097×10^{9}	9.322
8	7.02	7.20	3.958×10^{10}	10.50
9	7.31	7.45	2.153×10^{11}	11.33

*ϕ_L corrected to HDEHP 0.125% w/v assuming ϕ_L is proportional to $[\text{HDEHP}]^3$. The HDEHP in toluene used was variable from 0.25 to 1.0×10^{-4}% (w/v) for experiments 1 to 9.

to Biedermann and Ciavatta[5], hydrolysis of this metal starts at about -logH = 6.50. From our distribution data it is seen that $\log\phi_L$ against -logH shows the expected departure from the third power dependence on the latter at about -logH = 7 in accordance with the above observation. The change in ϕ_L over this limited -logH range where the distribution could be measured was so small that an analysis of the kind used for indium could not be carried out. However, it did not prove possible to extend the measurements sufficiently far beyond this range of hydrogen ion concentration because of the ionisation and consequent distribution of HDEHP between the phases.

The change in the HDEHP concentration in toluene was demonstrated by comparing distribution ratios for samples having the same initial HDEHP in toluene but pre-equilibrated with aqueous solutions of sodium perchlorate (3.00M) at different hydrogen ion concentrations (-logH of 4.00 and 10.0). The distributions of lanthanum were carried out from an aqueous solution at -logH = 4.00 and to prevent hydrogen ion concentration changes during these equilibrations the HDEHP, initially conditioned at -logH = 10.0, was washed with several portions of the aqueous sodium perchlorate solution having -logH = 4.00 before shaking with the metal ion. It was confirmed that a variation occurs in the distribution ratio with these two HDEHP solutions of the same initial concentration but preconditioned at different -logH.

It thus appears that the application of HDEHP to such hydrolytic studies mainly depends upon having a well defined relationship between the metal ion distribution ratio and the HDEHP concentration and factors such as the magnitude of the distribution ratio in the absence of hydrolysis and the hydrogen ion concentration below which hydrolysis becomes significant. The emulsification of HDEHP at higher -logH may also cause additional experimental difficulties. Extension of this work therefore awaits an extractant having the properties listed above.

Cation-Exchange Partition

In order to check the suitability of this method the measurements were made only on the indium-hydroxyl system. The cation-exchange distribution data is reported in table 5.4. The plot ϕ_R against -logH of the aqueous solution are presented in Fig. 5.2. It is found that the dependence of distribution, L, on -logH is divided into three parts. At the lower -logH values L is independent of hydrogen ion concentration and is equal to L_o. The region -logH = 3.44 - 3.88, for which

TABLE 5.4

Distribution of indium between a cation-exchanger* and an aqueous phase of ionic strength 3.000 at 25.0 ± 0.5°C.

pH	-logH	$[OH^-]\times10^{10}$	L	L_o	ϕ_R $(=L-L_o)$	l_o	$\phi_{1R}\times10^{-9}$
2.15	-	-	249.0	242	-	-	-
2.30	-	-	240.4	-	-	-	-
2.51	-	-	237.5	-	-	-	-
2.73	-	-	255.1	-	-	-	-
3.02	-	-	284.0	-	42.0	-	-
3.12	-	-	321.6	-	79.6	-	-
3.20	-	-	382.0	-	140.0	-	-
3.34	-	-	523.2	-	182.2	-	-
3.42	-	-	741.6	-	499.6	-	-
3.48	-	-	982.0	-	740.0	-	-
3.60	3.99	0.5888	1016	-	774.0	1334	12.29
3.72	4.09	0.7413	1332	-	1090	2754	20.59
3.80	4.16	0.8710	1564	-	1322	4335	26.16
3.90	4.26	1.096	1996	-	1754	7943	32.19
4.01	4.36	1.380	2439	-	2197	14960	42.09
4.10	4.43	1.622	3245	-	3003	25120	45.41
4.22	4.56	2.188	3728	-	3486	53090	65.03

*Zeo-Karb 225 (Grade SRC15) 8% cross-linked (DVB) and mesh range 100-200.

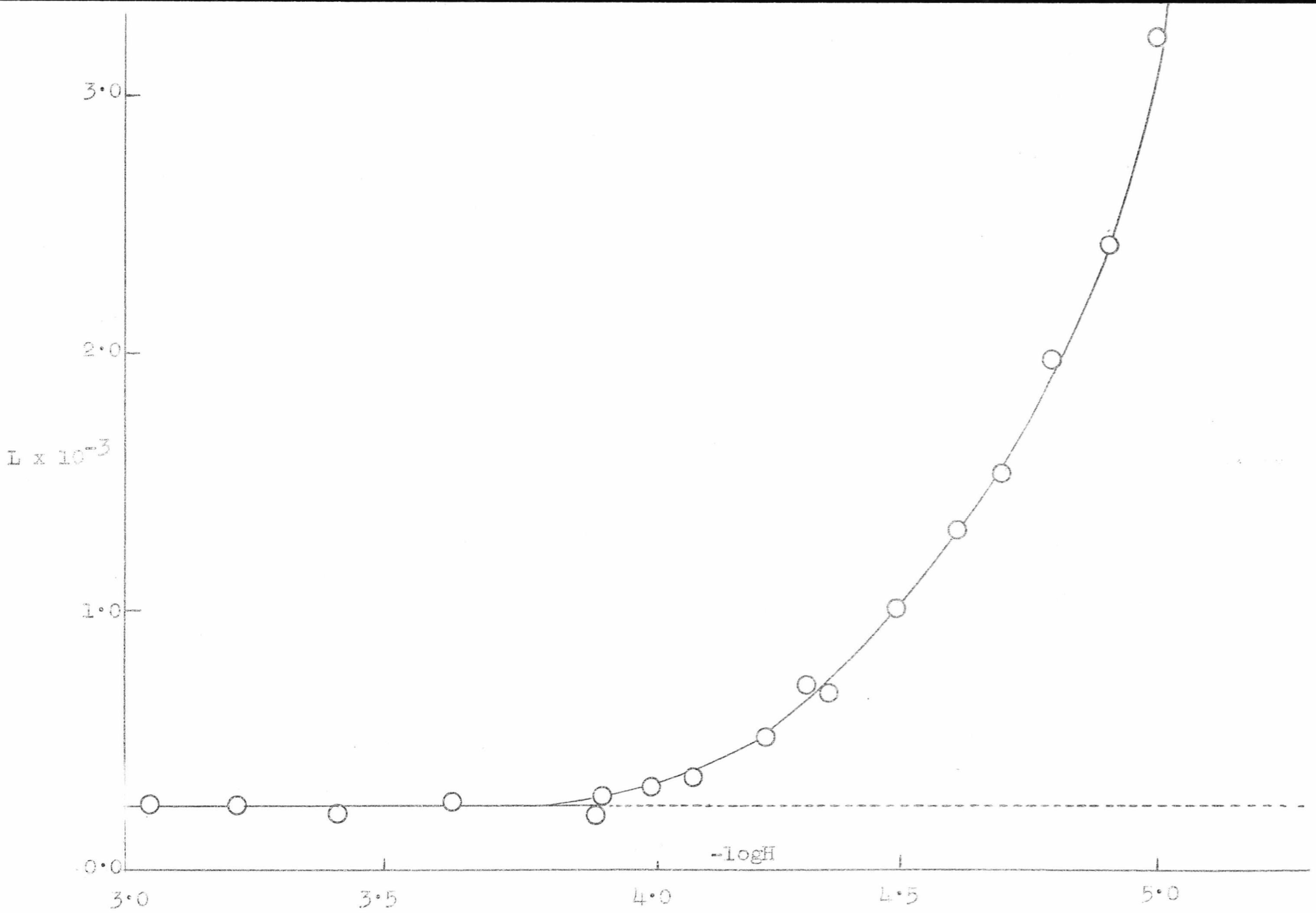


Fig. 5.2. The distribution ($L = [In]_R/[In]_{aq.}$) of indium between Zeo-karb-225, 8 per cent cross-linked, mesh 100-200 and aqueous $NaClO_4$ at various hydrogen ion concentrations, total ionic strenght 3·000.

a plot of $\log(L-L_0)$ or $\log\phi_R$ (putting $L-L_0 = \phi_R$) against $-\log H$ (Fig. 5.3) gives a straight line of slope 3, provides evidence that indium as In^{3+}_{aq} only is exchanging when sodium ions at the sulphonate exchange sites. If it is assumed that hydrolysis begins in the system studied at about $-\log H = 4.00$ (read from fig. 5.1) then the third region in the above plot beyond $-\log H = 4.00$ represents the hydrolysis region. The value of l_0 (distribution ratio in the absence of hydrolysis) can be calculated from the extrapolation (broken line) of the portion of straight line plot (Fig. 5.3) with slope of 3. ϕ_{1R} can be calculated from

$$\phi_{1R} = \left(\frac{l_0}{\phi_R} - 1\right) / [OH^-] \qquad (5.8)$$

The value of β_1 calculated from this plot agrees within experimental limitations with published values (Table 5.5). There are very large discrepancies among β_2 values (table 5.5). It is seen that beyond $-\log H = 4.00$ the additional mode of exchange exhibited by polystyrene type sulphonic acid exchanger as reported previously (Chapter III) is presumably due to the increase in secondary exchange capacity which is known from studies with lanthanides[11]. ϕ_R for lanthanides increases steeply with decreasing hydrogen ion concentration. As the hydrolysis of these metal ions as considered on current evidence only to start at $-\log H = 6.5$ the rapid increase

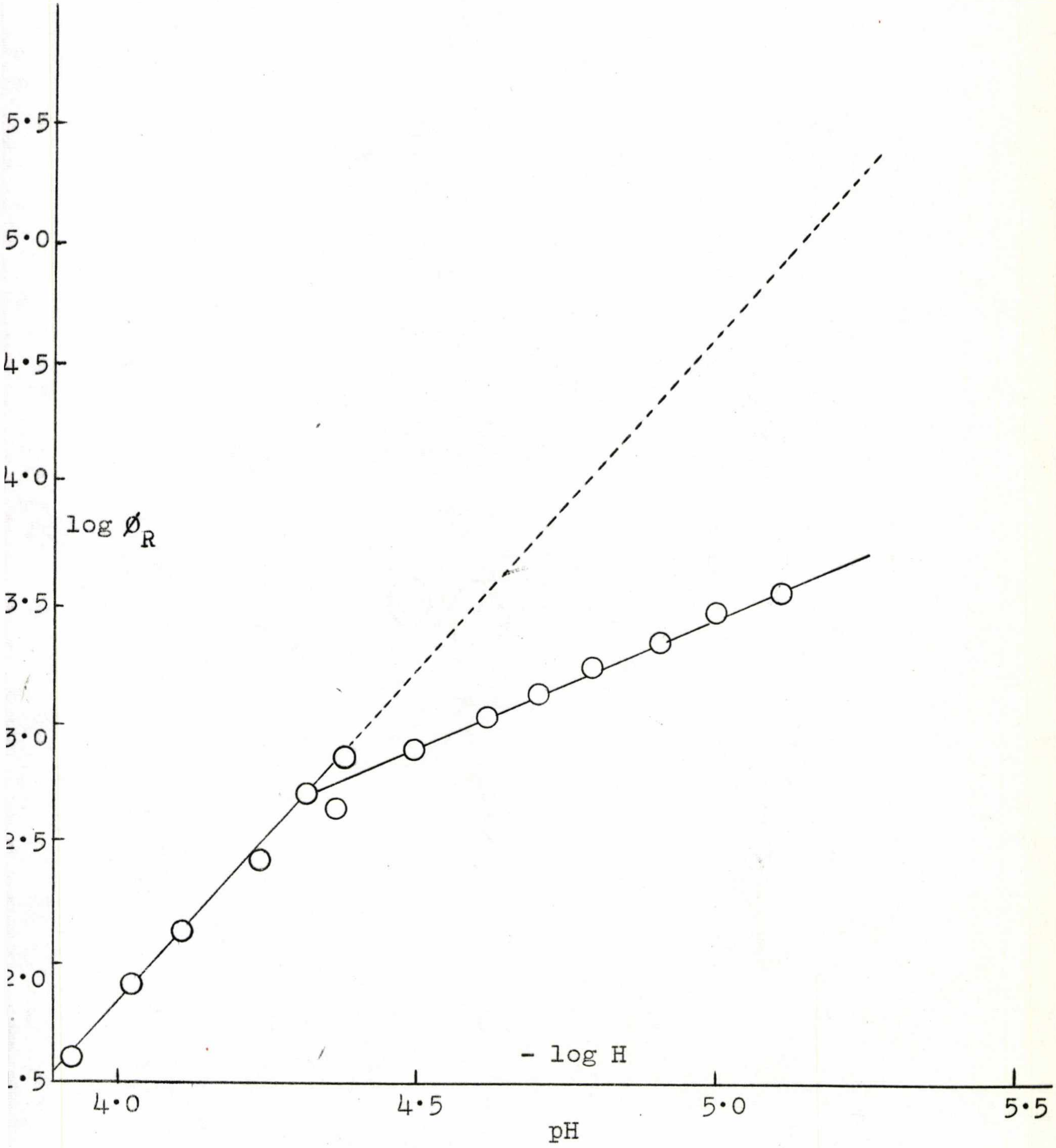


Fig. 5.3. The distribution of indium (Full line) between cation exchange resin and aqueous $NaClO_4$ at various hydrogen ion concentrations, total ionic strength 3·000

TABLE 5.5

Stability constants for the hydrolysis of indium in solution at ionic strength 3.00 and 25.0°C

Method	$\beta_1 \times 10^{-9}$	$\beta_2 \times 10^{-19}$	Ref
Dis.	3.9 ± 0.3	2.7 ± 0.3	p.w.
"	6.3	3.98	5
I.Ex.	4.0	25.0	p.w.
Pot.	6.3	12.6	3

I.Ex. = ion exchange method; p.w. = present work; Pot = potentiometric; Dis = liquid-liquid extraction.

in ϕ_R with increasing -logH is likely due to this secondary exchange process.

This process is of low capacity[11] (a few percent) relative to exchange at sulphonate sites, hence the loading of the resin with metal ion or increase in total indium concentration would be expected to cause its effect to be swamped. Unfortunately, with indium this could only be done at concentrations giving rise to the precipitation of hydrolysed indium species (estimated from the stability data). Additionally, there would be some uncertainty concerning polynuclear complex formation over the range of conditions of measurement.

It can be concluded that the ion exchange method is not suitable for the type of study envisaged unless we have some effective means of dealing with secondary cation exchange behaviour. For a successful study of this kind about 10^{-5}M metal ion[11] is required to give rise to the hydrolysed species soluble at that concentration of metal ion. Lanthanum and no doubt other lanthanides meet this requirement, but the formation of polynuclear complexes and other experimental limitations arising from secondary cation exchange may hamper this type of study using currently available solid exchangers.

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CHAPTER VI

A study of the complexes of europium(III) and americium(III) formed with propionate, lactate, alaninate and pyruvate

INTRODUCTION

In the previous chapters stability constant data for the formation of complexes of various metal ions with inorganic anions have been reported. Organic anions, especially from substituted fatty carboxylic acid have been used[1-4] in the separation of lanthanides and actinides by ion-exchange. There are plenty of data[1-9], both stability and thermodynamic, on the complex formation of lanthanides and to a lesser extent for actinides with acetate and related acid anions (e.g. glycolate, thioglycolate, glycinates, etc.). The data on the lanthanide and specially the actinide complexes with propionate and its derivatives (e.g. lactate, alaninate, pyruvate, etc.) are sparse. In order to compare the behaviour of these two groups measurements were undertaken in the determination of stability data for europium(III) and americium(III) in their complex formation with propionate, lactate, alaninate and pyruvate. As only tracer amounts of americium(Am-241) were available and in any case could be used, the experimental methods were restricted to the liquid-liquid extraction method for europium(III) and americium(III) systems. For comparison with the earlier work on these ligands and others, the measurements were made at an ionic strength of $\mu = 2.00$ ($NaClO_4$). From the knowledge of the possible partitioning of propionic acid into the HDEHP/toluene phase, unlike the other ligands undertaken in the present study the measurements on the propionate system were made potentiometrically using a glass-calomel electrode system and a modified Calvin-Wilson[11] pH titration method. The interaction of propionate with europium(III) was studied only because macro amounts of this metal ion, but not americium, can be used.

EXPERIMENTAL

All the common chemicals used were of reagent grade. The HDEHP, americium-241 and europium-152 and -154 mixture (containing carrier) were those described earlier in Chapter III except that the solutions were made up in 2M $NaClO_4$ and the HDEHP was pre-equilibrated with 2M $NaClO_4$.

Ligand Solutions

Propionate solution:- The source of propionate was propionic acid of puriss quality obtained from Koch-Light Laboratories Ltd., Colnbrook, Bucks, England. Propionic acid solutions were standardised by alkalimetric titration. The pK value of propionic acid was determined by titrating a 2M propionic acid solution potentiometrically with 2M sodium hydroxide. Similar measurements were made with dilute propionic acid solution at an ionic strength of 2 maintained with sodium perchlorate. The pK value is given in Table 6.1. The pH meter used in the present study and in other work described in this chapter was standardised against 0.05M potassium hydrogen phthalate.

Lactate solution:- Reagent grade lactic acid (supplied by B.D.H.) after cooking under reflux with a known amount of perchloric acid was neutralised with standard sodium hydroxide equivalent to the perchloric acid originally added. The solution was made up to an ionic strength of 2 with sodium perchlorate and the required pH was adjusted with sodium hydroxide and perchloric acid. The analysis for lactate was made by alkalimetric as well as potentiometric titration with sodium hydroxide. The pK value for lactic acid at $\mu = 2.00$ reported in Table 6.1 was determined as noted above.

Alaninate solution:- DL-d-alanine puriss supplied by Koch-Light Ltd., was used. The standard solution (determined by potentiometric titration) was made up to an ionic strength of $\mu = 2.000$ with sodium perchlorate and the required pH was adjusted with the help of sodium hydroxide and perchloric acid. In the strict definition the Zwitterion form of alanine at pH 3.60 does not contribute[8] to the ionic strength. However, it seems likely that its effect on the solvent medium would resemble that of a 1:1 electrolyte.

Table 6.1 - pK values for different carboxylic acids at an ionic strength $\mu = 2.00$ and 25.0±0.1°C

Acid	pK_1	pK_2
Propionic acid	4.35	-
Lactic acid	3.63	-
Alanine	2.50	9.65
Pyruvic acid	2.45	-

Consequently, the ionic strength of the aqueous solution was adjusted to 2.000 by assuming 1:1 electrolyte behaviour for the alaninate Zwitterion and adding an appropriate volume of concentrated sodium perchlorate solution. Since the total Zwitterion concentration varies between 0.01 and 0.2M, it makes little, if any, practical difference whether we include the Zwitterion concentration or not in the total ionic strength. The acid dissociation constants at $\mu = 2.000$ were determined by pH titration. In order to obtain the first dissociation constant excess known perchloric acid was added and the pK was calculated from the half titration point. The second dissociation constant was similarly calculated by further titration until the second end-point is reached. pK_1 and pK_2 at $\mu = 2.000$ are reported in Table 6.1.

Pyruvate solution:- Pyruvic acid (puriss), supplied by Koch-Light Ltd., and sodium pyruvate obtained from the Sigma Chemical Company, St. Louis, Missouri, U.S.A., were used as the sources of pyruvate ligand. The pyruvic acid solution was standardised by alkalimetric titration while sodium pyruvate was determined by an ion-exchange method. The sodium pyruvate solution was passed through an ion-exchanger in the hydrogen form and the acid (equivalent to pyruvate) thus liberated was determined by alkalimetric or potentiometric titration. Buffer stock solutions were prepared by mixing pyruvic acid and sodium pyruvate or by partial neutralisation of pyruvic acid by standard sodium hydroxide. The ionic strength and pH were adjusted as reported above. The pK value for pyruvic acid at $\mu = 2.000$ obtained by the pH titration method is reported in Table 6.1.

Pyruvic acid or the pyruvate anion are known[12-14] to be quite stable in aqueous solution where hydration can take place in solution. The purity of the sodium pyruvate and pyruvic acid was checked independently by N.M.R. and U.V. spectroscopic methods. The decomposition or any other change in pyruvate solution over a few minutes to two days following its preparation, was studied by observing the change in absorbance at 330 nm wave length of a sample at the pH and ionic strength of the present experimental run in an Hitachi Perkin-Elmer U.V. and visible range spectrophotometer. The absorbance did not change over the time interval of the measurements providing support for the view that the solutions were sufficiently stable for the purpose for which they were required.

Methods of measurement

Liquid-liquid extraction method:- The liquid-liquid extraction measurements made in this study for lactate, alaninate and pyruvate interaction with americium(III) and europium(III) are similar to those mentioned in Chapter III. All the measurements were made at $\mu = 2.000$ ($NaClO_4$), pH 3.60 and 25°C temperature.

Potentiometric method

Apparatus and procedure:- A Radiometer pH M-4d potentiometer with a G200B glass electrode and a K100 saturated calomel electrode (all supplied by Radiometer A/S, Copenhagen, Denmark) were used. The glass electrode was standardised against 0.05M potassium hydrogen phthalate solution and a Radiometer buffer solution type S1001.

All titrations and pH measurements were made in a thermostatted sample cell (250 ml capacity) at 25.0 ± 0.1°C. Rapid mixing was achieved by a mechanical stirrer which was stopped during the measurements. Nitrogen gas was passed through and over the solution to eliminate carbon dioxide. 100 ml of the mixture of europium perchlorate, propionate, perchloric acid and sodium perchlorate at an ionic strength of 2.000 were taken in the cell. After attaining constant temperature small aliquots (0.05 - 0.1 ml) of the standard sodium hydroxide (2.00M) were added with stirring and the pH was recorded when it attained a constant value (normally 2-3 minutes). The titrations were repeated for 100 ml of perchloric acid and sodium perchlorate and 100 ml of perchloric acid, propionate and sodium perchlorate separately at the same temperature. The strength of acid and ionic strength were kept the same in all the three titration runs. The amount of propionate in the presence and absence of europium was also kept the same. Three different sets of experiments were carried out depending on the concentration ratios of metal to acid to ligand. Each titration set was at least duplicated.

Results and Discussion

Preliminary distribution measurements showed that ϕ_L is dependent on the third power of the HDEHP concentration in the presence (separately) of constant and fairly high lactate, alaninate and pyruvate in the aqueous phase. Representative results are reported in Table 6.2. From these results it can be concluded that no other mechanism of extraction except that represented in equation 3.3 is taking place to any significant extent. In addition it may be deduced that the partition of these ligands is also negligible on the basis of this extraction behaviour.

Lactate systems

The HDEHP distribution results at pH 3.60 and ionic strength of 2.000 are reported in Table 6.3 for both europium(III) and americium(III) lactate systems. From the plot of ϕ_{1L} against lactate it is observed that more than two complexes are formed with each metal. Assuming the relation

$$\phi_{1L} = \beta_1 + \beta_2[L] + \beta_3[L]^2 + \ldots.$$

holds where [L] is the concentration of lactate, a least squares treatment using an electronic digital computer

Table 6.2 - Dependence of ϕ_L on HDEHP concentration in the presence of a constant ligand concentration and pH 3.60

Europium alaninate system; [Alaninate] = 7.53×10^{-2}M

Exp. No.	[HDEHP] % w/v	ϕ_L	ϕ_L^*
1	0.0125	0.800	0.814
2	0.025	6.518	-
3	0.030	11.30	11.26
4	0.050	52.09	52.14

*calculated on the basis of Experiment 2 assuming that ϕ_L is proportional to $[\text{HDEHP}]^3$.

Americium pyruvate system; [Pyruvate] = 3.754×10^{-2}M

Exp. No.	[HDEHP] % w/v	ϕ_L	ϕ_L^*
1	0.075	1.76	1.75
2	0.100	4.14	4.14
3	0.125	8.08	-
4	0.250	64.1	64.6

*calculated on the basis of Experiment 3 assuming that ϕ_L is proportional to $[\text{HDEHP}]^3$.

Europium lactate system; [Lactate] = 3.722×10^{-2}M

Exp. No.	[HDEHP] % w/v	ϕ_L	ϕ_L^*
1	0.05	0.752	-
2	0.075	2.53	2.54
3	0.100	6.04	6.01
4	0.125	11.71	11.75

*calculated on the basis of Experiment 1 assuming that ϕ_L is proportional to $[\text{HDEHP}]^3$.

Table 6.3 - Liquid-liquid extraction data for americium(III) and europium(III) lactate systems at ionic strength of $\mu = 2.00$ and $25.0 \pm 0.5^{\circ}C$

[Lactate] x 10^2	ϕ_{1L} x 10^{-3}	
	Am	Eu
0.2068	0.5005	0.4020
0.4136	0.5992	0.4751
0.6204	0.7496	0.5534
0.8272	0.8747	0.6437
1.034	1.034	0.7386
1.241	1.210	0.8012
1.448	1.367	0.9421
1.654	1.555	1.060
2.068	1.928	1.360
2.481	2.366	1.607
2.895	2.824	1.905
3.209	3.167	2.159
3.722	3.751	2.588
4.136	4.400	2.976
4.963	5.604	3.745
5.790	7.011	4.612
6.817	8.954	5.853
7.444	9.948	6.643
8.272	11.67	7.912

ϕ_{1L} values were obtained using 0.05% and 0.125% w/v HDEHP with $k_0 = 73.41 \pm 0.89$ (6 values) and 68.76 ± 1.02 (7 values) for europium(III) and americium(III) respectively in that order.

gives the values of β_1, β_2 and β_3 over the range of ligand studied. The overall stability constant data in addition to other published[6] values for these systems is reported in Table 6.4. There is fair agreement in β values for the europium lactate system with that of Choppin and Chopoorian[6]. Comparison cannot be made for the americium lactate system because of the unavailability of data at $\mu = 2.000$. However, when the results are compared with those for the europium(III) lactate it is seen that americium(III) forms much stronger complexes with lactate. A similar behaviour was observed by Grenthe[3] for europium and americium glycolate systems where the stability of americium glycolate complexes is appreciably higher than those for europium glycolates.

Alaninate system

Alaninate exists in three forms,

$$CH_3CHNH_3^+COOH \overset{pK_1}{\rightleftharpoons} CH_3CHNH_3^+COO^- \overset{pK_2}{\rightleftharpoons} CH_3CHNH_2COO^-$$

As seen from the pK values (Table 6.1) the anion $CH_3CHNH_2CO_2^-$ exists in large amount only above pH 10 whereas at pH values in the acid range the Zwitterion $CH_3CH(NH_3^+)CO_2^-$ exists as the predominant form of alaninate ligand. The rare earths and trivalent actinides hydrolyse[9] above about pH 5, therefore the measurements could only be made at low pH, e.g. 3.60 in the present study. At pH 3.60 about 90% of the alanine exists in the Zwitterion form.

Table 6.4 - Collected stability constant data for europium(III) and americium(III)

Metal ion	Ligand	Ionic strength	Method	β_1	β_2	β_3	Ref.
Eu^{3+}	Propionate	2.00	Pot.	$(0.86 \pm 0.06)10^2$	$(1.72 \pm 0.17)10^3$	$(7.01 \pm 0.26)10^3$	p.w.
	"	2.00	"	0.96×10^2	1.91×10^3	-	7
	Lactate	2.00	dis.	$(3.01 \pm 0.15)10^2$	$(3.60 \pm 0.10)10^4$	$(6.70 \pm 0.12)10^5$	p.w.
	"	2.00	dis.	3.37×10^2	3.94×10^4	7.49×10^5	6
	Alaninate	2.00	dis.	5.26 ± 0.11	2.63 ± 1.06	-	p.w.
	Glycinate	2.00	dis.	5.0 ± 0.3	-	-	8
	Pyruvate	2.00	dis.	$(0.94 \pm 0.01)10^2$	$(2.07 \pm 0.04)10^3$	$(6.09 \pm 0.27)10^3$	p.w.
Am^{3+}	Lactate	2.00	dis.	$(3.34 \pm 0.324)10^2$	$(5.83 \pm 0.21)10^4$	$(9.63 \pm 0.26)10^5$	p.w.
	Alaninate	2.00	dis.	5.66 ± 0.14	3.71 ± 1.34	-	p.w.
	Glycinate	2.00	dis.	4.9 ± 0.2	-	-	8
	Pyruvate	2.00	dis.	$(1.07 \pm 0.01)10^2$	$(2.20 \pm 0.03)10^3$	$(7.40 \pm 0.17)10^3$	p.w.

Pot = potentiometric method; dis = liquid-liquid extraction; p.w. = present work.

The distribution data for europium and americium is reported in Table 6.5. It is observed that under the conditions of measurements and from plots of ϕ_{1L} against [alaninate] only the first complex formation constant can be calculated for both the systems. ϕ_{1L} has scattered values showing a slight increasing trend with the increase of ligand concentration in the aqueous phase. A rough estimate of β_2 can also be made. Table 6.4 shows the values of stability constants for both systems. There is fair agreement in β_1 values for both theamericium and europium alaninate systems. However as for the lactate systems a slightly higher value of β_1 is observed for the americium system compared to that for the europium.

An experiment on europium was carried out at pH 4.50 to verify the assumption that with these metal ions the ligand complexed in the Zwitterion form. As compared to the other runs, this involves an increase in Zwitterion concentration of about 8%, whereas the concentration of the anion ($CH_3CHNH_2COO^-$) increased by a factor of about 80. At this pH assuming that complexing was due to the Zwitterion only a value of $\beta_1 = 5.3$ was obtained at 25°C. This result is in good agreement with the value obtained at pH 3.60 given in Table 6.4. No such agreement was found when calculations were made on the assumption that complexation with $CH_2CHNH_2COO^-$ was taking place. Moreover, the stability constants calculated on the basis of the concentration of

Table 6.5 - HDEHP distribution data for americium(III) and europium(III) alaninate systems at an ionic strength $\mu = 2.000$, pH = 3.60; T = 25.0 ± 0.5°C

	ϕ_{1L}	
[Alaninate] x 10^2	Am	Eu
0.9410	5.047	4.782
1.882	5.829	5.504
2.010*	-	5.411*
2.833	5.715	5.267
3.764	5.980	5.611
5.646	5.868	5.533
6.030*	-	5.488*
6.528	6.173	5.722
7.528	6.409	5.403
9.410	6.060	5.310
10.05*	-	5.452*
11.29	6.081	5.618
13.17	5.980	5.479
14.07*	-	5.587*
15.06	6.065	5.641
16.94	6.315	5.688
18.82	6.245	5.756

*measurements were made at pH 4.50 and 0.0025% w/v HDEHP. ϕ_{1L} were obtained using 0.025% and 0.075% w/v HDEHP with k_o = 9.169 ± 0.213 (5 values) and 14.95 ± 0.82 (6 values) for europium(III) and americium(III) respectively in that order.

this anion are quite unreasonable, e.g. ~ 7×10^6 from the data in Table 6.5. The reactions of glycine, the homolog of alanine with zinc(II), cadmium(II) and berylium(II), was studied by Krishman and Plane[15] using Raman spectroscopy. They concluded that glycine forms monodentate complexes by means of the Zwitterion at low pH values (ca 2.0 - 4.0). Further, if a comparison of the β_1 values for americium(III) and europium(III) alaninates is made with those for the glycinate[8] systems there appears to be good relative agreement. Choppin and Tanner[8] studied the glycinate system at pH 3.6 assuming that Zwitterion is complexing rather than the aforementioned anion. Their β_1 value (Table 6.4) for americium(III) is lower than that for europium(III) whereas alanine seems to form a stronger complex with americium(III) than with europium(III).

Pyruvate systems

The results for studies with pyruvate as ligand are reported in Table 6.6. From a plot of ϕ_{1L} against [pyruvate] it is observed that at least 2 or 3 complexes are present over the ligand range studied. A least squares analysis gives the values for β_1, β_2 and β_3 reported in Table 6.4. No comparison can be made in the stability results because of unavailability of data for this ligand in the literature as far as the author's knowledge is concerned. The stability of americium pyruvates are greater than those for

Table 6.6 - HDEHP distribution data for americium and curium pyruvate systems at an ionic strength of μ = 2.000; pH = 3.60; T = 25.0 ± 0.5°C

	ϕ_{1L} x 10^{-2}	
[Py] x 10^2	Am	Eu
0.3754	1.133	1.018
0.7508	1.242	1.104
1.126	1.337	1.182
1.502	1.420	1.278
1.877	1.510	1.365
2.252	1.618	1.451
2.628	1.700	1.522
3.003	1.801 (1.807)^b	1.615
3.378	1.901	1.701
3.754	2.001	1.798
4.505	2.202	2.000
5.256	2.454 (2.467)^c	2.201
6.006	2.650	2.402
7.508	3.133	2.829
8.250	(3.331)^a	
9.010	3.675	3.300
10.51	4.201 (4.177)^b (4.153)^a	3.820
12.01	4.759	4.350
14.51	5.399	4.802
15.02	6.060	5.439

a = pyruvate solution aged 10 hrs; b = pyruvate solution aged 21 hrs; c = pyruvate solution aged 2 days.

ϕ_{1L} values were obtained using 0.05% and 0.125% w/v HDEHP with k_0 = 73.41 ± 0.89 (6 values) and 68.76 ± 1.02 (7 values) for europium(III) and americium(III) respectively in that order.

corresponding europium complexes. To check whether pyruvate remains stable during the distribution study measurements were made on americium-241 distribution into HDEHP using the aqueous phase containing different aged pyruvate solutions. Table 6.6 shows that ϕ_{1L} at different ligand concentrations, obtained from pyruvate solutions 6 - 48 hrs old, have the same values. This suggests that pyruvate, under the present experimental conditions, remains sufficiently stable in aqueous solution.

Europium(III) propionate system

The treatment of the pH titration results was that due to Irving and Rossotti[10]. In consideration with pH titration curves 1, 2, 3 (Fig. 6.1) representing acid, acid + ligand and acid + ligand + metal ion titrations the values of ligand number $\bar{n}_A$ and $\bar{n}$ for ligand bound to proton and ligand bound to metal ion respectively were calculated from

$$\bar{n}_A = \left[C_L^o - \frac{(v_2-v_1)(N+E)}{v_0+v_1} \right] / C_L^o$$

and $$\bar{n} = \frac{(v_3-v_2)[E+N+C_L^o(1-\bar{n}_A)]}{\bar{n}_A C_M (v_0+v_2)}$$

where C_L^o = total initial propionate concentration in solution,

v_0 = total initial volume of solution in the cell,

N = strength of sodium hydroxide,

E = strength of acid perchloric,

C_M = total metal ion concentration in the cell solution.

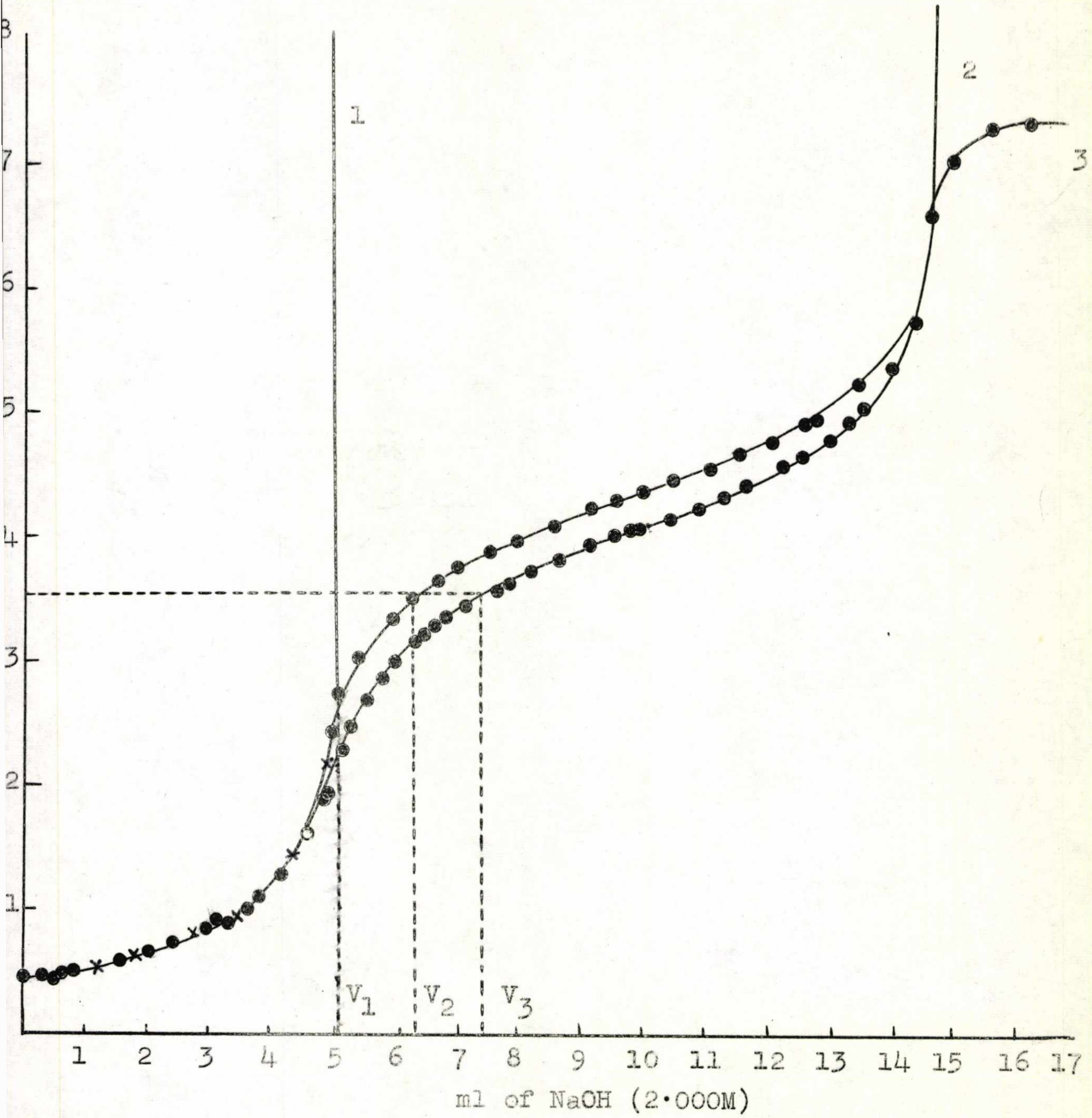

Fig. 6.1. pH titration curve for the europium (III) propionate system. $[\mathrm{Eu}]_{\mathrm{total}} = 2\cdot21 \times 10^{-2}\mathrm{M}$; $\mathrm{TL}^{\circ} = 0\cdot301\mathrm{M}$; $\mu = 2\cdot000$ $V_0 = 100\cdot0\mathrm{ml}$; $E = 0\cdot1\mathrm{M}$; $N = 2\cdot00\mathrm{M}$; $T = 25\cdot0 \pm 0\cdot1^{\circ}\mathrm{C}$. Curves 1,2, and 3 represent titration of perchloric acid, perchloric acid + propionic acid and perchloric acid + propionic acid + europium (III) in that order.

v_1, v_2 and v_3 are volumes of alkali added to give a common pH value on the three titration curves.

The value of free propionate [L] at different pH values was calculated from the experimentally measured pK value according to the relation

$$pH = pK + \log_{10} \frac{[L]}{(C_L - \bar{n}C_M) - [L]}$$

Knowing $\bar{n}$ and [L], values for β_m were calculated by the method described in Chapter I.

Representative data from analysis of the titration curves for two runs are reported in Table 6.7. A least squares analysis gave at least the stability constants corresponding to the first three europium(III) propionate complexes. The β_m values, with other published results[7], are reported in Table 6.4. Fair agreement is observed for β_1 and β_2 values when compared with those reported by Choppin and Graffo[7].

DISCUSSION

From the present measurements and others[1-9], it is seen that the stability constant of these metal ions in their complex formation with carboxylate ligands is in the order α-hydroxyisobutyrate > lactate > glycolate > pyruvate > propionate > acetate > alaninate > glycinate. This shows that the presence of a hydroxyl group on the carbon adjacent to the carboxylate group enhances metal complex formation.

Table 6.7 - pH titration data for europium(III)-propionate system at $\mu = 2.000$ and $25.0 \pm 0.1^\circ C$

RUN I: $C_M = 2.21 \times 10^{-2}M$; $C_L^o = 0.301M$.
$v_o = 100.0$ ml; $E = 0.100M$; $N = 2.00M$.

$[L] \times 10^3$	3.012	4.737	6.853	8.082	9.961
$\bar{n}$	0.2181	0.3256	0.4408	0.4971	0.5782
$\frac{X-1}{[L]} \times 10^{-2}$	0.8751	0.9125	0.9605	0.9808	1.018
$[L] \times 10^3$	13.53	16.89	21.95	26.95	35.73
$\bar{n}$	0.7111	0.8221	0.9774	1.118	1.287
$\frac{X-1}{[L]} \times 10^{-2}$	1.068	1.128	1.219	1.281	1.484
$[L] \times 10^3$	42.47	50.11	62.35	76.35	87.66
$\bar{n}$	1.386	1.513	1.620	1.788	1.828
$\frac{X-1}{[L]} \times 10^{-2}$	1.601	1.761	2.001	2.428	1.751

RUN II: $C_M = 3.315 \times 10^{-2}M$; $C_L^o = 0.301M$.
$v_o = 100.0$ ml; $E = 0.100M$; $N = 2.00M$.

$[L] \times 10^3$	5.687	8.182	10.56	13.64	19.65	
$\bar{n}/[L]$	66.44	61.25	56.50	52.41	46.22	
$\frac{X-1}{[L]} \times 10^{-2}$	0.9276	0.9676	1.027	1.086	1.188	
$[L] \times 10^3$	24.83	29.56	36.44	45.22	54.31	67.11
$\bar{n}/[L]$	42.53	39.45	36.38	31.95	28.77	25.01
$\frac{X-1}{[L]} \times 10^{-2}$	1.288	1.370	1.487	1.709	1.905	2.251
$[L] \times 10^3$	78.72	83.91	95.76	102.8	112.4	
$\bar{n}/[L]$	21.85	20.44	18.67	17.21	15.94	
$\frac{X-1}{[L]} \times 10^{-2}$	2.542	2.649	2.958	3.238	3.589	

X is defined in Chapter I. For other notations see the text of this Chapter.

A carbonyl group has the same but less effect in enhancing complex formation. The alaninate system, on the other hand, is different in its behaviour at pH 3.60 from other substituted fatty acids. If it is accepted that the ligand at pH 3.60 is $CH_3CH(NH_3^+)COO^-$, then not only is this a monodentate ligand like propionate, but in addition there may be electrostatic repulsion between the europium(III) or americium(III) cation and the substituted ammonium ion of the ligand. This may largely account qualitatively for the weakness of the interaction as determined by the free energy change.

Additionally it is observed that propionate, lactate and alaninate complexes are stronger than those of the homologous acetate, glycolate and glycinate complexes showing that the methyl group plays a part in enhancing complexation.

The main factor, affecting the relative stability of the europium and americium complexes investigated here, are the ionic radius and the properties of the outer electron shells. If the radius factor is the more important one, then europium with its smaller ionic radius is expected to form stronger complexes than americium. (This is shown by inorganic ligands with a few exceptions).

This was not the case for the systems in the present investigation. As to the properties of the outer electron shell, both elements have the same structure apart from a difference of one unit in the principle quantum number. The

5f orbitals are more affected by the environment than the 4f orbitals, which means that the former are more available for bond formation[16]. Americium is thus expected to form stronger complexes than europium, if the properties of the outer electron shells are more important than the radius factor. This seems to be the case for the systems in the present investigation.

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CHAPTER VII

Summary and General Discussion of the Work

From the studies reported in previous chapters it is apparent that the partition of trivalent rare earths, actinides, scandium and indium into a toluene solution of HDEHP (abbreviated further to H_2D_2) from an aqueous phase containing oxalate, sulphate, lactate, alaninate and pyruvate takes place through the extraction of $M(HD_2)_3$ over the range of ligand studied. When fluoride $[F^-] = (0.1 - 4.0)10^{-3}M$ is present in the aqueous phase MF_3 in addition to M^{3+} partitions into HDEHP when distributions were made with yttrium, trivalent lanthanides (Ln) and actinides (An). This was not found to be so for scandium and indium over the same fluoride range where only $M(HD_2)_3$ is the extracting species in the solution. From a more detailed study of yttrium, it is proposed that $MF_3.3H_xD_x$ is partitioning into HDEHP in addition to $M(HD_2)_3$. From the published data[1] and potentiometric measurements to check them in the course of the present work equilibrium constants for yttrium were used to set up a model for the extraction. From the model values for β_1, β_2 and β_3 can be computed from the partition data without reference to independent β measurements.

Values for the equilibrium constants obtained from the partition methods have been discussed in previous chapters in relation to other published values. The collected results for all the systems from the present measurements are reported in Table 7.1.

It has been shown[2] that when log K_m from the following equilibria

$$MF_{m-1}^{n-(p-1)} + F^- \overset{K_m}{\rightleftharpoons} MF_m^{n-p}$$

is plotted against m for systems where M^{n+} is scandium, iron(III), zirconium, hafnium, beryllium, aluminium, gallium and indium, straight line plots having slopes near unity are obtained. This is not observed for the fluoride complexes of yttrium, lanthanide(III) and actinide(III) ions studied in the present work; straight lines are not obtained. The slope obtained by joining values for m = 1 and m = 2 are 0.20 (La), 0.22 (Ac), 0.68 (Y), 0.34 (Ce), 0.32 (Eu), 0.18 (Gd), 0.67 (Am) and 0.51 (Cm). The small differences between K_1 and K_2 (where $K_1 = \beta_1$ and $K_1K_2 = \beta_2$) for lanthanum, europium, gadolinium and actinium could be attributed to a slow steric hindrance to coordination of a fluoride ion to the monofluoro aquo cation when compared with the corresponding scandium and yttrium systems. For americium and curium the differences are larger and the reason may lie in greater f electron influence in the bonding of ligands in the aquo and/or mixed fluoro aquo complexes.

TABLE 7.1

Collected equilibrium constants

Metal ion	Ligand	Ionic strength	log K_1	log K_2	log K_3
La^{3+}	F^-	0.5	2.69	2.49	2.60
	SO_4''	0.5	1.77	0.89	-
	C_2O_4''	0.5	4.47	3.54	-
Ce^{3+}	F^-	0.5	3.15	2.81	-
Eu^{3+}	F^-	0.5	3.40	3.08	-
	SO_4''	0.5	1.88	0.90	-
	Propionate	2.0	1.93	1.30	0.61
	Lactate	2.0	2.48	2.08	1.27
	Alaninate	2.0	0.72	-	-
	Pyruvate	2.0	1.97	1.34	0.47
Gd^{3+}	F^-	0.5	3.43	3.25	-
Ac^{3+}	F^-	0.5	2.72	2.50	2.68
	SO_4''	0.5	1.75	0.89	-
	C_2O_4''	0.5	4.47	3.53	-
Am^{3+}	F^-	0.5	3.39	2.72	2.89
	SO_4''	0.5	1.85	0.99	-
	C_2O_4''	0.5	4.82	3.78	-
	Lactate	2.0	2.52	2.24	-
	Alaninate	2.0	0.75	-	-
	Pyruvate	2.0	2.03	1.31	0.53
Cm^{3+}	F^-	0.5	3.34	2.83	2.90
	SO_4''	0.5	1.87	0.89	-
	C_2O_4''	0.5	4.80	3.82	-
Y^{3+}	F^-	0.5	3.91	3.23	3.16
Sc^{3+}	F^-	0.5	6.17	5.27	4.02
In^{3+}	F^-	1.0	3.67	2.58	2.34
	SO_4''	1.0	1.76	0.73	-
Fe^{3+}	F^-	0.5	5.18	3.93	2.94

It is seen from Table 7.1 that K_3 for fluoro complexes is usually equal to or greater than K_2 for these fluoride systems. This has been discussed by Paul et al[1] with reference to yttrium. On the basis of x-ray diffraction studies of YF_3[3] and $Y(OH)_3$[4] the metal ion has a coordination number of 9. The radius ratio Y^{3+} to F^- is 0.7, i.e. near the minimum[5] for a coordination of 9. Their argument is that when water molecules surround the yttrium ions, the coordination sphere becomes somewhat 'crowded' and hence replacement of water molecules by the smaller fluoride ions should relieve the strain and enhance the stability of the fluoride complexes. For yttrium ion and also for trivalent lanthanides and actinides this apparently does not occur until some water molecules have been replaced from the hydration sphere. However, there is no experimental evidence to support this argument and it will therefore not be taken further.

The proposed correlation[2] does not appear to hold for other ligands[6,7] for which widely differing values for the slopes are obtained. For sulphate and oxalate ligands however, the slope of unity is observed for all the systems studied. It is clear that the correlation cannot, however, be taken without qualification as a measure of the reliability of experimentally derived equilibrium constants or as a convenient method for estimating constants in the absence of experimental data. Careful measurement of enthalpy and entropy changes for these systems might provide information as to the origins of these differences in behaviour.

A comparison of the ratios K_1/K_2 as set out in Table 7.2 reveals that La < Eu > Gd and Ac < Am > Cm except for the sulphate systems of the actinides. Reasons for this trend remain obscure; the free energies of formation of the complex

$$ML^{3-p} + L^{-p} \longrightarrow ML_2^{3-2p}$$

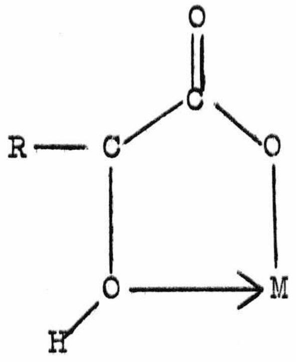
is lower for europium and americium than the corresponding quantities for the succeeding member in each series of elements. It does however seem to fit in with the view[8] that a break occurs at gadolinium and curium in plots of K_1/K_2 against atomic number for each series. Values are high numerically (6.5 - 11) for oxalate and sulphate complexes, but low (1.5 - 2, except for americium and curium) for the fluorides. Such values vary considerably when calculated for other ligands[6,7] attached to these metal ions. The ratios quoted for sulphate when applied to the Bjerrum[9] statistical model for stepwise stability constant ratios which was further discussed in detail by Manning[8] would suggest a mixture of inner and outer sphere ion-pairing as has been advocated by De Carvalho and Choppin[10] on the strength of other thermodynamic evidence.

TABLE 7.2

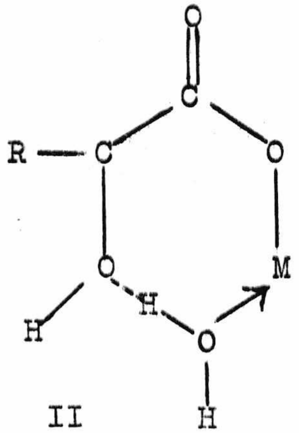
The ratio K_1/K_2 for lanthanides and actinides at ionic strength 0.5 and 25°C

Metal ion	K_1/K_2		
	F^-	$SO_4^{=}$	$C_2O_4^{=}$
La^{3+}	1.6	8.5	7.7
Eu^{3+}	2.0	11	9.6[15]
Gd^{3+}	1.5	7.4[15]	6.5[15]
Ac^{3+}	1.7	8.8	7.3
Am^{3+}	4.7	11	7.3
Cm^{3+}	3.3	9.5	9.4

The interaction of oxalate and lactate with these metal ions is considered[11,12] to occur through chelate formation because of the high stability of the metal complexes. The chelate can be formed in two different ways, (i) water may be replaced and a metal oxygen bond formed between the metal ion and the carboxylate or hydroxyl groups on the ligand (see I) or (ii) the bond may be formed through the oxygen of a water molecule of solvation and a hydrogen of the same molecule forming a hydrogen bond to the hydroxyl group of the ligand (see II).



I



II

The carboxylate group is presumably bonded in the same way in both I and II and furthermore in the same way as, say, in propionate. The changes in enthalpy and entropy terms are expected to be different for these two possible mechanisms. The entropy term is mainly influenced by the release of water from the hydration sphere of the central ion while the corresponding enthalpy change is determined by the difference in bond energies between coordinated water and the ligand. There is no existing thermodynamic data on the oxalates of the rare earths and actinides, but such data does exist for the bidentate lactate ligand[13].

TABLE 7.3

Europium systems[13] at $\mu = 2.000$

Ligand	ΔH_1	ΔS_1
Lactate	-1.94	5.1
α-hydroxy-isobutyrate	-1.51	7.5
Glycolate	-0.84	8.1

With these models in mind it is tempting to interpret the small ΔS_1 and large $-\Delta H_1$ values for lactate and similar chelate forming bidentate ligands as arising from the mechanism II above.

The argument proposed by Manning[8] to differentiate between inner and outer sphere ion-pairs on the basis of K_1/K_2 would thus appear to be an over-simplification probably because it ignores specific electronic interactions between the metal ion and the ligand.

The ratios for K_1 values for the lanthanide-actinide pairs set out in Table 7.4 are also of interest. It is seen that values vary from -7% to +10% from unity with a preponderance of values above unity. The ratios of the ionic crystal radii[14] for the lanthanide(III) to

TABLE 7.4

Ratios for K_1 values for lanthanide (Ln) - actinide (An) pairs at ionic strength 0.5 and 25°C

$K_1(Ln)/K_1(An)$	F^-	SO_4''	C_2O_4''
La/Ac	0.94	1.06	0.99
Eu/Am	1.01	1.09	1.11
Gd/Cm	1.09	1.09	0.93

actinide(III) pairs of ions are all close to 0.96. On an electrostatic 'hard sphere' model for ion pair interaction (with a common ligand) the small departure of this last mentioned ratio from unity would have an even smaller effect on the $K_1(Ln)/K_1(An)$ values. (The exact size of the effect would depend on the effective radii of the anions and cations.) The errors in the numerical values for $K_1(Ln)/K_1(An)$ will of course depend on the absolute errors associated with each K_1 value; these are probably not less than 5% so that an error in the ratio of around 10% is possible. The K_1 data are therefore not sufficiently accurate to enable definite conclusions to be drawn concerning possible ligand field effects in americium and curium complexes relative to europium and gadolinium respectively. However, the preponderance (5 out of 6) of values for $K_1(Ln)/K_1(An)$ above unity could be taken as qualitative evidence for some, perhaps slight, ligand field stabilisation in the pure aquo complexes of the actinide relative to the corresponding lanthanide. In addition to sufficient data on enthalpy and entropy changes for all the systems, perhaps greater overall accuracy (as opposed to precision) is required for $K_1(La)/K_1(Ac)$. Since ligand field stabilisation is not possible here for complexes of either cation the ratio can serve as a reference for comparison with others.

Ion-exchange of complex cations

The cation-exchange partition data shows that positively charged fluoro and sulphato metal cations exchange with the resin cations whereas there is no evidence for this occurring with oxalato complexes. The distribution coefficients, l_0, for free aquated metal ion and l_m, for partially complex aquated metal ion, for all the metal ions studied are summarised in Table 7.5 and Chapters III and IV.

Several factors[16] probably contribute to the observed changes; among these the effective size and the charge on the ion are undoubtedly of most importance. Fluoride is presumably a small ligand compared with the water molecule(s) it displaces on complex formation. Therefore the value of l_2 is larger than l_1 on the basis of effective size reduction although there is one charge unit less on MF_2^+ in comparison with MF^{2+}. It seems that size effect plays a bigger part on partition into the cation-exchanger probably on the grounds that less work (swelling energy) is required to be done against the resin structure in order to accommodate the smaller cation in that phase. This could be taken as evidence for the displacement of more water from the aquated metal ion on formation of MF_2^+ than on formation of MF^{2+}; hence the value of entropy measurement.

TABLE 7.5

Collected ion-exchange results at ionic strength $\mu = 0.5$ and 25°C

Metal ion	Ligand	l_0	l_1	l_2	l_0/l_1	l_0/l_2
La^{3+}	F^-	6783	622	6300	11	1
Y^{3+}	F^-	3270	297	715	11	5
Am^{3+}	F^-	5270	900	2306	6	2
	SO_4''	5480	101	-	54	-
Cm^{3+}	F^-	3245	617	1622	5	2
	SO_4''	3245	153	-	21	-
Eu^{3+}	F^-	5625	1000	-	6	-
	SO_4''	5625	65	-	87	-
Gd^{3+}	F^-	5145	1184	-	4^*	-
	SO_4''	4616	130	-	36^{15}	-
Sc^{3+}	F^-	2729	186	-	15	-
In^{3+}	F^- $\mu(1.0)$	365	31	-	12	-
	SO_4'' $\mu(1.0)$	365	12	-	29	-

*l_1 was calculated using β values obtained by a potentiometric method (Chapter II) whereas for the rest of the systems it was calculated from β values obtained by the liquid-liquid extraction method.

Comparison of the l_0/l_1 ratios for sulphato metal cations with those for the corresponding fluoro cations would suggest that the sulphato complex cation was appreciably larger, i.e. a larger ligand and less water released than for fluoro complex formation. That the difference in charges is not so important is supported by the low l_0/l_2 ratios observed for the fluoro complexes since MF^{+}_{2aq} and MSO^{+}_{4aq} carry the same charges.

The ion-exchange behaviour of these metal ions in the presence of fluoride can also be partly explained by regarding the ion-exchanger as a Donnan membrane system[16]. 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 electrolyte 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 8-10 percent cross-linking may be expected to have an internal counter ion concentration in the region of 6M, under the conditions whereby most equilibrium studies are carried out, free anionic ligand will be at a considerably lower concentration within the resin than without. Thus, for such ligands the expectation is that the distribution of complexes containing progressively higher ratios of ligand to metal will be less favoured since the necessary free ligand concentration does not exist within the resin phase to prevent the dissociation of such higher complexes.

The ratio l_0/l_1 for the europium-gadolinium and americium-curium pairs with sulphate show a similar trend in that the value for the second member of each pair is about half of that for the first. This trend is roughly maintained for fluoride although a comparison here requires caution since the lanthanide data are not too certain. It may again be a pointer to coordination changes in going from europium to gadolinium and from americium to curium. It is difficult to draw any other conclusions as to structural factors in relation to the other observed ratios. Perhaps if more data could be accumulated further correlations with other properties and ideas about the bonding and stereochemistry of the complex ions involved would become more obvious.

Potentiometric measurement of fluoride and stability constants for metal-fluoride systems

The membrane electrode used in the measurement of metal-fluoride ion association constants is very convenient for the measurement of free fluoride; it is, however, less sensitive than the iron(III)-iron(II) electrode and so is of more limited application in the measurement of equilibrium constants. For potentiometric studies leading to the calculation of reliable values for such constants, $[F^-]_f$ needs to be at least 10^{-6}M so that reasonably useful measurements will be restricted to metal ion systems where β_1 is about 10^6 M^{-1} or less. Thus, satisfactory values were not obtained for thorium, for which $\beta_1 = 3.6 \times 10^7$ (Dodgen and Rollefson[17]).

The insolubility of metal fluorides also tends to restrict the range of the $[F^-]_t$ to $[M]_t$ ratio accessible to study in a homogeneous aqueous solution. Conditions need to be chosen so that competition between lanthanum ion from dissolution of the membrane crystal and the metal ion being studied can be neglected. Likewise, for measurement of formal fluoride in water samples, fluoride bound to metal ions (calcium, magnesium, iron, etc.) is released by addition of EDTA and other ligands. Care could be needed particularly at low $[F^-]_t$ because of the possible solubilising effect of the ligand, particularly EDTA, on the lanthanum fluoride membrane.

Conclusions

Though a considerable effort has been made to obtain an understanding of the mechanism of extraction of trivalent rare earths and actinides into HDEHP in order to obtain equilibrium constants for fluoro complex formation, there is still insufficient reliable equilibrium data for these systems. If proper conditions are chosen, a careful study of the type reported in this thesis will certainly lead to more reliable data than hitherto available for all these metal fluoride systems. Reliable equilibrium data for fluoro complexes can then be used to get an understanding of the partition of metal fluorides into the resin. This may then assist in providing new separations of members of the lanthanide and actinide series from each other.

More detailed knowledge of thermodynamic parameters which play an important part in the insight of the interaction of a ligand with a metal ion in solution should be of assistance. Such data particularly for fluoride and oxalate is sparse.

Though a successful study of the determination of equilibrium constants for mononuclear indium species formed on hydrolysis of In^{3+}_{aq} has been made by partition methods as reported earlier, similar studies for trivalent rare earths and actinides await an extractant and ion-exchanger which is free from the limitations mentioned in Chapter V.

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