Tracer studies in the solution chemistry of heavy elements

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A. R. Sami

'TRACER STUDIES IN THE SOLUTION-CHEMISTRY OF HEAVY ELEMENTS'

THESIS

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MEMORANDUM

The work reported in this thesis was carried out at the Londonderry Laboratory for Radio-Chemistry, University of Durham between October, 1961 and September, 1964, under the supervision of Dr. S. J. Lyle, lecturer in Radiochemistry.

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. Where use has been made of the results and conclusions of other workers in relevant studies, care has been taken to ensure that the source of information is clearly indicated, unless it is of such a general nature that indication of source is impracticable.

a . R . Sari

ABSTRACT

Sorption of yttrium, lanthanum and cerium (III) ions on Zeo-Karb 225 (SRC 15) and De-acidite FF from perchlorate media has been studied at 25°C and a tracer concentration of the ions concerned. It has been found that the sorption of these ions on the resins in question follows nearly an identical pattern, and that the changes of the hydrogen-ion concentration in the pH range of 2.5-4 have only a very slight effect on the values of the distribution co-efficients. Taking yttrium-glycollate as a representative for the systems involving glycollate or other ligands and the trivalent rare-earth ions and those from the actinium series using yttrium-91 as a tracer and a perchlorate medium of μ = 0.50M, the effect of the cross-linking of a resin on the β_n values of the system in question has been studied and found to be negligible for the 2%, 4-5%, and 8% DVB resins provided the necessary corrections due to swelling of the resins are duly taken into account. An investigation of the same system with Zeo-Karb 225 (SRC 15) at different $^{V}/m$ ratios in the range of $^{15}/0.20$ and $^{15}/0.60$ has revealed that subject to the appropriate corrections due to swelling of the resin having been made, such changes of the $^{V}/m$ ratio have no significant effect on the β_n values of the system concerned. It has been further observed that a

treatment of a complexing solution with resins of different cross-linking practically entails no significant loss of the ligand species (glycollate) from the complexing solution.

Having made the above investigations of the resin/solution behaviour in perchlorate media at 25°C, the method (cation-exchange) was adopted for a tracer study of the systems involving yttrium, lanthanum, cerium (III), europium (III), actinium and americium (III) ions and chloride, fluoride, sulphate, oxalate, α-hydroxyisobutyrate and glycollate ligands. The step-stability constants have been computed by a graphic method based on a theory proposed by Fronaeus [78, 102]. The results obtained are generally in good agreement with those reported by other workers as a result of their investigation of the systems in question by ion-exchange, solvent-extraction, pH or potentiometric methods under comparable conditions, and have further shown the dependence of the chemistry of the concerned ions on the sizes of their respective crystal ionic-radii. The ratios of the β_I values for the lanthanum/actinium and europium (III)/americium (III) systems involving sulphate, oxalate and α-hydroxyisobutyrate ligands have been worked out and found to be in general near unity: this is an evidence in support of similar interactions between the metal ions of both the lanthanum and actinium series and the noted ligands in aqueous systems.

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CHAPTER I

INTRODUCTION

General

Our current ideas about the properties and behaviour of electrolytes are largely based on the experimental and theoretical work carried out during the last hundred and thirty years or so. A number of the experimental methods used by earlier workers are still in vogue though occasionally modified through the introduction of various refinements in instrumentation, technique and theory. A brief survey of the most significant contributions to our existing knowledge in this field is, therefore, pertinent.

A convenient starting point for this is provided by the formulation of the laws of electrolysis by Faraday (1833)[1]. Both he and Daniell assumed that electrolysis consists of the transport of electricity by charged particles, that is, ions, which are discharged at the electrodes. The first suggestion that ions are produced by the simple act of dissolving an electrolyte in water can be attributed to Clausius (1857)[2], who also envisaged a form of dynamic equilibrium between free ions produced by bond disruption and the unbroken molecules of the solute.

Arrhenius (1883)[3] propounded a more comprehensive theory on electrolytic dissociation, based on the conducting powers of the solutions. He postulated that inorganic salts, acids and bases, being such good conductors in aqueous solution, must be largely present as free ions; while most of the organic acids and bases, being relatively poor conductors in solution, must be partially dissociated. He further suggested that where incomplete dissociation occurs, the degree of dissociation, α_c, is concentration-dependent, tending to unity as concentration tends to zero.

Shortly after Arrhenius had made his views known, van't Hoff[4] reported the results of applying the gas-laws of Boyle and Charles to dilute solutions. He found that while with non-electrolytes, osmotic pressures could be expressed by $PV = RT$, where P = Pressure; V = Volume; T = Absolute temperature, it was not so with electrolytes. With ionic solutions, osmotic pressures, elevations of boiling points and depressions of freezing points were found to be higher than values obtained from the formulae applicable to non-electrolytes. He, therefore, introduced an empirical parameter, i, so that for an electrolyte the osmotic pressure is given by $PV = i\,RT$ where

$$i = \frac{\text{Experimental value of the property.}}{\text{Value of the property expected from the ideal formula.}}$$

At first it was thought that for a specific valency type i was constant, but in fact it varies slightly with concentration.

Combining his conductance data with van't Hoff's findings, Arrhenius tried to calculate the degrees of dissociation of electrolytes, assuming that at infinite dilution $\alpha_c = \Lambda/\Lambda_0$, where α_c = degree of dissociation; Λ = equivalent conductance; Λ_0 = conductance at infinite dilution.

The introduction of the 'law of mass-action' by Guldberg and

Waage(1864-79)[5] (also independently by van't Hoff, 1877[4]) provided the basis for a quantitative treatment of chemical equilibria. Ostwald[6] in 1889, making use of the Arrhenius theory and the law of mass-action, calculated the first dissociation constants, K^*, of 216 carboxylic acids. However subsequent failure to obtain a constant K'[7] value for Potassium Chloride was throught to be an anomaly of strong electrolytes. Jahn (1900)[8] proposed that for strong electrolytes $\alpha_c = \Lambda / \Lambda_o$ is not valid, because of the concentration-dependence of α_c. This contradicted the Arrhenius theory which assumed complete dissociation of strong electrolytes at all concentrations. Jahn sought to overcome this difficulty by the introduction of the concept of 'interionic forces of attraction and repulsion' which cause ionic mobilities (and hence β values(and also α_c) to be concentration-dependent. Noyes et al[9, 10] from their measurements of transport numbers also confirmed the concentration-dependence of ionic mobilities.

The extension of the concept of 'interionic forces' to the application of the 'law of mass-action' to ionic equilibria led Jahn[8] to introduce yet another concept viz., 'ionic activities'. Jahn argued that the interionic forces by restricting the free and random movement of ions in solution must render some of them ineffective as 'active masses', so that in the end it is not the total stoichiometric concentration but only a fraction of it (called the activity) which is available for taking part in the reaction. The activity of any ion in solution is expressed as:

$$a_i = \gamma_i \; c_i \quad , \text{ where}$$

a_i = activity of the ion; γ_i = activity co-efficient, and c_i = concentration (stoichiometric) of the ions in terms of molality i.e., moles per kilogramme of the solvent. If c_i is expressed in terms of molarity, i.e., moles per litre of the solution

$$a_i = y_i \; c_i \quad , \text{ where}$$

y_i = activity co-efficient (when concentration is expressed as a molarity).

The physical impossibility of having solutions containing only cations or anions, led to the idea of 'mean activities' of ions. Thus for, say, a 1:2 electrolyte, the mean molal activity co-efficient, $\gamma_{\pm}$, is related to the individual ionic values as:

$$\gamma_{\pm}^{3} = \gamma_i \, \gamma_j^{2}$$

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

Lewis and Randall (1900-20)[11], by making use of thermodynamic principles in particular the theorems of Gibbs[12], evolved more precise definitions of activities and also the methods for determining them from experimental data. In 1921[11], they introduced the concept of 'ionic strength' which is the measure of the total electrical field obtaining in ionic solutions containing several electrolytes. This, according to the authors, should determine the activity co-efficient of any particular ion in the solution. The 'ionic strength', I (or μ) is given by the expression:

$$I = 0{\cdot}5 \sum m_i z_i^2$$, where

m_i = molality of the ion.

z_i = charge of the ion.

$\sum$ = summation for all different ions.

The rule assumes complete dissociation of all the electrolytes.

The activity co-efficients can be obtained from experimental data, for example from measurements of the electromotive force (e.m.f.) of cells, freezing and boiling point determinations, vapour pressures, solubilities, rates of ionic reactions, and phase distribution studies. Another important contribution which accounts for all the significant factors is the theoretical treatment of electrolytic dissociation by Debye and Huckel[13-14] and its refinement by Onsager and Fuoss[15, 16, 17, 18, 19], to give the equation:

$$\log f_{\pm} = A\left[z_i z_j\right]\left\{ I/\left(1 + B\acute{a}\sqrt{I}\right) - Q\,(I)\right\} \qquad (1)$$

It is applicable over a wide range of ionic strength. A, B, and Q are empirical parameters, equal respectively to the products of several physical constants; a is the average cation-anion radius and z_i and $z_{\textcircled{i}\,j}$ the ionic valencies.

There are many different ways of studying electrolytic dissociation. One approach is to determine the true or thermodynamic dissociation constants for equilibria of the type:

$$ML \rightleftharpoons M^+ + L^-$$

K_c, the thermodynamic dissociation constant is given by:

$$K_c = \frac{a_m \; a_L}{a \; mL}$$

$$= \frac{[M] \; y_{\pm}^2}{[ML] \; y_{ML}} = \frac{\alpha_c^2 \, c \; y_{\pm}^2}{(1-\alpha_c) \; y_{ML}}$$

To establish K_c, methods are required to find α_c or the ratio $\alpha_c^2 \, c/(1 - \alpha_c)$, the activity co-efficients are then calculated using equation (1) if I is known. So far only the conductance method has been mentioned, the proper treatment of which is based on the equations of Onsager[15, 16, 17] and Onsager and Fuoss[18, 19]. Another approach is to study the number of stages of ion-association (or complex formation). This is, of course, the inverse of dissociation. The contemporary treatment owes much to the work of Niels Bjerrum[20, 21], on Chromium (111) - complexes with thiocynate. Following N. Bjerrum's work, although a number of experimental and computational techniques had been developed for the determination of stability constants between 1920-40, only comparatively few studies were made on systems containing several complex species. According to Rossotti and Rossotti some of the best work of this type concerns polybasic acids[22-26]. Other notable contributions are due to Møller[27]; Bates and Vosburgh[28] and Riley et. al.[29-32]

The impulse to further work was provided in 1941, when general methods for computing step stability constants from the experimental functions $\bar{n}$ (a) (= average number of ligands/central group) and α_0(a) (= $\frac{\text{free ligand concentration}}{\text{Total ligand concentration}}$), were described by J. Bjerrum[33] and Leden[34] respectively.

Many of the experimental techniques employed since 1941 (e.g. Potentiometry; conductivity; catalysis; liquid-liquid partition and solubility) are fundamentally the same as those used by earlier workers at the beginning of the century. Some of the more recent methods like spectrophotometry, polarography and ion-exchange combined with more refined methods of computing stability constants from experimental data have proved of great value to the chemists engaged in the study of chemical equilibria in solution.

As pointed out earlier, the activity of an ion is largely determined by the total ionic strength of a solution[11, 13, 14, 15, 16, 17, 18, 19]. It follows that at constant ionic strength, the activity of any particular ion will be constant. Thus in the study of equilibria if a high and constant ionic strength is maintained by the use of a back-ground electrolyte, it should be possible to control the activity of one of the reacting species over a large concentration range, and the assumption that its activity over that range is constant will be reasonably valid. Equilibrium constants can, therefore, be derived in terms of concentration rather than activities. This is a useful simplification. The earliest published report on the use of a constant ionic medium in the study of chemical equilibria involving association of ions is due to Grossman (1901)[88]. Biedermann and Sillen[35] have published an historical survey of the subject.

The limitations of the use of medium of constant ionic strength in the investigation of step equilibria are as follows:

(1) No information can be obtained about the complexes formed between the reacting species and the ions present in the medium.

(2) In dilute solutions, no distinction can be made between the solvated species containing different numbers of solvent molecules.

(3) Sillen[36] has pointed out that complications may arise if one of the ions of the medium can be converted to one of the reacting species by the addition or loss of a proton, e.g. in the study of the Hg^{2+} - NH_3 system in ammonium nitrate by the method of pH measurements, it might not be possible to distinguish between ammine (NH_3) and amide (NH_2^-) complexes on the one hand and ammine and hydroxyl ($\overset{-}{OH}$) complexes on the other.

(4) That the effect of complex formation on certain physical properties of the solution may almost be swamped by the effect of the presence of the background salt. If so, the change in the measured property attributable to complex formation is very small and therefore interpretation of the measurement is rendered difficul or impossible[37].

(5) The method is not applicable to the studies of chemical equilibria based on measurements of conductivities of solutions[37].

In the choice of the bulk electrolyte, the following points must be borne in mind:

(1) That in a given solvent, it is sufficiently soluble to give the required concentration.

(2) That it does not contribute to the measured physical property.

(3) That it does not complex with the species under investigation. Sodium and ammonium perchlorates meet the above requirements fairly well and are commonly used as bulk electrolytes in equilibrium studies.

Significance of Stability Constants

The stability constant is the measure of the degree of association which occurs in a solution containing two or more component species in equilibrium. Step stability constants are denoted by the symbol βn, where $n = 1, 2, 3 \ldots\ldots n$.

For a reaction of the type

$$M + nL \rightleftharpoons ML_n$$

βn (the overall stability constant) is given by $\beta_n = [ML_n] / [M][L]^n$ and is related to the equilibrium constants for the step equilibria, viz. k_1, k_2, k_3 etc. by the expression:

$$\beta_n = k_1 \times k_2 \times k_3 \cdots \times k_n$$

The step equilibria involved in a reaction of the above type are:

$$M^{n+} + L^{-} \rightleftharpoons ML^{(n-1)+}$$

$$ML^{(n-1)+} + L^{-} \rightleftharpoons ML_2^{(n-2)+}$$

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

$$ML^{+}_{n-1} + L^{-} \rightleftharpoons ML_n$$

so that

$$k_1 = \frac{[ML^{(n-1)+}]}{[M^{n+}][L^{-}]} ,$$

$$k_2 = \frac{[ML_2^{(n-2)+}]}{[ML^{(n-1)+}][L^{-}]}$$

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

$$k_n = \frac{[ML_n]}{[ML^{+}_{n-1}][L^{-}]} .$$

Now the fact that the stability constant βn is found to be appreciably greater than zero is perhaps one of the most convincing pieces of evidence for the existence of the complex MLn in solution. Moreover, if all the stability constants for a given system are known, it is possible, in principle, to calculate the equilibrium concentration or activity of each of the species present under a known set of experimental conditions. Such an exact knowledge of the composition of the solution is desirable for a correct interpretation of its optical and kinetic properties, of its partition equilibria and of its biological behaviour. The values of the stability constants can also be used to predict the conditions for complete or maximal formation of a given complex. Reliable information of this type may be of great importance in planning analytical and separative procedures, e.g., in cases where the species in question is highly coloured or can be precipitated from solution, extracted into organic solvent or sorbed on an ion-exchanger or a chromatographic column.

Moreover the equilibrium constant K. for any reaction is related to the corresponding free-energy change by the expression:

$$- RT \ln K = \Delta G = \Delta H - T\Delta S$$

where ΔG, ΔH and ΔS represent the changes of free energy, enthalpy and entropy in that order in a hypothetical unit-concentration scale as the corresponding equilibrium constant K. The step stability constants, therefore, give a measure of the value of ΔG associated with the reactions:

$M + nL \rightleftharpoons ML_n$. (overall reactions)

and $M_{n-1} + L \rightleftharpoons ML_m$. (step reactions)

The corresponding changes of entropy of complex formation may be obtained by combining the stability constant with the enthalpy change of the complex formation which is best measured calorimetrically; but may also be obtained by determining the stability constant at a series of temperatures. Analysis of β_n and K_n into their component heat and entropy terms is essential to the further understanding of many factors viz., size, shape, and electronic structure of the central group and the ligand; and also the temperature and the composition of the solvent which influences

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the stability of the complex[38].

Partition methods with particular reference to ion-exchangers for the study of chemical equilibria

Partition methods for studying chemical equilibria are based on the distribution of one of the reacting species in solutions at equilibrium between two phases. By maintaining the necessary conditions of equilibrium and changing the concentration of one of the reacting species, the distributions of the particular species between the two phases are studied and the information obtained is made use of in the computation of the stability constants. Liquid-Liquid partitioning or solvent extraction, solubility and ion-exchange methods are all included in this category.

Solvent extraction:

The use of this method for the study of chemical equilibria was first suggested by Nernst[88], and it was applied for the investigation of a number of chemical equilibria involving metal ions and organic acids[89, 90, 91] as early as the turn of the present century. The very successful application of this technique to the extraction and purification of fission-products, rare-earth and actinide elements along with a wide range of other inorganic substances in the last two decades, encouraged its further application to the study of the solution chemistry of these elements. According to Irving, Rossotti and Williams[92, 93, 94], the extraction of electrolytes into organic solvents can be classified as follows:

(1) those due to the formation of inner complexes of metals with reagents such as dithizone and acetylacetone.

(2) those due to the formation of metal acido-complexes such as the well-known extraction of $FeCl_3$ by ether from aqueous HCl as $HFeCl_4$.

(3) those due to the association of salts or ion-pairs containing large anions or cations e.g., tetraphenyl arsonium perrhenate and Ferrous tris 1:10 phenanthroline with long chain alkyl sulphates or sulphonates.

Thenoyltrifluoroacetone and alkyl- or aryl-substituted phosphoric acids are also being used for solvent extraction studies of chemical equilibria. A number of extensive reviews[95, 96, 97] have appeared in recent years on this subject. The principles involved in the study of the chemical equilibria by this technique are the same as in an ion-exchange method.

Solubility Method:

The derivation of quantitative information about association equilibria from measurements of solubilities of sparingly soluble solids in aqueous solutions containing complexing agents has been in practice for a long time. Molecular complexes of picric acid were studied by this method at the end of the last century[98, 99]. The use of a medium of constant ionic strength for controlling the activity co-efficients of various species in solution in the study of the association equilibria by this method was introduced by Edmonds and Birnbaum[100].

Ion-exchange Method:

The first reports of the use of ion-exchangers for the investigation of complex ions were published in 1902 by Guenther-Schulze[39, 40]. Using an inorganic zeolite, he studied the Cl^--complexes of some divalent cations. He assumed that the presence of Cl^- ions on the exchanger was due to the sorption of MCl^+. The discovery of organic exchangers in 1935 by Adam and Holmes[41] stimulated further interest in the use of the ion-exchangers, due particularly to their greater stability in acid media. Samuelson[42] in 1946, carried out similar experiments as Guenther-Schulze using an organic cation-exchanger and established that the presence of chlorine on zeolite was due to adsorption of the chloride and not on account of the exchange of ML^+ species as suggested by Guenther-Schulze. The work of Guenther-Schulze[39,40] led Gustavson[43-51] to investigate complexes of chromium using inorganic and organic exchangers over the period 1924-46. He also suggested the use of anion-exchangers for examination of the aqueous phase.

Samuelson[52-54] used anion-exchangers in studies of the structure of Graham's salt. He also employed a cation-exchanger to determine the composition and stability of the metaphosphato-ferrate complex. Further studies on chromium (III) -complexes, involving organic acidshaving been made[56-58], eventually led to the determination of the compositions and stabilities of the alkaline-earths (including Radium) complexes with various organic acids[59-65]. The use of radioactive tracers or very low metal concentrations simplifies experimental technique as well as formulation of necessary equations for calculation of stability constants. Investigations along this line were begun in 1944[55]. The technique which is now well established has been extensively used for the investigation of the complexes of the rare-earths and transuranic elements with a host of organic and inorganic ligands[66-73]. Anion exchangers have also been used particularly to deduce information regarding anion-complexes resulting from the interaction of Zirconium, Niobium, Palladium and Iron etc. and the halides[74, 75, 76]. The paper of Schubert[77] dealing with the effect of temperature and ionic strength on the interaction of Strontium^{89,90} and citrate ions using Dowex 50 and Strontium^{89,90} as a tracer also includes a review of the subject up to 1950. Since then, the most outstanding contribution is the treatment of ion-exchange data for computation of successive stability constants by Fronaeus[78]. This treatment will be dealt with at an appropriate place in this text. The treatment of experimental data in general for calculating stability constants of complexes of the type ML_n, derives mostly from the contributions of Bjerrum[79], Sullivan and Hindmann[80], and Irving and Rossotti[81]. The least squares method of Rydberg[82] which dispenses with the graphic methods of computing complexity constants and allows the use of high speed digital computers is a valuable time-saving contribution.

Cation-Exchange Equilibria

Cation-exchangers are compounds of high molecular weight in ionised form with sodium, ammonium and hydrogen cations. The commercial products are usually formaldehyde or polystyrene resins which contain phenolic, sulphonic or carboxylic acids groups either in the acidic (H^+-form) or salt form (e.g. Na^+-form). They are insoluble in water and organic solvents. When equilibrated with a solution containing metal ions or other cations e.g. ML_n^{z+}, they take part in the exchange reactions of the type:

$$zH^+_R + ML_n^{z+} \rightleftharpoons ML_n^{z+}{}_R + zH^+ \qquad (1)$$

and

$$zNa^+_R + ML_n^{z+} \rightleftharpoons ML_n^{z+}{}_R + zNa^+ \qquad (2)$$

The subscript R indicates the resin phase.

It is evident from the above equilibria that the study of the overall distribution of a central group M between the resin and the aqueous phases can give valuable information about the species present in the aqueous solution.

The partition co-efficient of the cation ML_n^{z+} ($o \leqslant n \leqslant C_+$, where C_+ is the maximum value of n for a cation complex) between an aqueous phase and the Na-form of the exchanger may be expressed in term of the equilibrium constant, Kn, for reaction (2) above as:-

$$Pn = \frac{\left[ML_n^{z+}\right]R}{\left[ML_n^{z+}\right]aq}.$$

$$= K_n \frac{\left[Na^+\right]\ R.}{\left[Na^+\right]\ aq.}$$

and should be constant if the ratio $\frac{\left[Na^+\right] R}{\left[Na^+\right] aq.}$ is constant. This condition is easily fulfilled if the aqueous solution contains a constant high concentration of Na^+ ions and the exchange is low.

Similarly, if M is likely to be hydrolysed either in the resin phase or in solution, it is essential to use the resin in the hydrogen form and a strong acid as a back-ground electrolyte[83, 86, 87]. The use of constant ionic medium as pointed out earlier will ensure that the activity co-efficients of various ions in the aqueous phase remain constant. It has been further discovered that the partition co-efficient is dependent on the load $\left[ML_n^{Z+}\right]$ R, and is reasonably constant if the load on the resin is very low. According to Fronaeus[84, 85], at low concentration, the cationic species M^{z+}, ML^{z-1} (if L is singly negatively charged) have the same effect on the activity co-efficients in the resin phase. He, therefore, recommends that quantitative information about complex formation in the aqueous phase be obtained from measurements which refer to constant and low loads on the resin. These conditions are readily fulfilled when radio-tracers are used in equilibrium studies. The chief draw-back of the ion-exchange technique for study of equilibria is that it involves computation and interpretation of $C_+ + 1$ parameters in addition to the required step stability constants. Of all the treatments suggested, that of Fronaeus[78/102] is normally employed in the more recent and refined work.

Computation of the Successive Stability Constants by the Method of Fronaeus

The overall stability constant β_n for a reaction of the type:

$$M + nL \rightleftharpoons ML_n$$

is defined as:

$$\beta n = \frac{[ML_n]}{[M][L]^n}$$

This is related to the formation constant k_n where

$$k_n = \frac{[ML_n]}{[ML_{n-I}]\ [L]}$$

by

$$\beta n = k_I \ x, \ k_2 \ x, \ \ldots\ldots\ldots \ k_n,$$

In cation-exchange study of equilibria of the above type, a known volume of a solution containing M^{z+}, L^{y-} (which is varied) and back-ground salt to maintain high and constant cationic strength, is equilibrated with a known weight of the resin in a suitable form, and the distribution co-efficient, is found.

$$\phi = \frac{C_{MR}}{C_M} \quad \text{, where}$$

C_{MR} = Concentration of metal on the resin in all its forms viz. M_R, ML_R, $ML_{2\,R}$ etc.

and C_M = Concentration of metal in the solution in all its forms viz. M, ML, ML_2

If M is a trivalent cation, and L has a single negative charge, we can write ϕ as:

$$\phi = \frac{[M^{3+}]_R + [ML^{2+}]_R + [ML_2^{+}]_R \ldots\ldots}{[M^{3+}] + [ML^{2+}] + [ML_2^{+}] + [ML_3]} \qquad (1)$$

$$\lim_{L^- \to 0} \phi = \phi_0 = l_0 = \frac{[M^{3+}]_R}{[M^{3+}]} \quad \ldots\ldots\ldots\ldots\ldots \qquad (2)$$

the value of l_0 is found experimentally, using aliquots of metal solution alone and treating them with known weights of resin.

Considering the step equilibria, viz.,

$$M^{3+} + 3\,Na\,R \rightleftharpoons M^{3+}R + 3\,Na^{+}$$

$$K_I = \frac{[M^{3+}]_R}{[M^{3+}]} = l_0 \quad \ldots\ldots\ldots\ldots\ldots \qquad (3)$$

$$ML^{2+} + 2\,Na\,R \rightleftharpoons ML^{2+}{}_R + 2\,Na^{+}$$

$$K_2 = \frac{[ML^{2+}]_R}{[ML^{2+}]} = l_I \quad \ldots\ldots\ldots\ldots\ldots \qquad (4)$$

$$ML_2^+ \; + \; Na\,R \rightleftharpoons ML_{2\,R}^+ \; + \; Na^+$$

$$K_3 = \frac{[ML_2^+]_R}{[ML_2^+]} = l_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

so that

$$[M^{3+}]_R = l_o \, [M^{3+}] ,$$

$$[ML^{2+}]_R = l_I \, [ML^{2+}], \text{ and}$$

$$[ML_2^+]_R = l_2 \, [ML_2^+]$$

substituting these values in equation (1), we have

$$\phi = \frac{l_o [M^{3+}] + l_I [ML^{2+}] + l_2 [ML_2^+]}{[M^{3+}] + [ML^{2+}] + [ML_2^+] + [ML_3]} \ldots (6)$$

Further by definition:

$$[ML^{2+}] = \beta_I [M^{3+}] [L] ,$$

$$[ML_2^+] = \beta_2 [M^{3+}] [L]^2 ,$$

and $$[ML_3] = \beta_3 [M^{3+}] [L]^3$$

So by further substitution equation (6), becomes:

$$\phi = \frac{l_o + \beta_I \; l_I \, [L] + \beta_2 \, [l_2 \, [L]^2}{I + \beta_I \, [L] + \beta_2 \, [L]^2 + \beta_3 \, [L]^3}$$

$$\phi = l_o \left\{ \frac{I + \frac{\beta_I \, l_I}{l_o} [L] + \frac{\beta_2 \, l_2}{l_o} [L]^2}{I + \beta_I [L] + \beta_2 [L]^2 + \beta_3 [L]^3} \right.$$

Let $\frac{\beta_I \, l_I}{l_o} = l_I'$; and $\frac{\beta_2 \, l_2}{l_o} = l_2'$, so that

$$\phi = l_o \left\{ \frac{I + l_I' [L] + l_2' [L]^2}{I + \beta_I [L] + \beta_2 [L]^2 + \beta_3 [L]^3} \right. \quad \ldots\ldots\ldots\ldots \quad (7)$$

From equation (7)

$$l_o \, \phi^{-I} = \frac{I + \beta_I [L] + \beta_2 [L]^2 + \beta_3 [L]^3}{I + l_I' [L] + l_2' [L]^2 + \cdots\cdots}$$

$$\text{or } l_o \, \phi^{-I} - I = \frac{\beta_I [L] + \beta_2 [L]^2 + \beta_3 [L]^3 - l_I' [L] - l_2' [L]^2}{I + l_I' [L] + l_2' [L]^2}$$

Dividing by $[L]$

$$\frac{l_o \phi^{-I} - I}{[L]} = \frac{\beta_I + \beta_2 [L] + \beta_3 [L]^2 - l_I' - l_2' [L]}{I + l_I' [L] + l_2' [L]^2}$$

$$\frac{l_o \phi^{-I} - I}{[L]} = \frac{(\beta_I - l_I') + (\beta_2 - l_2') [L] + \beta_3 [L]^2}{I + l_I' [L] + l_2' [L]^2}$$

The quantity $(l_o \phi^{-I} - I)/[L]$ is called ϕ_I. Thus

$$\phi_I = \frac{(\beta_I - l_I') + (\beta_2 - l_2')[L] + \beta_3 [L]^2}{I + l_I'[L] + l_2'[L]^2} \quad \ldots\ldots (8)$$

$$\lim_{[L]\to 0} \phi_I = \phi_I^o = (\beta_I - l_I') \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

At sufficiently low ligand concentrations, terms like $\beta_3 [L]^2$, $l_I' [L]$ and $l_2' [L]^2$ should be negligible, so that

$$\phi_I = (\beta_I - l_I') + (\beta_2 - l_2')[L] \quad \ldots\ldots\ldots\ldots\ldots (10)$$

Now a plot of ϕ_I vs. $[L]$ should approach linearity, with intercept $\beta_I - l_I' = \phi_I^o$ and slope $(= \beta_2 - l_2')$.

From the knowledge of the quantities viz., l_o, ϕ, ϕ_I^o and $[L^-]$, another function f is calculated, being:

$$f = \frac{l_o \phi^{-I} \left\{ (\beta_I - l_I')[L] - I \right\} + I}{[L^-]^2}$$

$$= \frac{\beta_I \phi_I^o + \beta_2 \phi_I^o [L] + \beta_3 \phi_I^o [L]^2 - \beta_3 [L] - (\beta_2 - l_2')}{I + l_I'[L] + l_2'[L]^2} \quad \ldots (11)$$

$$\lim_{[L^-]\to 0} f = f^o = \beta_I \phi_I^o - (\beta_2 - l_2') \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

Knowing f, fo, ϕ_I, ϕ_I^o, the following quantities are calculated

$\Delta f = f - fo$, and

$\Delta\phi_I = \phi_I - \phi_I^o$

By rearranging equations for ϕ_I and f, we have

$$\beta_I = \frac{\Delta f}{\Delta \phi I} + \beta_3 \frac{[L]}{\Delta \phi I} + \beta_4 \frac{[L]}{\Delta \phi I} - l_2' \phi_I \frac{[L]}{\Delta \phi I} \quad \ldots\ldots\ldots \quad (13)$$

on further rearranging

$$\frac{\Delta f}{[L]} = \beta_I \frac{\Delta \phi I}{[L]} - \beta_3 - \beta_4 [L] + l_2' \phi_I \quad \ldots\ldots\ldots \quad (14)$$

It is usually assumed that a plot of $\frac{\Delta f}{[L]}$ against $\frac{\Delta \phi I}{[L]}$, is linear; an assumption which is of course only valid if the terms β_3, β_4 and $l_2'\phi_1$, are negligible, the slope of the line then gives β_I. The quantities $\frac{\Delta f}{[L^-]}$ and $\frac{\Delta \phi I}{[L^-]}$ sometimes tend to be nearly constant, so that this method is no longer applicable. In such cases, following equation 13 a value of β_I, may be obtained by taking the arithmetical mean of the reliable $\frac{\Delta f}{\Delta \phi I}$ values; this assumes that in equation 13, the terms $\beta_3 \frac{[L]}{\Delta \phi I}$, $\beta_4 \frac{[L]}{\Delta \phi I}$, etc. are negligible.

Knowing β_I, the quantity $(\beta_2 - l_2')$ is calculated from

$$(\beta_2 - l_2') = \beta_I \phi_{\frac{o}{I}} - fo \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

This is followed by the calculation of another function,

$$g = \frac{l_o \phi^{-I} (\beta_2 - l_2') + (f - \beta_I \phi_I)}{[L]}$$

$$= \beta_2 \phi_I - \beta_3 - x_4 [L] \quad (16)$$

If the term $x_4 [L]$ is negligible, which will be the case if a higher complex is not formed, a plot of g vs. ϕ_I is linear with slope = β_2, and intercept = $-\beta_3$.

Outline of the work undertaken

The present work deals with certain aspects of the solution-chemistry of some of the Rare-earths and elements of the Actinium Series. The equilibria involving the trivalent cations of these elements and oxalate, glycollate, α-hydroxyisobutyrate, Fluoride, Chloride and Sulphate ligands have been investigated by a cation-exchange method using media of constant cationic strength (NH_4^+ or Na^+, depending on the form of the resin used) and at constant temperature. The data obtained were treated after the manner of Fronaeus[78] for the computation of the step stability constants. The choice of the ligands namely, oxalate, glycollate and α-hydroxyisobutyrate, Fluoride and Sulphate was made on account of the extensive use of these in the separation of Rare-earths and elements of the Actinium Series from each other and other elements by precipitation and ion-exchange elution techniques.

A number of papers regarding the study of these systems by potentiometric, electromotive force measurement, solvent extraction and ion-exchange techniques have appeared in recent years and will be referred to at appropriate places in this text. The study of the Chloride systems of Yttrium (111) and Cerium (111) was undertaken because in the earlier work done in this laboratory[101], ammonium chloride had been used as a back-ground salt and the results obtained from the study of Yttrium (111) and Cerium (111) complexes with glycollic and α-hydroxyisobutyric acid etc. were found to be at variance with some of the results reported in the literature since 1960.

The work is divided into two parts. Part I is an extension of the work previously carried out in this laboratory[101], and deals with an investigation of the factors which were thought to have a bearing on the method and had not hitherto been adequately studied. Account was taken in Part II, of the results of the Part I work in planning the study of the equilibria mentioned above.

PART I

SORPTION OF YTTRIUM (III) ON ZEO-KARB 225 (SRC 15) AND DE-ACIDITE FF.; EFFECT OF CROSS-LINKING OF A RESIN ON YTTRIUM (III)-GLYCOLLATE SYSTEM; EFFECT OF A VARYING V/M RATIO ON YTTRIUM (III)-GLYCOLLATE SYSTEM AND THE STUDY OF YTTRIUM (III) α- HYDROXYISOBUTYRATE AND CHLORIDE SYSTEMS.

CHAPTER II

EXPERIMENTAL

Introduction

The use of synthetic ion-exchange materials for the separation of mixtures of chemically similar elements of the lanthanum and actinium series is now a well-established practice especially at the tracer level. In such separations, the solution containing a mixture of the elements is passed down a column of a suitable ion-exchanger. The sorbed metal ions are then selectively eluted with such buffers as glycollate, lactate or α-hydroxyisobutyrate. The efficiency of the separation by these acids increases in the order: glycollate, lactate, α-hydroxyisobutyrate[103]. This cannot be explained unless the nature of the equilibria involved and the composition of the association products formed in the ionic solution are adequately known. In recent years, particularly since 1960, a wealth of data and results have been published on the study of the equilibria involving these and other ligands and elements of the rare-earth and actinium series by potentiometric[104, 105, 106], ion-exchange[107, 108, 109] and solvent extraction[110, 111, 112] methods. Prior to these and other equilibria of some of the rare-earths and elements of the actinium series by cation-exchange, a series of preliminary investigations were undertaken regarding partition behaviour subject to change of pH, cross-linking of resin and $^{v}/m$ ratio (where v = volume of solution in millilitres, and m = weight of resin in gm.). The possibility of a change in the concentration of a ligand in solution due to adsorption of the latter on the resin was also studied; the ligand selected for the purpose was glycollic acid, the reason being that the same ligand had been used earlier in experiments dealing with the effects of cross-linkage of resin etc. on Yttrium (111)-glycollate system. The data and results of all these investigations and those of Yttrium (111)-glycollate, α-hydroxyisobutyrate and chloride systems are all contained in this chapter. The choice of Yttrium-91 as a tracer for this preliminary work was based on the following consideration:-

(1) Yttrium-91 is one of the comparatively inexpensive rare-earth isotopes, and it has a reasonably long half-life ($^{t}/_{\frac{1}{2}}$ = 61 days).

(2) The β^--particles emitted by this isotope are sufficiently energetic permitting an accurate assay of the metal in the liquid phase by β counting in G.M. liquid counters.

(3) Yttrium, on account of its ionic radius, and chemical behaviour similar to Gd and Tb, may be taken as a representative for all rare-earths.

(4) Yttrium is consistently trivalent. Therefore, the possibility of complications arising out of a

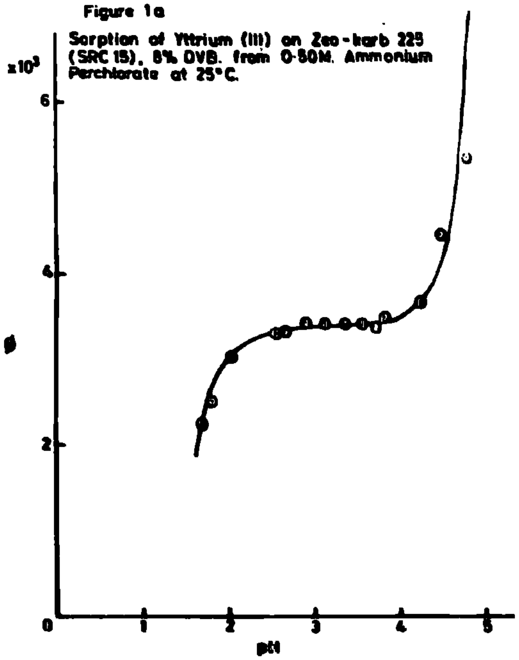


Figure 1a

Sorption of Yttrium (III) on Zeo-karb 225 (SRC 15), 8% DVB. from 0·50M. Ammonium Perchlorate at 25°C.

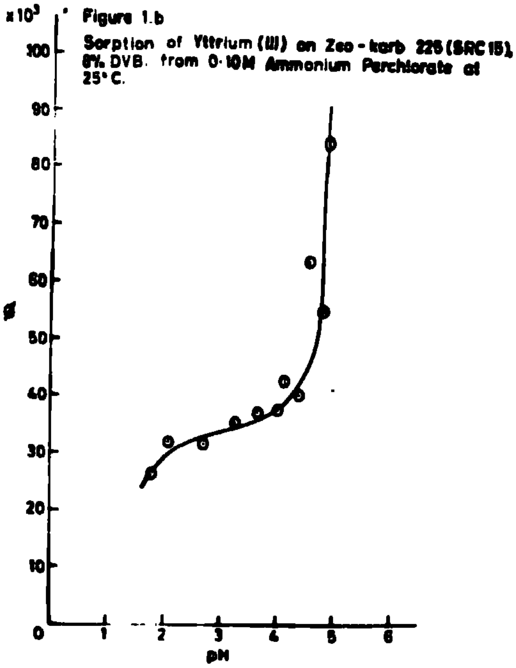


Figure 1.b

Sorption of Yttrium (III) on Zeo-karb 225 (SRC 15), 8% DVB. from 0·10M Ammonium Perchlorate at 25°C.

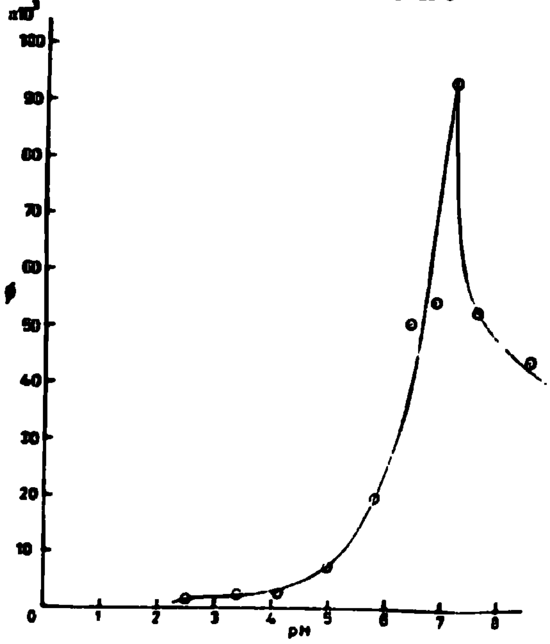


Figure 1.c

Sorption of Yttrium (III) on Zeo-karb 225 (SRC 15), 8% DVB from 0·50M Ammonium Perchlorate at 25°C.

Figure 2.

Sorption of Yttrium (III) on De-acidite F.F. from 0·50M Ammonium Perchlorate at 25°C.

change of valence state of the element in solution are ruled out.

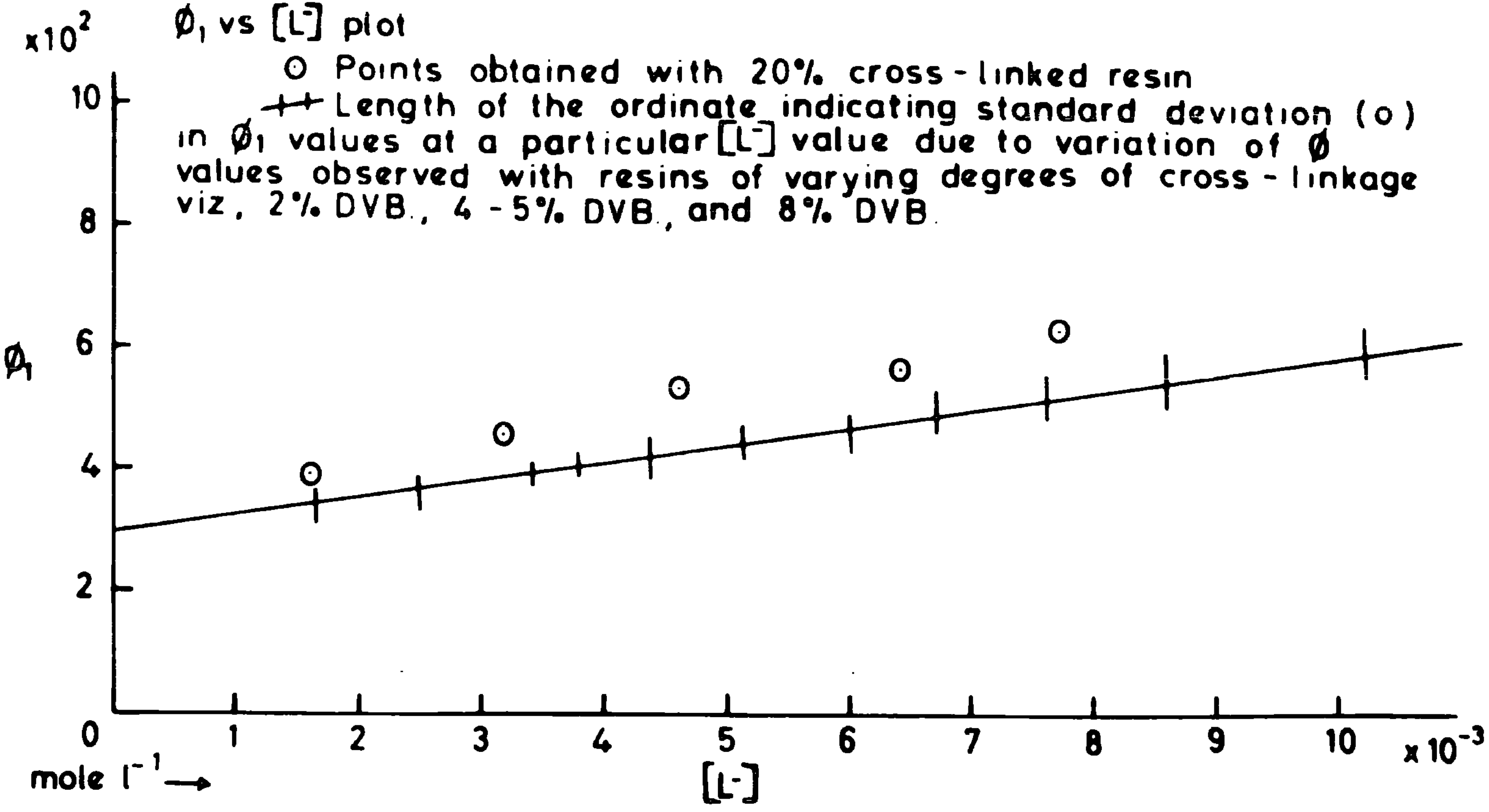
Sorption of Yttrium (111) on Zeo Karb 225 (SRC 15): 8% DVB, 100-200 mesh (Ammonium-form) in the presence of 0.5M and 0.1M Ammonium perchlorate and at 25°C.

A series of solutions containing the same amount of the tracer (Yttrium-91) and enough of solid ammonium perchlorate to give 0.5M or 0.1M strength were prepared in 25 ml. and 50 ml. standard flasks, and adjusted to different hydrogen ion concentrations ranging from pH 1.5 to 4.5 using standard aqueous ammonia and perchloric acid solutions. Equal and known volumes of each were mixed separately with the same and known weights of the resin and equilibrated for nearly two days in a constant temperature (25°C) water-bath as in the general procedure (vide appendix iii). The initial and final β-activities of the solutions were measured in a Geiger-Müller liquid counter, and the distribution-co-efficients calculated by the method detailed in appendix iv. Isotherms were obtained by plotting ϕ against pH (vide figures Ia,b,c).

Sorption of Yttrium (111) on De-acidite FF. in the presence of 0.5M Ammonium perchlorate and at 25°C.

De-acidite FF. was converted to the perchlorate-form. A known weight of it was placed in a series of polythene capsules and mixed with equal volumes of Yttrium-91 solutions in 0.5M ammonium perchlorate and adjusted to different pH

Figure 3
Effect of the Degree of cross linking of the Resin on Yttrium (III) Glycollate System in 0 50M Ammonium Perchlorate at 25°C
ϕ_1 vs $[L^-]$ plot



⊙ Points obtained with 20% cross-linked resin

+ Length of the ordinate indicating standard deviation (o) in ϕ_1 values at a particular $[L^-]$ value due to variation of ϕ values observed with resins of varying degrees of cross-linkage viz, 2% DVB., 4-5% DVB., and 8% DVB.

values. The capsules were sealed and placed in a constant temperature water-bath to equilibrate (vide appendix iii). As in the previous experiment, ϕ values were obtained from measurements of initial and final solution activities, and plotted against pH's (vide figure 2).

Investigation of the Yttrium (111)-Glycollate system with cation-exchangers having different degrees of cross-linking in 0.5M Ammonium perchlorate and at 25°C.

In this investigation, the general procedure laid out in appendix iii was followed. pH's of the solution were kept between 3 and 4 to avoid erratic distributions (vide figures 1a, b, c). The data obtained with resins of different degrees of cross-linking and the results calculated from them are collected in the tables below:- (ALSO SEE FIG. 3)

TABLE I

Data and results obtained with Zeo-Karb 225 (SRC 15): 8% DVB 100-200 mesh (ammonium form)

Weight of resin taken = 0.40 g.

Volume of complexing solution per equilibration =15 ml.

Volume of tracer solution in 25 ml. of the complexing solutions = 1 ml.

Time allowed equilibration 24 hours.

pH of solutions = 3.34 ± .01

l_0 (I - I0) = 3630 ml.g^{-1} l_0 (II - I7) = 328I ml.g^{-1}

(a)

[L] mole/litre	ϕ ml.g^{-1}	ϕ_I M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\phi_I$ M^{-1}	g M^{-3}
-	-	300 ± 10	0.65 x 10^5	-	-	-
.00084	2859	323	0.69	0.4 x 10^4	23.3	-
.00168	2346	326	0.82	1.7	25.7	-
.00252	1828	391	0.81	1.6	91.1	-
.00341	1537	400	0.91	2.6	99.8	-
.00420	1295	429	0.98	3.3	129	-
.00518	1073	460	1.07	4.2	160	-
.00604	928	482	1.14	4.9	182	-
.00681	782	535	1.26	6.1	235	-
.00766	759	494	1.23	518	194	1.19 x 10^7
.00863	644	537	1.34	6.9	237	1.27
.0175	232	752	2.00	13.5	452	1.81
.0262	119	1013	2.77	21.2	713	2.43
.0350	71	1295	3.60	29.5	995	3.11
.0437	49	1515	4.27	36.2	1215	3.64
.0874	13	2923	8.48	78.3	2628	7.03
.1398	4	5313	15.58	149.3	5013	12.75
.1748	3	7413	21.83	211.8	7113	17.79

(b) Results

Reaction medium and conditions	pH range	pK HL	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
0.5M NH_4 ClO_4 t = 25°C	3.34 ± .01	3.46*	297.1	2.4×10^4	x

*See appendix (vi)b

TABLE II

Data and results obtained with 4-5% cross-linked resin (Zeo-Karb 225 (SRC 12): 100-200 mesh; NH_4-form).

Resin weight used per equilibration = 1 g.

Volume of complexing solution per equilibration = 20 ml.

Resin swelling correction factor (σ) = 0.9676*

pH = 3.31 ± 0.01

*vide appendix (vii)

$\phi_I^0 = 300 \pm 10$ M^{-1}; $f_o = 6.5 \times 10^4$ M^{-2} $l_o = 1767$ $ml.g^{-1}$

(a)

$[L^-]$ mole/litre	ϕ $ml.g^{-1}$	ϕI M^{-1}	f M^{-2}	Δf M^{-2}	$\Delta\phi I$ M^{-1}	g M^{-3}
.00169	1140	325	8.26×10^4	1.76×10^4	25.35	-
.00334	765	393	9.00	2.50	92.79	-
.00507	567	417	10.21	3.71	117.31	1.10×10^7
.00676	413	485	11.81	5.31	184.83	1.20
.00771	373	485	12.15	5.65	184.67	1.25
.0103	270	539	13.85	7.35	239.26	1.40
.0128	194	631	16.35	9.85	330.90	1.61
.0257	70	943	25.79	19.29	643.18	2.42
.0333	46	1122	31.19	24.69	821.76	2.88
.0446	31	1257	35.54	29.04	956.11	3.23
.0625	17	1649	47.24	40.74	1346.48	4.23
.0695	14	1802	51.89	45.39	1502.42	4.63

*Mean of 5 values corrected for swelling of the resin

(b) Results

Reaction medium and conditions	pH	pK' HL	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
= 0.5M t = 25°C	3.31 ± .01	3.46	302.28	2.57×10^4	5×10^5

TABLE III

Data and results obtained with 20% cross-linked resin (Zeo-Karb 225 (SRC 23): ammonium form; 100-200 mesh).

Weight of resin used per equilibration = 0.1 g.

Volume of complexing solution used per equilibration = 15 ml.

l_o = 9200 ml. g^{-1}

	$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_I M^{-1}
1.	.001636	5651	384
2.	.003227	3717	457
3.	.004643	2648	533
4.	.006454	1979	565
5.	.007737	1574	626
6.	.015470	580	960
7.	.039230	107	2166
8.	.080670	17	6696

$\phi_I^0 = 320 \pm 20$ M^{-1}

pH = 3.29 ± .01

TABLE IV (a)

Data and results obtained with 2% cross-linked resin (Zeo-Karb 225 (SRC 7): ammonium form; 100-200 mesh).

Weight of resin used per equilibration = 2.0 g.

Volume of complexing solution used per equilibration = 20 ml.

Correction factor σ for resin swelling = 0.8508

pH = 3.37 ± .01

l_o = 470 ml.g^{-1}

Batch 1

No.	$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_I M^{-1}
1.	.002055	341	184
2.	.003203	252	270
3.	.004109	240	233
4.	.006084	172	285
5.	.007378	144	307
6.	.008325	136	295
7.	.010410	113	304
8.	.012650	92	325
9.	.021080	52	381
10.	.054040	18	465
11.	.108100	8	534

TABLE IV (b)

Data and results obtained with a different batch of 2% cross-linked resin (Zeo-Karb 225 (SRC 7): ammonium form; 100-200 mesh).

Weight of resin used per equilibration = 1.0 g.

Volume of complexing solution used per equilibration = 40 ml.

Resin swelling correction factor, σ = 0.8894

pH = 3.26 ± .01

l_0 = 728 ml. g^{-1}

Batch 2

No.	$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_I M^{-1}
1.	.003814	287	403
2.	.004392	244	452
3.	.006423	173	500
4.	.008915	115	598
5.	.010821	88	672
6.	.013500	72	675
7.	.015180	59	747

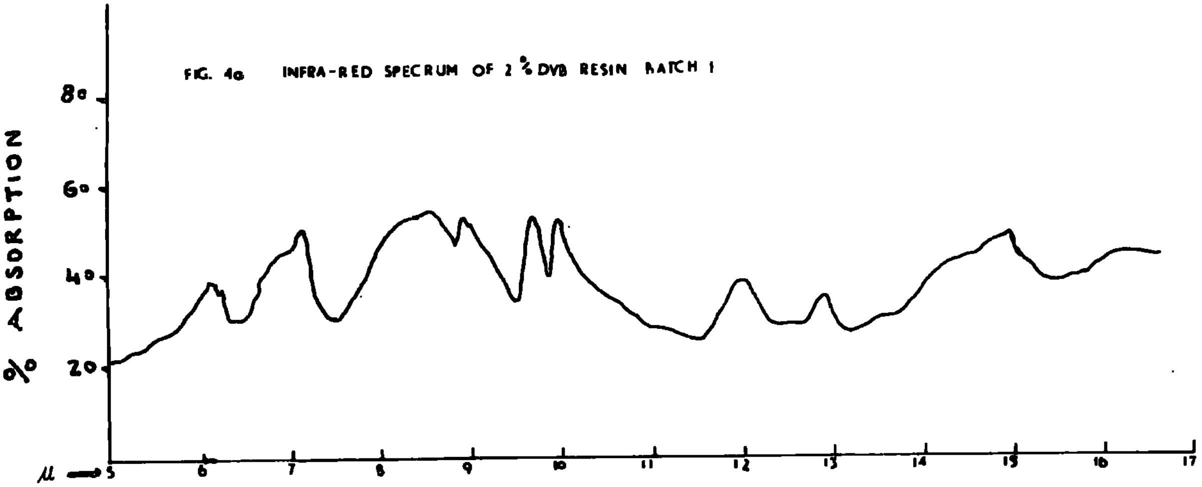


FIG. 4a INFRA-RED SPECRUM OF 2 % DVB RESIN BATCH I

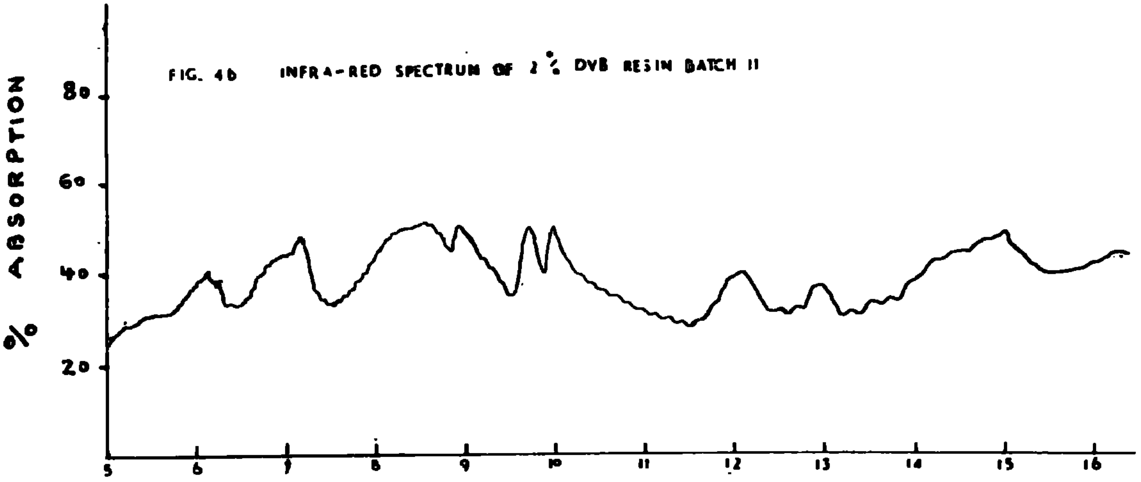


FIG. 4b INFRA-RED SPECTRUM OF 2 % DVB RESIN BATCH II

Infra-red Spectrophotometric Examination of the two batches of resin (Zeo-Karb 225 (SRC 7): 2% DVB, ammonium form, 100-200 mesh)

The discrepancies in the values of the function ϕ_1, calculated from the data obtained with resin from two different batches (vide supra, tables IV (a) and IV (b)) suggested the possibility of some basic differences in the composition or structure of the two resins. To check on this possibility, the infra-red spectra of the two resins were obtained by a method outlined in the appendix (VIII). The comparison of the two spectra (vide figure 4) however, does not clearly indicate any qualitative difference of composition or structure between the two resins. The very obvious difference in the two batches of the resin was that of colour. The resin from batch I was much darker in colour than that from batch II and on washing with hydrochloric acid gave an effluent which was much darker in colour than the one obtained from the latter.

Effect of the varying $^{v}/m$ ratio on the Yttrium (III)-Glycollate system in 0.5M Ammonium perchlorate

In this investigation, eight per cent cross-linked resin was used. The choice was based on the results of the preceding experiment (vide figure 3). It is evident from figure 3, that the effect of the degree of cross-linkage of the resin used is not very serious regarding ϕ_I, (between 2-8% DVB) and hence the subsequent values of the stability constants of the complexes involved. However, 8 to 10% degree of cross-linkage seems a happy medium.

TABLE V (a)

$^{v}/_{m} = {}^{15}/_{0.2}$

pH = 3.21 ± 0.01

$l_o = 3587^{*}\ ml.g^{-1}$

No.	$[L^-]$ mole/litre	ϕ $ml.\ g^{-1}$	ϕ_I M^{-1}
1.	.00142	2359	367
2.	.00284	1809	346
3.	.00426	1255	436
4.	.00568	987	464
5.	.00710	821	474

*Mean of 12 values, obtained with varying $^{v}/_{m}$ ratios - resin weight used/15 ml. of solution was varied between 0.2 g. to 0.6 g.

TABLE V (b)

$^v/_m = {}^{15}/_{0.4}$

pH = 3.21 ± 0.01

l_o = 3587 ml. g^{-1}

No.	$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_I M^{-1}
1.	.00142	2422	339
2.	.00288	1605	429
3.	.00438	1219	443
4.	.00576	953	479
5.	.00719	739	536

TABLE V (c)

$^v/_m = {}^{15}/_{0.6}$

pH = 3.21 ± .01

l_o = 3587 ml. g^{-1}

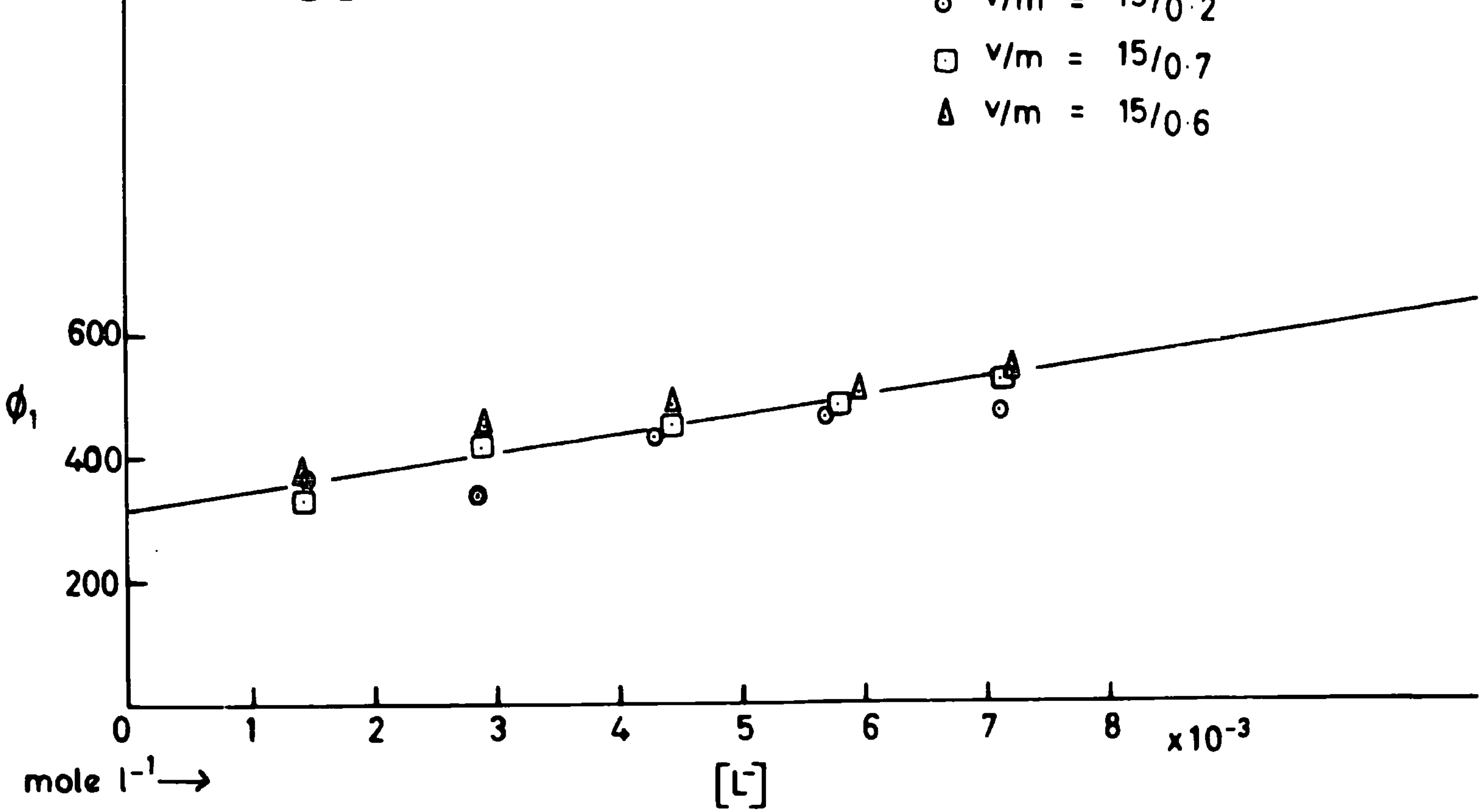
No.	$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_I M^{-1}
1.	.00144	2340	370
2.	.00288	1552	455
3.	.00438	1142	489
4.	.00593	898	505
5.	.00720	736	538

NOTE: The results of the above investigation are graphically shown in figure 5.

Figure 5

Effect of the variation of v/m ratio on Yttrium(III) Glycollate System in 0·50 M Ammonium Perchlorate at 25°C.

ϕ_1 vs $[L^-]$ plot.



The determination of glycollic acid in Solutions previously in contact with ion-exchange resins.

The study of chemical equilibria by a cation-exchange method is based on the assumption that while free and partially complexed metal ions are sorbed onto the resin, the free ligand concentration is not affected. The investigation of the glycollic solutions previously contacted with resins of varying cross-linkage was undertaken to check the validity of this assumption. The loss of free ligand species, though ruled out by the exchange mechanism of a cation-exchanger, is nevertheless possible due to a vander Waals adsorption process. The following methods were tried for determining glycollic acid concentration in solutions which had previously been treated with cation-exchangers of varying cross-linkage:-

(1) Ultra violet spectrophotometry - The method had to be abandoned because solutions which had been in contact with resins showed complete absorption in the U.V. region. This, incidentally, suggested that during equilibrations, some resin might be passing into solution. To check on this, and to establish the nature of soluble resinous matter, 4-5% cross-linked resin (H-Form) was shaken with water for several hours. After the insoluble matter had settled down, the supernate was decanted off and centrifuged to ensure the complete removal of the suspended matter. The solution was evaporated to

FIG. 7a INFRA-RED SPECTRUM OF 4-5 % DVB RESIN (H-FORM)

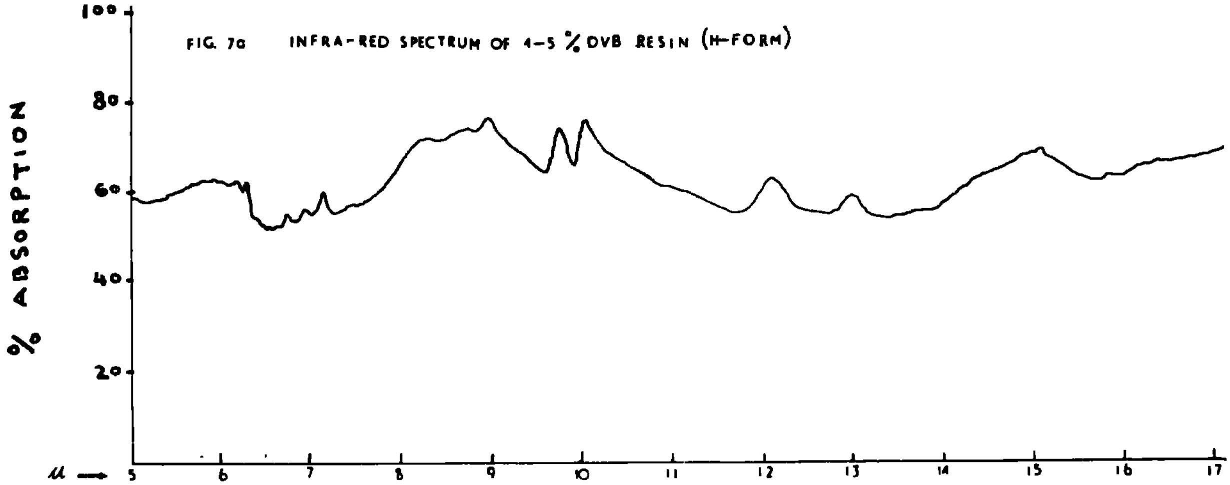
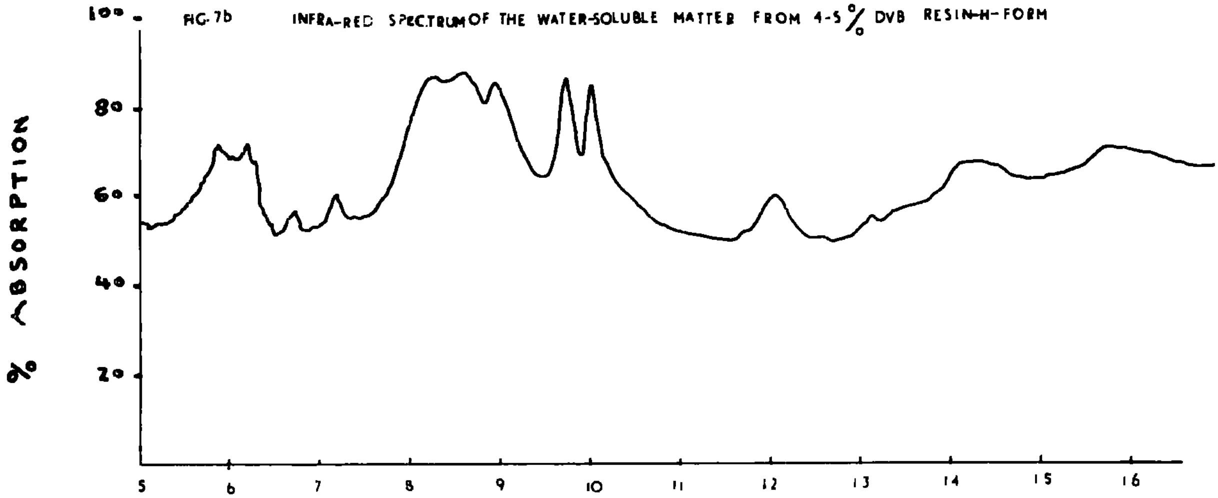


FIG. 7b INFRA-RED SPECTRUM OF THE WATER-SOLUBLE MATTER FROM 4-5 % DVB RESIN-H-FORM



dryness. The residue was collected in a clean dry test tube and dried under vacuum for several hours. Finally its infra-red absorption spectrum was obtained (vide appendix viii) and compared with that of the original sample. The comparison showed the two to be identical (vide fig. 7).

(2) Cerium (IV) oxidation of Glycollic acid[113] - The method was abandoned on account of poor reproducibility of results.

(3) Chromium (VI) 'Heat of dilution' method[114] - Essentially the method given in the original paper was followed. However, for 3 to 8 mg. quantities of glycollic acid in 2 to 5 ml. of a sample only 7 ml. of conc.-sulphuric acid was added for initial oxidation (instead of 10 ml.) and afterwards a further addition of 10 ml. was made instead of 30 ml. This prevented a tendency towards excessive reduction of chromium (VI). Larger amounts of glycollic acid require proportionally more conc. sulphuric acid in the oxidation steps and consequently greater dilution afterwards if a chemical indicator is used in the subsequent titration. It was found in practice to be more convenient to add an excess of 0.1M. iron (II) solution to the chromium (VI) remaining after the oxidation and to titrate with a standard chromium (VI) solution using N-phenylanthranilic acid as indicator than to titrate chromium (VI) with iron (II) to a potentiometrically determined end-point as previously recommended. The method could not be used successfully for

determining glycollic acid in solutions which had previously been in contact with resins of low cross-linkage (2% DVB and 4-5% DVB) due to high and inconsistent blank values.

(4) Estimation of Glycollic acid by chromotropic acid[115]- The method was re-examined in detail to ensure its successful application to the systems under investigation, using crude and refined grades of the reagent. The procedure finally adopted is as follows:-

0.200 ml. of a sample containing 15 to 130 μg. of glycollic acid and 0.5 ml. of a chromotropic acid (Na-salt) solution are transferred to a boiling tube fitted with a ground glass stopper. 5 ml. of conc. sulphuric acid are added in small portions and mixed in such a way as to prevent an excessive localised heat release. It is then stoppered and suspended in a boiling water-bath for 15 to 20 minutes (if refined reagent is used) or 30 to 40 minutes (if crude reagent is used), cooled under a tap of running water and diluted with water to 50 ml. in a standard flask. The optical density of the coloured solution is finally measured at 570 mμ. against a reference solution prepared by following the same procedure but using water or an appropriate salt solution instead of the glycollic acid sample. A calibration curve is prepared by the same procedure. The Beer-Lambert relationship is obeyed for 15 to 130 μg. of glycollic acid using 1 cm. glass cells. With a somewhat longer heating time and using crude reagent (the colour produced with a crude reagent is less sensitive to heating time than the one obtained with a purer stuff), the law is obeyed up to 180 μg. Colour is stable up to 24 hours. The concentration of sulphuric used is also critical. Therefore, in a particular run the solution to acid ratio must be the same in all samples including those taken for a calibration curve. The acid used must, moreover, be from the same container. Figure 8 shows a typical calibration curve obtained with a recrystallised reagent. The broken line indicates the position after nearly 24 hours.

The effect of lactic acid on such a determination of glycollic acid has also been studied. The results are contained in table VI b.

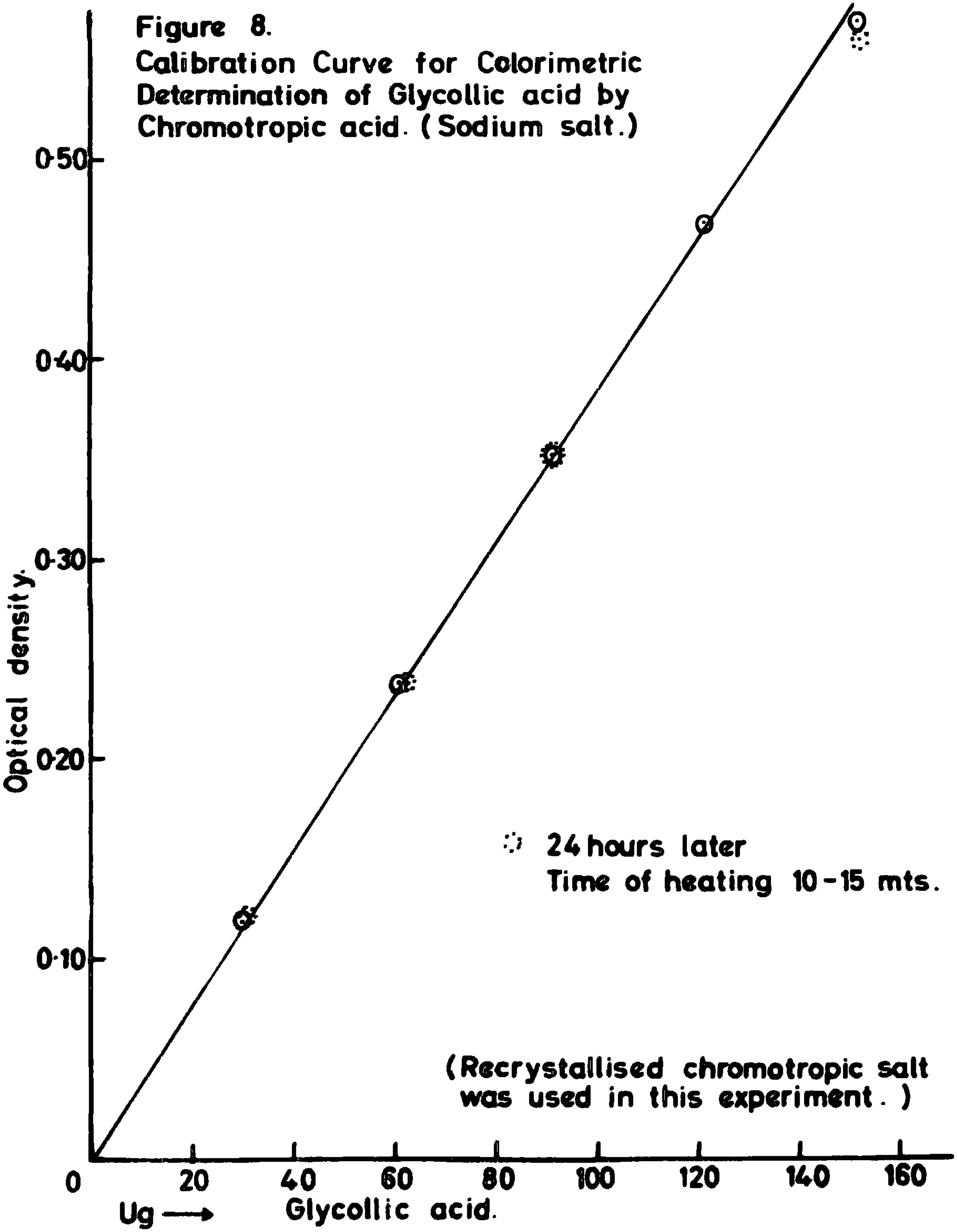


Figure 8.
Calibration Curve for Colorimetric Determination of Glycollic acid by Chromotropic acid. (Sodium salt.)

⁘ 24 hours later
Time of heating 10 - 15 mts.

(Recrystallised chromotropic salt was used in this experiment.)

TABLE VI (a)

Glycollic acid determination; a comparison of results

Resin Cross-linkage	Glycollic acid taken (μg)	Glycollic acid found (μg) Spectrophotometrically*	Titrimetrically μg
2%	60.8	60.8	-
	121.6	123	-
	182.5	183*	-
4-5%	60.8	61.6	-
	60.8	60.1	-
	121.6	120	-
	121.6	122	-
8%	60.8	61.5	62.0
	60.8	60.1	61.7
	121.6	121	123
	121.6	122	121
20%	91.3	90.5	91.2
	152.1	151*	150

*Heating time 50 minutes; reagent sample B. The reference solution was provided by a 'blank' determination run on 0.200 ml of 0.5M NH_4ClO_4 which had been equilibrated with resin in the same way as the glycollic acid sample.

TABLE VI (b)

The effect of lactic acid on the determination of Glycollic acid by the chromotropic acid method.

Glycollic acid taken (μg)	Lactic acid present (μg)	Glycollic acid found* (μg)
15.2	-	16
15.2	5.0	16
30.4	-	30.5
30.4	9.0	30.5
60.8	-	60.8
60.8	18	61.0
60.8	36	60.8
60.8	41	61.0
60.8	46	60.8
60.8	54	57.0
60.8	72	54.5
60.8	90	41.5

*Heating time for colour development was 45 to 50 minutes. Reagent sample A was used. The reference solution was prepared from a 'blank' run on 0.5M NH_4ClO_4 previously equilibrated with resin.

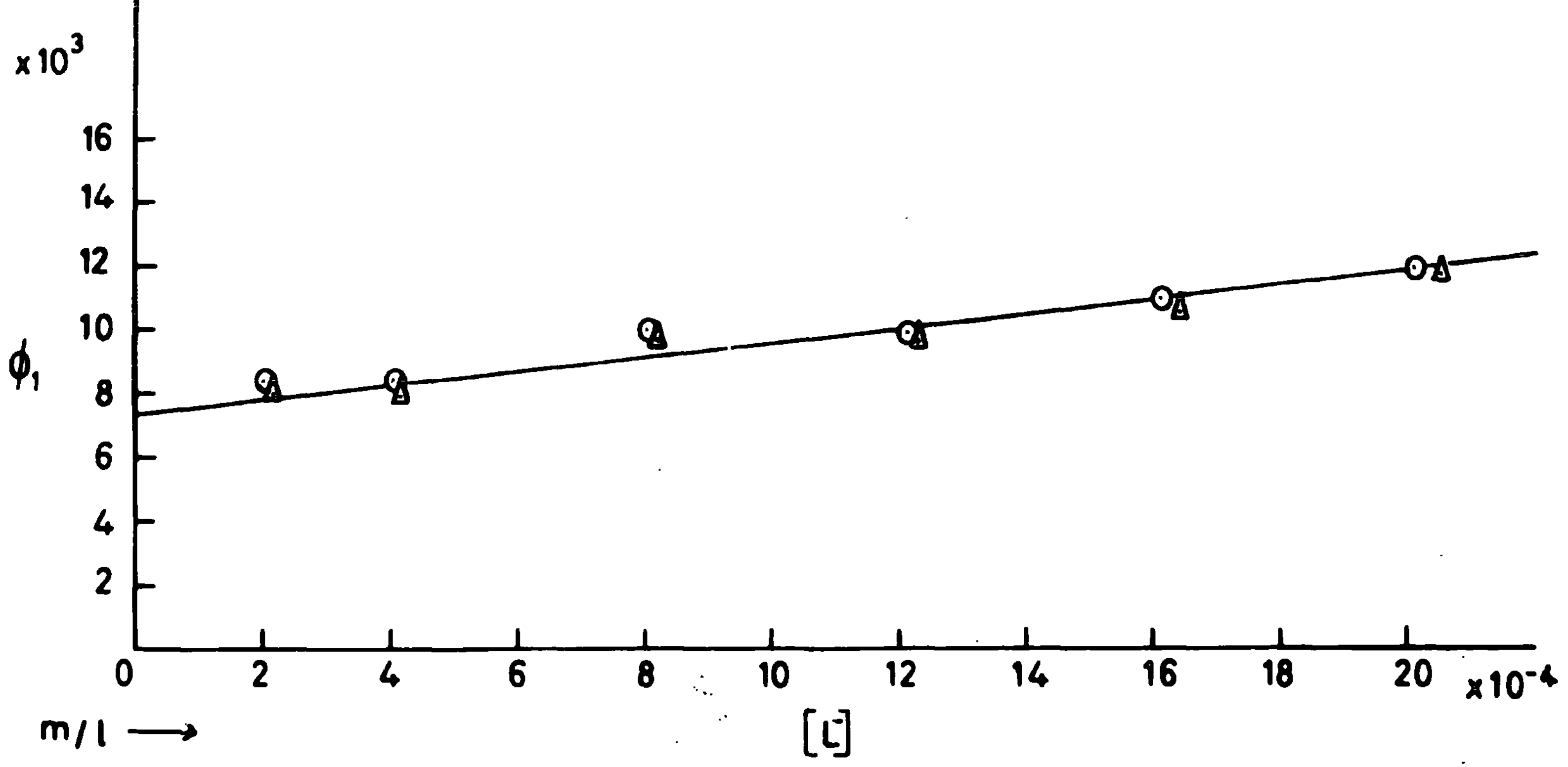
Figure 6.

Yttrium (III)- α Hydroxyisobutyrate in 0·5 M NH_4ClO_4 at 25°C.

ϕ_1 vs $[L^-]$ plot.

Δ pH measurements made with S.C.E./glass system using saturated Na Cl solution as salt bridge.

⊙ pH measurements made with S.C.E/glass system using saturated K Cl as salt bridge.



Study of Yttrium (III)-α-hydroxyisobutyrate equilibria in 0.5M ammonium perchlorate at 25°C

The study was carried out with 8% cross-linked resin (cation-exchanger) following the usual procedure. The $^{V}/m$ ratio was kept the same throughout to avoid unnecessary application of a resin-swelling correction which is required if the ratio is reduced beyond a certain limit (vide fig. 5). The pH of the equilibrium solutions was maintained between 3 and 4. The pK value of the acid was determined by the method used for a similar measurement on glycollic acid (vide appendix (vi)). The results of the study are collected in the tables VII (a) and VII (b). Table VII (a) contains values of $[L^-]$ and ϕ_1, derived from the pH values measured with a saturated Calomel/glass electrodes system having saturated potassium chloride as a salt-bridge. Table VII (b) contains results derived from measurement of pH with a saturated Calomel glass electrodes system using saturated sodium chloride solution as a salt-bridge. The plots of the function ϕ_1 derived from the data of Table VII (a) and VII (b) against $[L^-]$ almost coincided (vide fig. 6), indicating that change of the salt-bridge in the electrode system was without effect on the values of the step stability constants (derivatives of the functions ϕ_1 and $[L^-]$).

TABLE VII (a)

$^{v}/m = {}^{20}/0.1$

pH = 3.60 ± .01

pK_{HL} = 3.78

l_o = 3590* ml.g^{-1}

No.	$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_1 M^{-1}
1.	.0002017	3070	839
2.	.0004034	2692	827
3.	.0008068	1996	990
4.	.001210	1634	989
5.	.001614	1305	1086
6.	.002017	1051	1198
7.	.002415	889	1268
8.	.002824	772	1293
9.	.003227	637	1436

Plot of ϕ_1 against $[L^-]$, on extrapolation to o. ligand concentration gave ϕ_1^0 = 750 ± 50. M^{-1}

*Mean of 8 values.

TABLE VII (b)

$^{v}/_{m} = {}^{20}/_{0.1}$
pH = 3.41 to 3.45
$pK_{(HL)} = 3.61$

$[L^-]$ mole/litre	ϕ $ml.g^{-1}$	ϕ_1 M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\ \phi_1$ M^{-1}	g M^{-3}
-	3590	750 ± 30	3.63×10^5	-	-	-
.000204	3070	828	2.38×10^5	$\times 10^5$	-	$\times 10^8$
.000409	2692	816	4.51	-	-	-
.000807	1996	977	4.45	0.82	239.8	-
.001226	1634	976	5.48	1.85	226.1	2.08
.001635	1305	1072	6.07	2.44	322.0	-
.002044	1051	1182	6.75	3.12	432.0	2.31
.002420	889	1248	7.33	3.70	498.0	2.52
.002824	772	1276	7.77	4.14	526.0	-
.003270	637	1417	8.59	4.96	667.0	2.82
.004088	488	1555	9.69	6.06	805.0	3.12
.004958	351	1859	11.71	8.12	1109.0	3.67
.005341	308	1999	12.63	9.00	1249.0	3.92
.005885	328	1688	11.06	7.43	938.0	3.44
.006002	250	2184	14.03	10.40	1434.0	4.31
.00667	232	2236	14.61	10.98	1498.0	4.46
.006865	203	2436	15.81	12.18	1686.0	4.80

TABLE VII (c)

Results:

Reaction medium and temperature	pH	pK_{HL}	β I M^{-1}	β 2 M^{-2}	β 3 M^{-3}
= 0.5M NH_4ClO_4 t = 25°C	3.41 to 3.45	3.62	750 ± 30	2.1×10^5	-

Investigation of the Yttrium (III)-Chloride System in 0.5M Ammonium Perchlorate and at 25°C

The investigation was made in the usual way using Yttrium-91 as a tracer and 8% cross-linked cation-exchanger (Zeo-Karb 225 - SRC 15). The pH of the equilibrium solutions was maintained at 3.50 ± 0.01. The $^{v}/m$ ratio throughout the run was kept the same, namely, $^{20}/0.05$. The ligand range used was 0.05 to 0.48 mole per litre. The isotope concentration of the solutions before and after equilibration was determined radiometrically by β-counting using a Geiger Müller liquid counter (vide appendix (viii)). The pH of the solutions was measured by a Doran Universal pH meter using a saturated Calomel glass electrodes system and a saturated solution of potassium chloride as a salt-bridge. The time allowed for the establishment of the equilibrium was 24 hours. The stoichiometric concentrations of the ligand solution have been used for the calculation of the function ϕ_1. The results of the investigation have been collected in the following table.

TABLE VIII

$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_1 M^{-1}	f M^{-2}	Δf M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}
-	4955	-	-	-	-	-
0.05	4213	3.52	-	-	-	-
0.10	3717	3.33	-	-	-	-
0.15	3504	2.76	0.45	0.35	0.76	0.46
0.20	3008	3.24	0.30	0.20	1.24	$\underline{0.16}$
0.25	2612	3.59	0.82	0.72	1.59	0.45
0.30	2251	4.00	1.33	1.23	2.00	0.62
0.35	2081	3.95	2.33	2.23	1.95	1.14
0.40	1758	4.55	2.73	2.63	2.55	1.03
0.45	1532	4.96	3.34	3.24	2.96	1.09
0.48	1532	4.65	3.78	3.68	2.65	1.39
-	-	2.00	0.10	-	-	-

The agreement between the β_I values (Table VIII), is not very good. Therefore no attempt was made at the further calculations of β_2 and β_3. Rejecting the value (underlined in Table VIII), and taking the mean of the rest β_I is computed to be = 0.88 ± 0.34. M^{-1}

DISCUSSION OF RESULTS

Sorption of Yttrium (III) on Zeo-Karb 225 (SRC 15), 8% DVB and De-acidite FF from ammonium perchlorate solutions follows the same pattern which is independent of the concentration of the background salt (vide figures 1a,b,c, and 2). The values of the distribution co-efficients (ϕ) are nearly independent of pH in the range of pH 2.5 and 4.0. Below pH 2.5 the ϕ values tend to decrease sharply while beyond pH 4.0 they rise steeply passing through a maximum at pH 6.5 and dropping suddenly to low values thereafter (see figure 1c). This pattern of sorption for Yttrium (III) on ion-exchangers is comparable to what Haissinsky et. al[133] observed concerning the adsorption of cerium (III) on platinum, silver, glass and other surfaces at different hydrogen-ion concentrations. These authors have suggested that the adsorption of the lanthanides on platinum is due to the electrostatic attraction of a primary layer of adsorbed anions and is subject to changes of pH on account of the competitive adsorption of hydrogen ions on platinum. The figure given below illustrates this mechanism:

$$\begin{array}{l}
C^+\ C^+\ -\ A^-A^-\ -\ H^+\ H^+ \\
H^+\ H^+\ -\ A^-A^-\ -\ C^+\ C^+ \\
H^+\ H^+\ -\ A^-A^-\ -\ H^+\ H^+ \\
C^+\ C^+\ -\ A^-A^-\ -\ H^+\ H^+ \\
H^+\ H^+\ -\ A^-A^-\ -\ C^+\ C^+ \\
C^+\ C^+\ -\ A^-A^-\ -\ H^+\ H^+
\end{array}$$

According to this assumption, it is evident that when a cation is outnumbered in solution by hydrogen ions (low pH), it will be forced to stay in solution or as in the present case the values of ϕ are low. With decreasing hydrogen ion concentration (increasing pH), the competition for sites by hydrogen ions decreases and hence an increase in the values of ϕ. The plateau regions in the isotherms (figures 1a,b,c and 2) indicate a balanced state of affairs between the competing ions. The sudden increase in the values of ϕ beyond pH 4.0 is difficult to explain on the basis of the competitive sorption of the hydrogen ions alone. Haissinsky et. al. explained the adsorption of ruthenium on platinum at higher pH by further postulating that the decrease in the potential of platinum with increase in pH favours the discharge of cations and hence greater adsorption, and have demonstrated such a diminution of potential in platinum experimentally. In the present case, if, it is assumed that an increase in pH causes a decrease of Donnan's Potential in a cation-exchanger, the steep rise in the values of the distribution co-efficients for yttrium (III) may then be explained on the basis of a break down of the primary anionic layer around the resin particles and a favoured sorption of yttrium (III) because of its higher charge and smaller ionic radius than the competing hydrogen ions. The steep fall in the values of ϕ beyond pH 6.5 may be attributed to the formation of colloidal miscelles slightly adsorbable or poorly adherent to the surface due to the partial hydrolysis of the ions[133].

Regarding the influence of the degree of cross-linking of a resin on yttrium (III)-glycollate system, it has been observed that up to 8% DVB it is not very serious (vide figure 3). The standard deviations observed in the values of ϕ_1 at a constant concentration of a ligand (shown by the length of the ordinates in figure 3) obtained with 2% DVB, 4-5% DVB and 8% DVB resins are not beyond the expected limits (± 5%). It might be observed that the values of the distribution co-efficients are subject to errors due, inter alia, to the imperfections within the resin. According to Freeman[134], these errors are consistent and may be neglected. In the present investigations such errors were minimized by using the mean values of the distribution co-efficients obtained from replicate measurements. It was further noticed that the corrections due to the swelling of the resin were more important in the case of a low DVB resin than those with a higher degree of cross-linkage. The higher trend of ϕ_I values (vide figure 3) obtained with 20% cross-linked resin seems anomalous and is difficult to explain unless some kind of a 'selectivity reversal' due to the 'polyfunctionality'

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of the resin and the ligand effect (apart from complexing of yttrium (III)) is assumed. The only case of 'selectivity reversal' reported so far concerns the exchange of sodium and hydrogen ion on highly cross-linked resins (15% DVB and higher). Reichenberg et. al.[161] in their exchange study of the Na^+/H^+ system found that the value of K_H^{Na} i.e. the selectivity co-efficient of the resin for Na^+ ions decreased sharply with increase in $X_{NaR.}$ i.e. the equivalent ionic concentration of sodium on the resin. They attributed this reversal of selectivity initially to the effect of the 'polyfunctionality' of the resin[161] but later suggested that it was due to the influence of the sulphonic groups[162] in the resin. In the present case since $X_{y(III)R}$ is nearly constant on account of the fact that only tracer amounts of yttrium were used, the 'selectivity reversal', if any, must be due either to the influence of the 'polyfunctionality' of the resin alone or some sort of a combined effect due to the ligand (apart from complexing) and the 'polyfunctionality' of the resin or the sulphonic groups in it. A resin of 8% cross-linkage appears to be a reasonable choice on account of its smaller water uptake (compared to resins of lower cross-linkage) and balanced selectivity (compared to resins of higher cross-linkage).

The variation of $^{v}/m$ ratio over the range of $^{15}/0.2$ and

$^{15}/.6$ does not seem to have any effect on the values for β_n in yttrium (III)-glycollate system, provided the necessary corrections due to the swelling of resin are made (vide figure 5).

The results of the investigation regarding the likely removal of glycollic species from the solutions by the cation-exchangers of various degrees of cross-linking due to vander Waal's adsorption phenomenon during equilibrations of yttrium (III)-glycollate solutions with these resins, show that the concentration of glycollic acid in solution is not affected by the resins in questions, namely, the cation-exchangers of 2%, 4-5%, 8% and 20% DVB (vide table VI a). This is fortunate for otherwise the calculation of $[L^-]$ function would become more involved and less reliable so that the $_n$ values derived from it would not be valid. On the basis of the above, it was assumed that like glycollic acid, the concentrations of other ligands (namely α-hydroxyisobutyrate, chloride, sulphate, fluoride and oxalate) included in the ensuing studies would not be affected by the resin. In the colorimetric determination of glycollic acid in solutions which had been previously treated with resins, by chromotropic acid (sodium salt) lactic acid up to 46 μg per 61 μg of glycollic acid per sample was found to be without effect (vide table VI b).

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Yttrium (III)-α-Hydroxyisobutyrate System

As indicated in appendix viii, the conventional salt-bridge, namely, saturated solution of potassium-chloride was replaced by a saturated solution of sodium chloride in the saturated calomel half-cell, for the measurement of pH in the present investigations. This introduced a constant difference of -0.19 ± 0.01 pH unit in the measured values of pH against those obtained with the conventional cell-system and the salt-bridge. This necessitated re-determination of a pK value for the acid under the desired conditions (vide appendix iv). A pK value of 3.61 for α-hydroxyisobutyric acid for $\mu = .50$ and at 25°C is in good agreement with a value of 3.78 derived from the measurements of the pH values of α-hydroxyisobutyric solutions with a conventional cell assembly and salt-bridge[101]. The results obtained from a parallel run of measurements of ϕ_1 and $[L^-]$ functions based on the measurements of pH values with identical cell-systems but different salt-bridges show a good agreement within limits of experimental error (vide figure 6). The β_n values obtained in the present investigation and those reported in literature are given in table IX.

It will be evident from the perusal of these results, that β_I and β_2 values obtained in the present work are in good agreement with those reported at serial no. 2 and 3 in

TABLE IX Yttrium (III) α-Hydroxyisobutyrate - Results

Reaction medium, temperature, pH	Method	pK_{HL}	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}	Reference
0.50M NH_4 ClO_4 t = 25°C; pH = 3-4	i. ex.	3.61	750 ± 30	2.1×10^5	x	Present work
0.50M NH_4 Cl t = 25°C; pH = 3-4	i. ex.	3.78	661	2.34×10^5	1.6×10^6	101
2M Na ClO_4 t = 25°C	Pot. titra.	-	730	2.8×10^5	2.0×10^7	135
0.2M Na ClO_4	i. ex.	-	1300	4×10^4	2×10^7	136

i. ex. = ion exchange

Pot. titra. = Potentiometric titration

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the said table IX. It may be objected to that in view of the difference of media, the agreement between the set of results given at serial numbers 1 and 2 is only fortuitous. It may be pointed out in answer to this objection that since the complexing of yttrium (III) by chloride ions is almost negligible compared to α-hydroxyisobutyrate ions (vide tables IX and XI), the agreement between the said results cannot be but genuine. Regarding the agreement of the results of the present work with those reported by Choppin[135] (serial no. 3, table IX), in spite of the difference in the strength of the media, it might be mentioned that according to I. Grenthe[156], in europium (III)-glycollate system a β_I value valid for $\mu = 0.5M$ should be reduced by 10% for comparison with values obtained at $\mu = 2M$. Taking this as a maximum limit for yttrium (III) α-hydroxyisobutyrate system, Choppin's value of 730 for β_I (at $\mu = 2M$) should be 800 (for $\mu = 0.5M$). The difference between this and the β_I value reported in the present work namely 750 ± 30 is not unreasonable, considering the probability of experimental and other errors involved in the two techniques. Further, in view of the non-availability of a computation similar to I. Grenthe's (156) for the relative sizes of β_I, at ionic strength below 0.5M, the values for β_n reported by Spitsyn[136] cannot be commented upon.

Yttrium-glycollate System:

The β_n values for the yttrium (III)-glycollate system obtained from the present investigation and those reported in literature are summarized in Table X. In the light of the computation suggested by I. Grenthe[156] for comparison of β_n values obtained for europium (III)-glycollate system at $\mu = 0.5M$ and $\mu = 2M$, our value of 270 for β_I (valid for $\mu = 2M$) seems to be in good agreement with those reported by Sonesson[137], Choppin[135] and Lyle et. al.[101]. The β_n values reported by Spitsyn[136] cannot be commented upon for reasons already explained in the discussion of yttrium (III)-α-hydroxyisobutyrate results.

Yttrium (III)-Chloride System:

The variations in the values of the function ϕ_1 (vide Table VIII, page 49) over the range of a ligand concentration used in the present investigation, though partly ascribable to the imperfections in the resin (vide page 52), do indicate the weakness of the chloride complexes of yttrium (III). The β_I values for yttrium (III) and some other trivalent elements of the lanthanum and actinium series are collected in Table XI. The relative weakness of yttrium (III)-chloride complex, namely, YCl^{2+} vis a vis $AmCl^{2+}$ and $CmCl^{2+}$ may be attributed to two causes, (i) the absence of

TABLE X Yttrium (III)-Glycollate System - Results

Reaction medium, temperature and pH	Method	pK_{HL}	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}	Reference
0.50 NH_4ClO_4 t = 25°C; pH = 3-4	i. ex.	3.46	$297^{@}$ 302^{*}	2.40×10^4 2.57×10^4	 5×10^5	Present work
2M $NaClO_4$ t = 25°C	Pot. titra.	-	239	2.30×10^4	4×10^5	135
2M $NaClO_4$ t = 20°C	Pot. titra.	-	295	2.5×10^4	5×10^5	137
0.50 NH_4Cl t = 25°C	i. ex.	-	290	1.6×10^4	1.45×10^4	101
0.2M $NaClO_4$	i. ex.	-	600	5.1×10^4	1×10^6	136

i. ex. = ion exchange

Pot. titra. = Potentiometric titration.

@Results obtained with 8% cross-linked resin.

*Results obtained with 4-5% cross-linked resin.

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a crystal field stabilization[135,160,163] in yttrium, and (ii) the probability of 5f-orbital hybridization[144,164] in americium and curium. The absence of a crystal field stabilization in yttrium (III) is attributed to its electronic configuration, namely, $[Kr]^{3+}$ which is not considered to be suitable for such stabilization[163]. The probability of 5f-orbital hybridization in transuranic elements is attributed to (i) the large distance of 5f-electrons from the nuclii, (ii) their imperfect shielding by 6d and 7s electrons, (iii) their greater spatial extension and (iv) their proximity (in terms of energy) to 6d and 7s electrons. The hybridized orbitals are known to be more strongly polarized and hence capable of stronger bonding with ligands which in turn may determine the electronic structure of an element in a given oxidation state in solution[165].

The conclusions arrived at from the preceding discussion of results in particular and the present investigations in general are summarized as follows:-

(1) Sorption of yttrium (III) on Zeo-karb 225 (SRC 15) and De-acidite FF from ammonium perchlorate solutions is almost independent of the hydrogen ion concentrations of the solutions in the pH range of 2.5 and 4.0.

(2) The cross-linking of a resin and the variations of

the ${}^{v}/m$ ratio in the range of ${}^{15}/.2$ and ${}^{15}/.6$ have no significant effect on the values of the function ϕ_{I} (and hence also on β_n values) in yttrium (III)-glycollate system, provided corrections due to the swelling of the resin are duly made. A resin of 8-10% DVB. appears to be a good choice for use in the study of such equilibria on account of its low water-uptake and balanced selectivity for the cations concerned.

(3) The stabilities of yttrium (III) complexes with α-hydroxyisobutyrate, glycollate and chloride ligands are in the following order:-

α-hydroxyisobutyrate $>$ glycollate $\gg$ chloride

(4) The concentration of glycollic acid in ammonium perchlorate solutions is not affected by treatment of these solutions with cation-exchanger of 2 to 20% DVB.

(5a) The chromium (VI) 'heat of dilution' method is satisfactory for a quantitative determination of glycollic acid in ammonium perchlorate solutions which have previously been contacted with cation-exchangers of 8-20% DVB, provided the amount of glycollic acid is in the range of 1-2 mg/ml of a solution.

(5b) The determination of glycollic acid in perchlorate solutions which have been in contact with cation-exchangers of 2-20% DVB. by chromotropic acid (sodium salt) is quite satisfactory. The Beer-Lambert law is obeyed up to 130 μg amounts of glycollic acid per 0.20 ml. of the sample solutions. The colour produced is stable up to 24 hours (vide figure 8).

(6) It has been observed that subject to the accuracy of the available data most of the assumptions made in the theory[78], regarding the use of ion-exchangers for the quantitative study of the step equilibria, are reasonably valid.

Precautions:

(1) As far as possible a resin from the same batch should be used throughout.

(2) The resin must be stored in dry, well stoppered bottles. Samples for use may be kept in desiccators.

(3) As far as possible the $^{v}/m$ ratio should not be altered in a particular experiment. Alternatively resin-swelling correction appropriate to the $^{v}/m$ ratio used should be determined and applied.

(4) To minimize variations in the values of distribution

ratios, measurements should be made in replicates and the mean values taken for the calculation of the function, ϕ_I.

(5) The pH of all the solutions used should be nearly the same. Utmost care should be taken in the measurement of the pH of a solution especially when it is required to be used for the calculation of the ligand concentration in the solution.

(6) Chemicals of the highest available degree of purity should be used.

(7) Stocks of doubtful composition should be discarded.

(8) Instruments used for the measurement of radio activities must be frequently checked for efficiency and reproducibility.

(9) Cross contamination of solutions should be scrupulously avoided.

(10) The radio-chemical purity of the tracers used must be ascertained.

(11) All the possible precautions necessary for minimizing random statistical errors in counting rates should be observed.

TABLE XI Stability Constants for M^{*}(III)-Chloride Complexes

Metal ion	Ionic radius A	Reaction medium	Temperature and pH	Method	β_{I} M^{-1}	Reference
Y (III)	0.98	0.50M $NaClO_4$	t = 25°C pH = 3-4	i. ex.	0.88 ±	P.W.
Y (III)	0.98	μ = 1M $HClO_4$	t = 25°C	solv. ext.	0.93 ± 0.11	138
La (III)	1.06	μ = 1M $HClO_4$	t = 22 ± 1	solv. ext.	0.9 ± 0.3	139
La (III)	1.06	"	"	"	1.4	140
La (III)	1.06	4M $NaClO_4$	t = 25°C pH = 2	solv. ext.	0.62 ± .15	141
Ce (III)	1.03	"	"	i. ex.	0.6 - 0.7	142
Ce (III)	1.03	μ = 1M $HClO_4$	t = 22 ± 1	solv. ext.	0.9 ± 0.3	139
Ce (III)	1.03	μ = 1M	"	solv. ext.	0.95 ± 0.10	138
Eu (III)	0.95	μ = 1.0M	t = 20 ± 2	i. ex. solv. ext.	(0.94 to 0.59) ± 0.14 (0.97 to 0.77) ± 0.15	143
Eu (III)	0.95	μ = 1M	t = 22 ± 1	solv. ext.	0.9 ± 0.3	139
Eu (III)	0.95	μ = 1M	t = 26 ± 1	i. ex.	1.35 ± .1	153

Con'd.

TABLE XI (Con'd)

Metal ion	Ionic radius A	Reaction medium	Temperature and pH	Method	β_I M^{-1}	Reference
Am (III)	0.99	4.0M $NaClO_4$	t = 25°C	solv. ext.	0.72 ± .12	141
Am (III)	0.99	μ = 0.5M	-	i. ex.	1.7	144
Am (III)	0.99	μ = 1 M	t = 26 ± 1	i. ex.	1.41	153
Cm (III)	0.98	μ = 0.5M	-	i. ex.	1.5	144
Am (III)	0.99	μ = 1	-	solv. ext.	0.25	154

P.W. = Present work.
i. ex. = ion exchange method.
solv. ext. = solvent extraction.

*M = a trivalent rare-earth or actinide ion.

PART II

A CATION-EXCHANGE STUDY OF THE SOLUTION-CHEMISTRY OF SOME OF THE TRIVALENT CATIONS OF THE LANTHANUM AND ACTINIUM SERIES OF ELEMENTS WITH REFERENCE TO CHLORIDE, FLUORIDE, SULPHATE, OXALATE, α- HYDROXY-ISOBUTYRATE, GLYCOLLATE LIGANDS.

CHAPTER I

The Study of the Complexes of Lanthanum (III) with Fluoride, Sulphate, α-hydroxyisobutyrate and Oxalate Ligands

Introduction:

The complexes of lanthanum (III) with fluoride, sulphate, α-hydroxyisobutyrate and oxalate ligands in 0.5M or 1M sodium perchlorate and at 25°C have been studied by the cation-exchange method, using lanthanum-140 as a tracer. The procedure employed for a similar study of the Yttrium (III) complexes (already discussed) was used. The tracer, lanthanum-140, was obtained from Barium-140 by a solvent-extraction method using a cupferron-chloroform mixture after the manner of Toshiyasu Kiba, Shigeru Ohashi and Toyoo Maeda who used it for an identical separation of Yttrium-90 from Strontium-90, from a mixture of fission products[116]. The anion-exchange method of separating lanthanum-140 from barium-140[165], apart from being tedious and lengthy, did not give good, clean separation in my hands. Investigation of the lanthanum (III)-complexes was undertaken, because lanthanum as a precursor of the lanthanides could provide a clue to the behaviour of these elements in general. The view that the chemical behaviour of the elements in question depends on the size of their ionic radii and charge could alone be proved or disproved by such an investigation of the complexes of lanthanum (III) and some other elements of the series with the same ligands, under precisely the same conditions and by the same technique. Further, although the information obtained from the isotherms regarding the distribution of Yttrium (III) between the aqueous and resin phases, could be made use of for planning similar studies on lanthanum (III), it was decided to obtain similar isotherms with lanthanum (III) and cerium (III) as well with a view to being on a surer ground regarding the similarity of the distribution behaviour of these elements.

Separation of Lanthanum-140 from Barium-140:

A drop or two of the Barium-140 isotope solution were taken in a polythene bottle, and diluted to 5 ml. with distilled water. Added 1.6 ml. of 9M aqueous ammonia, 10.4 ml. of 0.9M ammonium acetate solution and 3 ml. of 5% solution of cupferron in water. Shook the mixture for a couple of minutes in an electric shaker followed by an addition of 5 ml. of chloroform and 10 to 15 minutes shaking. Separated the two phases. Treated the aqueous phase with more of the cupferron-chloroform mixture (3:5 by volume) and separated the organic phase after the mixture had been shaken for 10 to 15 minutes. The organic phases obtained in the above treatments of barium-140, were then stripped with 3N nitric acid for lanthanum-140. A portion of the solution was used for following the decay of the isotope (lanthanum-140) to provide a check on its radiochemical purity. The rest of the solution was evaporated to a small volume and finally ignited in a platinum crucible. The lanthanum-140 was taken up from the crucible with 1 ml. of perchloric acid. The perchloric acid solution was diluted with distilled water and neutralised to the required pH with a standard sodium hydroxide solution. The cationic strength was made up to 0.5M or 1M as required by adding solid sodium perchlorate.

Check on the purity of lanthanum-140:

The purity of lanthanum-140 was ascertained from its decay. The decay curves obtained by plotting counting rate against time in hours on a semi-log graph paper showed it to have a half-life in good agreement with the literature value of 40.2 hours. The decay of the isotope was followed by counting its β-activity in a gas flow type proportional counter. The source for counting was prepared in the following manner:

One mililitre of the isotope (La-140) was taken and diluted to 15 mls. with distilled water. Added 5 mg. of lanthanum (III) carrier and then an excess of a warm saturated solution of ammonium oxalate to it with stirring. Heated in a water-bath at 60°C for a few minutes (2 to 3 minutes) to digest the precipitate. Cooled in ice water with stirring.

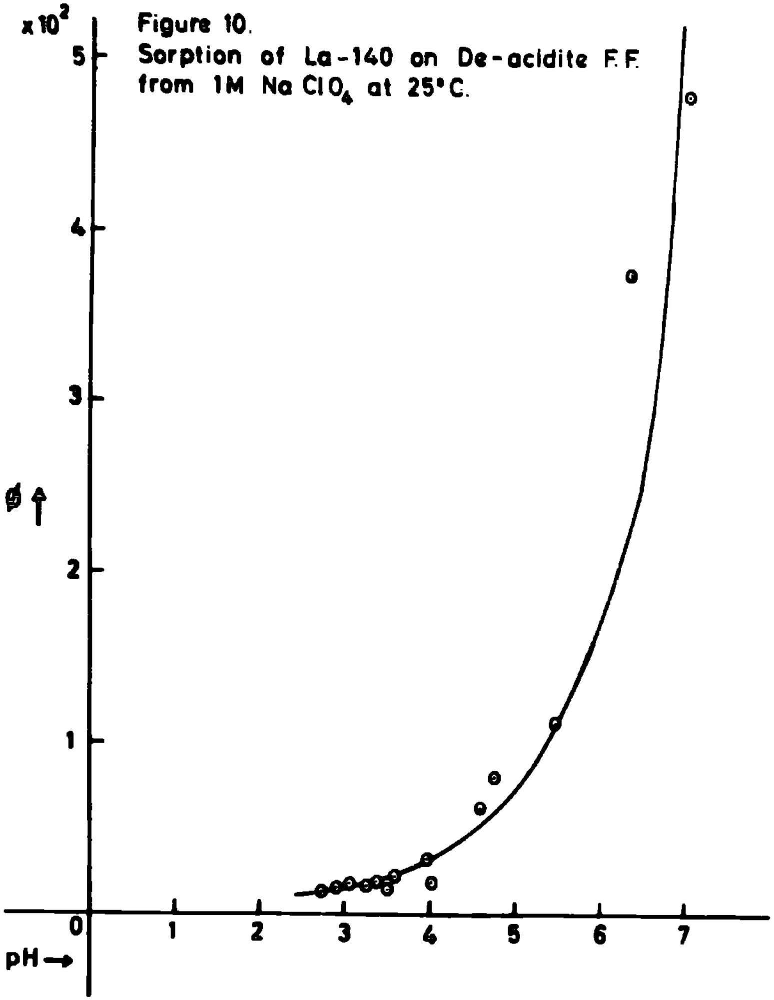


Figure 10.
Sorption of La-140 on De-acidite F.F. from 1M NaClO$_4$ at 25°C.

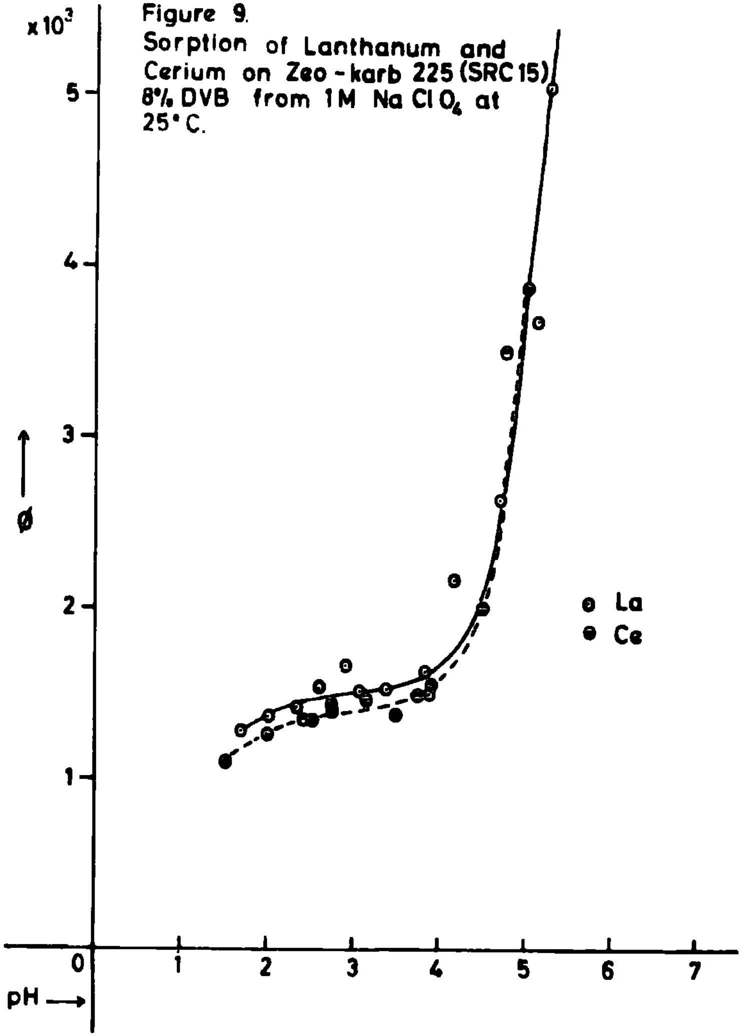


Figure 9.
Sorption of Lanthanum and Cerium on Zeo-karb 225 (SRC 15) 8% DVB from 1M NaClO$_4$ at 25°C.

Filtered off the precipitate onto a fibre-glass filter disc, and washed with ethanol and ether in that order. Dried in a vacuum dessicator and counted in gas proportional counter.

Sorption of Lanthanum (III) on De-acidite-FF (perchlorate form) from 1M Sodium perchlorate and at 25°C:

To study the sorption of Lanthanum (III) on De-acidite-FF (ClO_4^--form), the method used for a similar investigation with Yttrium (III) was followed. The $^V/m$ ratio used in this study was $^{40}/0.05$. The lanthanum-140 was used as a tracer. The solution activities before and after equilibration were measured by β-counting using Geiger-Müller liquid counting tubes (vide appendix viii). The results of the investigation are shown in figure 10 .

Sorption of Lanthanum (III) on Zeo-Karb 225 (SRC 15): 8% DVB, 100-200 mesh (Sodium-form) from 1M sodium perchlorate at 25°C:

The investigation was carried out in precisely the same manner as employed for a similar study on Yttrium (III) (page 27). The $^V/m$ ratio was $^{40}/0.05$, and time allowed for equilibration was between twelve to sixteen hours. The results obtained are shown in figure 9 .

The study of the Lanthanum (III)-Fluoride system:

The investigation was made in the usual way using Zeo-Karb 225 (SRC 15), 8% DVB, 100-200 mesh (sodium-form) as a cation-exchanger but under varying experimental conditions as detailed below:-

(1) In run (a), 0.5M sodium perchlorate was used as a medium and 0.1M sodium fluoride solution as a ligand (vide appendix iig(1)). The pH of the solution was kept between 3 to 4. The $^{v}/m$ ratio used was $^{15}/0.4$.

(2) In runs (b) and (c) the ligand solution consisted of 0.45M sodium fluoride + 0.05M hydrofluoric acid, and the medium solution was obtained by mixing sodium perchlorate and perchloric acid in a proportion so that the resulting solution was 0.45M in sodium perchlorate and 0.05M in perchloric acid (vide appendix iig(2)). The $^{v}/m$ ratios used were $^{15}/0.2$ and $^{15}/0.05$ respectively.

The data and results of the investigation are collected in the following table:-

<u>Data and Results:</u>

The concentration of free ligand viz., $[F^-]$ available for complex formation with lanthanum (III), was calculated from the total stoichiometric concentration of $[NaF]$ or $[HF]$ in the solution and the equilibrium pH of the solution using the relationship:

$$K_{HF} = \frac{[H^+]\ [F^-]}{[HF]} = 1.23 \times 10^{-3}$$ [148]

TABLE I

	$[L^-]$ mole/litre	ϕ ml. g^{-1}	$1_o\,\phi^{-1}$	ϕ_1 M^{-1}
	-	3216	-	-
(a)	1.70×10^{-3}	1735	1.8536	502
	3.55	1123	2.8638	525
	5.39	891	3.6094	484
	7.37	1587	2.0265	139*
	-	4212	-	-
(b)	3.65×10^{-5}	4168	1.0106	290*
	7.30	4083	1.0316	433
	10.95	4001	1.0527	481
	-	-	-	-
	18.25	3848	1.0946	518
		4035		
(c)	3.65×10^{-5}	3965	1.0177	485
	4.75	3947	1.0223	469
	5.48	3929	1.0270	493
	6.58	3894	1.0362	655*
	7.30	3894	1.0362	496
	8.43	3859	1.0456	541

$$\phi_1 = 493 \pm 28 \quad M^{-1}$$

Results:

The perusal of Table I, shows that over the ligand concentration range of 3.65×10^{-5} to 7.37×10^{-3} mole/litre, ϕ_1, values fluctuate without a trend. The obvious conclusion is that only one complex namely, LaF^{+2}, is being formed. Therefore ϕ_1 must be constant and give the value of β_1. The constancy of ϕ_1, with the exception of the values marked *, is evident from the above Table. The mean of 11 values gives:

$$\phi_1 = \beta_1 = 493 \pm 28 \ M^{-1}$$

Temp.	Medium	K_{HF}	pH	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
25°C	0.5M $NaClO_4$	1.23×10^{-3}	1.18 and 3.64 - 3.98	493 ± 28	x	x

Investigation of the Lanthanum (III)-Sulphate System in 1M Sodium Perchlorate at 25°C:

The system has been studied in the usual way. The $^{V}/m$ ratio used has been = $^{15}/0.4$ throughout. The pH of the equilibrated solutions varied between 3.50 and 3.70. The resin employed was Zeo-Karb 225 (SRC 15), 8% DVB, 100-200 mesh (Na-form). Lanthanum-140 was used as a tracer and its 'concentration' in solution before and after equilibrations was measured radiometrically by counting of β-particles in a Geiger Müller liquid counting tube (vide appendix viii) Stoichiometric concentrations of the ligand have been used for the calculations of the function ϕ_1, assuming that at the given pH, sodium sulphate was completely dissociated. The data and results are given in Tables II (a) and II (b):

TABLE II (a)

$[L^-]$ mole litre^{-1}	ϕ ml. g^{-1}	ϕ_1 M^{-1}
-	368	-
0.040	201	21
0.056	154	25
0.080	134	22
0.084	130	22
0.100	109	24
0.112	108	21
0.120	88	27
0.140	86	23
0.200	51	31

Over the range of the ligand concentration used, it seems only one complex, namely, $LaSO_4^+$ is being formed (vide values in the above table which are nearly constant).

Assuming that it was so, a mean value of ϕ_1 was taken as a measure of its stability ($= \beta_I$). Therefore

$\beta_I = 24 \pm 3\ M^{-1}$

TABLE II (b)

Results:

Reaction medium, temperature and pH range	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
1M $NaClO_4$ t = 25°C pH = 3.50 - 3.70	24 ± 3	x	x

The Study of the Lanthanum (III)-Oxalate Equilibria in 0.5M Sodium Perchlorate at 25°C:

The ligand solution used in this investigation consisted of 0.1M sodium oxalate, 0.3M sodium perchlorate and perchloric acid. The pH of the equilibrium solutions was maintained at 3.70 ± .01. The $^{v}/m$ ratio used in these equilibration was $^{15}/.05$. The pK2 value for the oxalic acid was determined experimentally in 0.5M sodium perchlorate and at 25°C (vide appendix vi). The concentration of the free ligand was calculated from the pH of the solutions and the pK2 of the acid using the Henderson's equation (vide appendix v(a)). For equilibrations and treatment of the radiochemical data, the procedure described in appendices iii and iv were followed. The essential data and results of the investigation are collected in the following Tables:-

Ɨ

TABLE III (a)

$[L^-]$ mole/ litre	ϕ $ml.g^{-1}$	ϕ_1 M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
7.04×10^{-5}	2097	0.356×10^5	0.0914×10^{10}	0.020×10^{10}	0.071×10^5	0.282×10^5	0.00437×10^{15}
8.80	1522	0.369*	0.0951	0.025	0.080	0.313	0.00466
10.56	1413	0.398	0.1028	0.033	0.113	0.292	0.00481
12.32	1306	0.376	0.0998	0.030	0.091	0.320	0.00487
14.08	1042	0.430	0.1123	0.032	0.145	0.221	0.00523
17.60	674	0.488*	0.1274	0.057	0.203	0.281	0.00581
26.40	412	0.556*	0.1482	0.078	0.271	0.288	0.00674
35.20	247	0.714*	0.1914	0.121	0.429	0.282	0.00857
44.00	184	0.775*	0.2100	0.140	0.490	0.286	0.00936
52.80	135	0.887*	0.2414	0.170	0.602	0.282	0.01070
	7356ǂ						
	6458**						
		0.285×10^5	0.070×10^{10}				

Mean value of $\beta_1 = (0.288 \pm 0.010) \times 10^5$ M^{-1}

*Values obtained with l_o = 6458; remaining values were obtained using l_o = 7356 $ml.g^{-1}$

ƗTwo separate resin samples were employed in these measurements.

ǂMean of six values.

**Mean of eight values.

TABLE III(b)

Reaction medium & temperature	pK_2	pH	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
0.5M $NaClO_4$ t = 25°C	3.80 ± .01	3.70 ± .01	(2.88 ± 0.10) x 10^4	1.25 x 10^8	3.30 x 10^{10}

The Study of the La (III)-α-Hydroxyisobutyrate Equilibria in 0.5M Sodim Perchlorate at 25°C:

The study was carried out as usual using Lanthanum-140 as a tracer and Zeo-Karb 225 (SRC 15): 8% DVB (100-200 mesh; Na-form) as a cation-exchanger. The pH of the equilibrium solutions was maintained at 3.49 ± 0.01. The $^v/m$ ratio used in this study was $^{15}/.05$. The ligand solution used was 0.5M α-hydroxyisobutyric acid adjusted at pH 3.50 ± .01 and $\mu = 0.5$ with respect to the cations (vide appendix ii (c)). The time allowed for the equilibria to establish was over twelve hours. The concentrations of the isotope in the aquecus phase before and after the equilibration were determined radiometrically by β-counting of the solutions using a Geiger Müller liquid counting tube (vide appendix viii). The essential data and the results of the investigation over the ligand concentration range of 4 x 10^{-3} mole/litre to 6 x 10^{-2} mole-litre are given in the following Tables:-

TABLE IV (a)

$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_1 M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta \phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
*4.315 x 10^{-3}	4456	129	3.50 x 10^4	-	-	-	-
*8.178	3398	245‡	3.62	1.12 x 10^4	65	172	1.81 x 10^6
*9.863	1901	264	3.90	1.40	84	167	1.89
*1.227 x 10^{-2}	2387	267‡	4.10	1.60	87	184	2.05
1.680	1694	299‡	4.67	2.17	119	182	2.29
2.129	1259	334‡	5.29	2.79	154	181	2.55
2.588	1024	347‡	5.60	3.10	167	186	2.67
2.980	781	405‡	6.54	4.04	225	178	3.07
3.451	666	416‡	6.80	4.30	236	182	3.17
4.314	324	473	7.84	5.34	293	181	3.61
5.176	240	539	9.02	6.52	359	181	4.10
	6942						
	10218‡						
		180 ± 15	2.5 x 10^4				

Mean value of β_1 = 181 ± 3.74 M^{-1}

*Ligand concentration viz. $[L^-]$, were calculated from the observed pH values of the solution, which for some unknown reason had deviated from the expected value of 3.49 ± .01. The maximum deviation was noted in solution no. 3, being equal to - 0.19 pH units.

‡The values were calculated with l_o = 10218; the actual l_o value obtained in the particular run.

TABLE IV (b)

Results:

Reaction medium and temperature	pK_{HL}	pH	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
0.5M $NaClO_4$ t = 25°C	3.61	3.49 ± .01	181 ± 3.74	7.8×10^3	7.5×10^4

CHAPTER II

The Study of the Cerium (III)-Complexes with Chloride, Sulphate and Oxalate Ligands

Introduction:

The present work on the complexes of cerium (III) is in fact an extension of the work which had already been done in this laboratory[101] in the chloride media with such organic ligands as acetate, lactate, glycollate and α-hydroxyisobutyrate. Since the results obtained did not show very good agreement with those which appeared in the literature subsequently and had been obtained by ion-exchange and other techniques in perchlorate media[117,118,119], it was thought that the probable complexing of the cerium (III) by chloride ions might be the cause of this disagreement. It, therefore, became imperative to study the cerium (III)-chloride system in a perchlorate medium using an ion-exchange technique. As will be seen later, this investigation did reveal a significant complexing of cerium (III) by chloride ions, though the results of similar investigations published in recent years by the solvent extraction technique suggest a different story[120,121]. The study of the cerium (III)-sulphate system was undertaken with a view to checking on the reported results of a similar study by Fronaeus[122]. The agreement in the values of the successive stability constants with those reported by Fronaeus was found to be very close. The investigation was extended to the cerium (III)-oxalate system in order that the results obtained from similar studies involving other members of the lanthanum series and the oxalate, could be compared between themselves.

These investigations have been made with cerium-144-praesodymium-144 as a tracer and Zeo-Karb 225 (SRC 15): 8% DVB as a cation-exchanger in 0.5M or 1M sodium perchlorate solutions. The pH of the equilibrium solutions were maintained between 3.0 and 4.0. The tracer concentrations were determined radiometrically by β-counting of the tracer solutions before and after equilibration using a Geiger-Müller liquid counting tube (vide appendix viii) after praesodymium-144 had attained equilibrium with its parent. A preliminary distribution study of cerium-144 between the resin and aqueous phases vis-a-vis a varying hydrogen ion concentration of the solution was made to make sure that cerium (III), did not behave differently from yttrium (III) and lanthanum (III) in this respect. The similarity of yttrium (III), lanthanum (III) and cerium (III) distribution isotherms obviated the necessity of similar investigations with other elements of the lanthanum series.

Sorption of Cerium (III) on an 8% cross-linked cation-exchanger from 1M Sodium Perchlorate at 25°C:

Sorption of cerium (III) on Zeo-Karb 225 (SRC 15) (100 to 200 mesh) was studied precisely in the manner employed for similar investigations with yttrium (III) and lanthanum (III), using cerium-144 as a tracer. The isotherm obtained is shown in figure 9.

Investigation of the Cerium (III)-Chloride system in 0.5M Ammonium Perchlorate at 25°C:

The cerium (III)-chloride system was studied much in the manner as employed for the study of yttrium (III)-chloride system, using cerium-144 as a tracer and 8% cross-linked cation-exchanger (Zeo-Karb 225 - SRC 15). The essential data and the results of the investigation are given below:

$^{v}/m$ = $^{20}/.05$

pH = 3.56 ± 0.01

Range of ligand concentration = 0.05 to 0.35 mole/litre.

Time allowed for equilibrations = 24 hours.

TABLE V (a)

$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_1 M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
0.00	12666	2.53	2.60	-	-	-	-
0.05	11113	2.76	4.00	1.40	0.23	-	-
0.10	9856	2.85	3.00	0.40	0.32	1.25	4.6
0.15	8880	2.84	4.87	2.30	0.31	-	-
0.20	7496	3.45	4.25	1.70	0.92	1.84	7.1
0.25	6597	3.68	4.64	2.00	1.15	1.74	7.3
0.30	5589	4.22	5.11	2.50	1.69	1.48	6.7
0.35	5290	3.98	6.04	3.40	1.45	2.34	10.2

Mean $\beta_1 = 1.73\ M^{-1}$

TABLE V (b)

Results:

Reaction medium temperature and pH	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
0.5 NH_4ClO_4 t = 25°C pH = 3.56	1.73	2	x

Note:

In the above investigation, addition of hydrazine hydrate to the tracer solution did not make much difference in the distribution of the tracer between the resin and aqueous phases, showing that cerium was predominantly in the tervalent state in solution.

Investigation of the Cerium (III)-Sulphate System in 1M Sodium Perchlorate and at 25°C:

The cerium (III)-sulphate system was studied under nearly the same conditions as those used by Fronaeus[122]. Zeo-Karb 225 (SRC 15) was used as a cation-exchanger and cerium-144 as a tracer. The pH of the solutions was maintained at 3.80 ± .01. The $^{V}/m$ ratio was $^{15}/.2$, and over twelve hours were allowed for equilibrations. The concentration of the isotope in solutions before and after the equilibration were measured radiometrically as usual by β-counting of the active solutions. The results of the investigations are collected in Tables VI (a) and VI (b). It may also be mentioned here that in the calculation of the functions ϕ_1, f and g, the stoichiometric concentrations of the sulphate ions in the solutions were used as 'ligand' concentrations, assuming that under the conditions sodium sulphate is almost completely dissociated to give only sulphate ions.

TABLE VI (a)

$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_1 M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
-	1107	33.8	920	-	-	-	-
0.012	756	38.7	901	-	-	-	-6.54×10^3
0.024	559	40.8	1087	167	7.0	23.9	+6.51
0.036	452	40.2	1181	261	6.4	40.8	10.55
0.048	357	43.8	1272	352	10.0	35.2	10.41
0.060	292	46.5	1360	440	12.7	34.6	10.93
0.072	250	47.6	1417	497	13.8	36.0	11.44
0.084	196	55.3	1614	694	21.5	32.3	12.40
0.096	181	53.3	1598	678	19.9	34.1	12.53
0.120	132	61.4	1849	929	27.6	33.7	14.21
0.144	105	66.3	2014	1094	32.5	33.7	15.31
0.168	86	70.7	2169	1249	36.9	33.8	16.38
0.216	60	80.8	2513	1593	47.0	33.9	18.74

Rejecting the first two values of β_1, which carry large errors due to the sizes of Δf and $\Delta\phi_1$ and taking the mean of the remaining values, $\beta_1 = 34 \pm 1.$ M^{-1} The plot of $\Delta f/L^-$ against $\Delta\phi_1/L^-$ was also tried and found to be linear with a slope equal to 34 (= β_1). (vide figure 11c)

TABLE VI (b)

Results:

Reaction medium, temperature and pH	β_1 M^{-1}	β_2 M^{-2}	β_3 M^{-3}
1M $NaClO_4$ t = 25°C pH = 3.80 ± .01	34 ± 1	271	800

Investigation of the Cerium (III)-Oxalate System in 0.5M Sodium Perchlorate and at 25°C:

The system was investigated with 8% cross-linked cation-exchanger (Zeo-Karb 225 (SRC 15)). Cerium-144 was used as a tracer. The $^V/m$ ratio was kept the same throughout, namely, $^{15}/.2$. The pH of the equilibrium solutions was also kept the same at 3.80 ± 0.01. The ligand solution was prepared as described in appendix ii (e). The concentration of the free ligand was calculated from its stoichiometric concentration, the pH of the solution and the pK_2 of oxalic acid which was determined experimentally (vide appendix vi) by Henderson's equation (vide appendix v(a)). At pH 3.80 ± .01, and using the pK_2 value of 3.80 ± .01 (vide appendix vi), the concentration of free ligand,

$$[L^-] = 0.50\ [HL]$$

where

$[L^-]$ = concentration of free ligand.

$[HL]$ = Stoichiometric concentration of the ligand.

The concentrations of the isotope, before and after equilibration were measured radiometrically as described in appendix viii. The essential data and results of the investigation are given in tables VII (a) and VII (b).

TABLE VII (a)

$[L^-]$ mole/litre	ϕ $ml.g^{-1}$	ϕ_1 M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
-	7117	0.32×10^5	0.087×10^{10}	-	-	-	-
6.0×10^{-5}	1849	0.48	0.13	0.043×10^{10}	0.16×10^5	0.269×10^5	0.74×10^{13}
9.0	1264	0.52	0.14	0.053	0.20	0.265	0.82
1.4×10^{-4}	731	0.63	0.18	0.093	0.31	0.300	1.11
1.8	529	0.70	0.20	0.113	0.38	0.297	1.23
2.0	440	0.77	0.22	0.133	0.45	0.296	1.35
2.2	360	0.86	0.25	0.163	0.54	0.302	1.53
2.4	331	0.86	0.25	0.163	0.54	0.302	1.54
3.0	231	1.00	0.30	0.213	0.68	0.313	1.83
4.0	148	1.19	0.36	0.273	0.87	0.314	2.17

Ignoring the first two values of β_1 and taking the mean of the rest, we have:

$$\beta_1 = 0.303 \pm 0.002 \times 10^5 \ M^{-1}$$

TABLE VII (b)

Reaction medium, temperature and pH	pK_2 (Oxalic acid)	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
0.5 Na ClO_4 t = 25°C pH = 3.80 ± .01	3.80 ± .01	$3.03 \pm 0.02 \times 10^4$	1.87×10^8	4×10^{11}

CHAPTER III

The Study of the Complexes of Europium (III) with Sulphate, Oxalate, α-Hydroxyisobutyrate and Glycollate Ligands

Introduction:

The complexes of Europium (III) with sulphate, oxalate, α-hydroxyisobutyrate and glycollate ligands have been studied under the same conditions as those used for similar studies involving these ligands and lanthanum, cerium and yttrium. Europium - 152 + 154 was used as a tracer, and its concentrations in solution before and after equilibration were determined radiometrically by counting γ-radiations in the energy range of 1.00 to 1.28 Mev. using a well-type Sodium Iodide (Thallium-activated) crystal and a single channel pulse-height analyser (vide appendix viii) Zeo-Karb 225 (SRC 15), 8% DVB, 100 to 200 mesh in the sodium form was used as a cation-exchanger.

Investigation of the Europium (III)-Sulphate system in 1M Sodium Perchlorate at 25°C:

The Europium (III)-Sulphate system was investigated using nearly the same conditions as those used in the studies of the lanthanum (III)- and cerium (III)-sulphate systems. A $^{v}/m$ ratio of $^{10}/.1$ was used throughout, and the pH of the solution was maintained between 3.70 and 3.80. 0.5M sodium sulphate solution was used as a ligand. The results of the investigation are contained in Tables VIII (a) and VIII (b).

TABLE VIII (a)

$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_1 M^{-1}	f M^{-2}	Δf M^{-2}	$\Delta \phi_i$ M^{-1}	β_1 M^{-1}	g M^{-3}
-	1100	32.30	880	-	-	-	-
0.01	829	32.69	1017	-	-	-	-
0.02	656	33.84	1016	-	-	-	-
0.03	529	35.98	1039	159	3.68	43.21	1.21 x 10^4
0.04	444	36.94	1077	197	4.64	42.46	1.22
0.05	383	37.44	1106	226	5.14	43.97	1.25
0.06	323	40.09	1165	285	7.79	36.58	1.25
0.07	293	39.35	1170	290	7.05	41.13	1.28
0.08	251	42.28	1241	361	9.98	36.17	1.32
0.09	217	45.21	1317	437	12.91	33.84	1.37
0.10	198	45.55	1339	459	13.25	34.64	1.40
0.11	170	49.73	1448	568	17.43	32.59	1.49
0.12	162	48.25	1426	546	15.95	35.02	1.48
0.13	135	54.98	1602	722	22.68	31.83	1.64
0.14	124	56.25	1645	765	23.95	31.94	1.68

Mean value of $\beta_1 = 36.95 \pm 4.34$ M^{-1}.

TABLE VIII (b)

Results:

Reaction medium, pH and temperature	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
1.0M $NaClO_4$ pH = 3.70 to 3.80 t = 25°C	37 ± 4	354	1200

Investigation of the Europium (III)-Oxalate System in 0.5M Sodium perchlorate at 25°C:

Europium (III)-oxalate equilibria were investigated under precisely the same conditions as those employed for a similar study of the cerium (III)-oxalate system. The essential data and the results of the investigation are collected in Tables IX (a) and IX (b):

TABLE IX (a)

$^{v}/_{m} = {}^{15}/_{0.2}$

pH = 3.80 ± 0.01

$pK_{2(HL)}^{*} = 3.80 \pm 0.01$

$[L^-] = 0.5\ [HL]$

*Measured as described in appendix vi

TABLE IX (a)

$[I^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_I M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
-	3431	0.65 x 10^5	0.36 x 10^{10}	-	-	-	-
2 x 10^{-5}	1336	0.78	0.44	0.08 x 10^{10}	0.13 x 10^5	0.615 x 10^5	0.0465 x 10^{15}
4	719	0.94	0.54	0.18	0.29	0.621	0.0575
6	465	1.06	0.62	0.26	0.41	0.634	0.0665
8	320	1.22	0.72	0.36	0.57	0.631	0.0767
-	3155	-	-	-	-	-	-
1 x 10^{-4}	232	1.26	0.76	0.40	0.61	0.656	0.0808
2	79	1.94	1.20	0.84	1.29	0.651	0.1245
3	39	2.66	1.66	1.30	2.01	0.647	0.1700
4	28	2.79	1.76	1.40	2.14	0.654	0.1788
5	17	3.69	2.34	1.98	3.04	0.651	0.2362
6	14	3.74	2.38	2.02	3.09	0.654	0.2394
7	10	4.49	2.87	2.51	3.84	0.654	0.2878
1 x 10^{-3}	7	4.50	2.88	2.52	3.85	0.655	0.2879
2	1.72	9.16	5.91	5.55	8.51	0.652	0.5847
3	0.68	15.58	10.08	9.72	17.93	0.651	0.9964
4	0.32	24.96	16.16	15.80	24.31	0.650	1.5972

$\beta_I = 0.652 \pm 0.025 \times 10^5\ M^{-1}$ (First four values rejected)

$= 6.52 \pm 0.25 \times 10^4\ M^{-1}$

TABLE IX (b)

Results:

Reaction medium, pH and temperature	$pK_{2(HL)}$	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
0.5 $NaClO_4$ pH = 3.80 ± .01 t = 25°C	3.80 ± .01	6.52×10^4	6.27×10^8	1.5×10^{12}

Investigation of the Europium (III)-α-Hydroxyisobutyrate Equilibria in 0.5M Ammonium perchlorate at 25°C:

The Europium (III)-α-hydroxyisobutyrate system has been studied in the usual way, using Zeo-Karb 225 (SRC 15), 8% DVB (ammonium-form) as a cation-exchanger and Europium-152 and 154 as a tracer. At low ligand concentrations, the $^v/m$ ratio used was $^{15}/.2$. At high ligand concentrations it was decreased to $^{15}/.4$. The ligand solution was 0.5M α-hydroxyisobutyric acid neutralised to pH 3.51 ± 0.01 and had an ammonium ion concentration of 0.5M made up by the addition of ammonium perchlorate (vide appendix ii (c)). The pH of the equilibrium solutions was in the range of 3.27 to 3.49 when low ligand concentrations were used. At higher ligand concentrations, a constant pH of 3.59 was maintained. The ligand concentration varied over the range 2.7×10^{-3} to

6.4×10^{-2} mole $litre^{-1}$. The 'concentration' of the isotope in the solution was determined radiometrically as described in the introduction and in appendix viii. The essential data and the results of the investigation are given in the Tables X (a) and X (b).

TABLE X (a)

$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_1 M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
-	5646'	-	-	-	-	-	-
-	5859'''	-	-	-	-	-	-
-	6118''	-	-	-	-	-	-
-	5763''''	-	-	-	-	-	-
-	-	515 ± 25	1.90×10^5	-	-	-	-
2.712×10^{-3}	1845'	760	3.01	1.11×10^5	245	453	5.18×10^7
3.287	1785''	738	3.12	1.22	223	547	5.81
3.546	1576'''	766	3.24	1.34	251	534	5.92
3.868	1390'	793	3.38	1.48	278	532	6.10
4.471	1410''	747	3.33	1.43	232	625	6.17
5.019	1062'	860	3.74	1.84	345	533	6.64
6.365	791'	964	4.26	2.36	449	526	7.49
7.062	708'''	1030	4.58	2.68	515	520	7.83
7.957	628''	1098	4.92	3.02	583	520	8.34
8.178	528'	1185	5.28	3.38	670	504	9.14
1.008×10^{-2}	452'''	1187	5.44	3.54	672	527	9.06
1.096	365'	1320	6.06	4.16	805	517	10.01
1.260	306''	1507	6.98	5.08	992	512	11.38
1.334	221''''	1879	8.66	6.76	1364	496	14.03
1.703	170''	2054	9.68	7.78	1539	505	15.46
2.157	111''	2509	11.99	10.09	1994	506	18.91
2.166	92''''	2815	13.43	11.53	2300	502	21.16
2.487	81''''	2820	13.60	11.70	2305	508	21.28
2.901	55''''	3577	17.32	15.42	3062	503	26.97
4.885	23''''	5097	25.31	23.41	4582	510	38.56
5.374	17''''	6271	31.22	29.32	5756	509	47.43
5.862	13''''	7540	37.63	35.73	7052	509	57.02
6.341	11''''	8232	41.18	39.28	7717	509	62.26

Mean value of $\beta_I = 516^* \pm 13$ M^{-1}

*Values underlined were rejected in taking the mean.

Note: (Table X (a))

The experiment was completed in four runs. The l_0 values obtained for each run separately are given at the top of the Table X (a) in column 2 and they are marked ', '', ''', ''''. The ϕ values obtained in the presence of the ligand corresponding to these are also marked identically. In each individual run the ϕ_1 values were calculated from the appropriate l_0 and ϕ values.

TABLE X (b)

Results

Reaction medium & temperature	pH range	$pK_{(HL)}$	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
0.5M NH_4ClO_4 25°C	3.27 to 3.59	3.61	516 ± 13	7.67 x 10^4	10^6

Investigation of the Europium (III)-Glycollate System in 0.50M Ammonium Perchlorate at 25°C:

Europium (III)-Glycollate equilibria in 0.5 M ammonium perchlorate have been studied by the method employed for a similar study involving yttrium (III) and the glycollate ligand. The necessary solutions were prepared in the manner described in appendix ii. The cation-exchanger used was Zeo-Karb 225 (SRC 15) of 8% cross-linkage and in the ammonium form. The procedure used for equilibration and the treatment of the radiochemical data are described in appendices iii, iv, respectively. The $^{v}/m$ ratio was kept the same throughout the run. The pH of the equilibrium solutions was also kept constant at 3.36. A europium-152 + 154 mixture was used as a tracer and its 'concentration' in solution before and after equilibration was determined radiometrically by γ-counting in the energy range of 1.00 to 1.28 Mev. as described in appendix viii. The essential data and results are given in Tables XI (a) and XI (b).

TABLE XI (a)

$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_1 M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
-	4006	290	0.22×10^5	-	-	-	-
0.00177	2270	433	0.46	0.24×10^5	143	168x	1.69×10^7
0.00354	1506	470	1.37	1.15	180	639x	4.72
0.00445	1124	575	1.03	0.81	285	284	3.59
0.00532	896	652	1.21	0.99	362	273	4.01
0.00714	744	613	1.34	1.12	323	347	2.51
0.00885	482	826	1.79	1.57	536	293	5.25
0.0133	267	1054	2.48	2.26	764	296	6.73
0.0177	167	1298	3.19	2.97	1008	295	8.28
0.0221	111	1586	4.01	3.79	1296	292	10.11
0.0266	78	1896	4.89	4.67	1606	291	12.09
0.0310	56	2276	5.96	5.74	1986	289	14.52

Rejecting the first two values and taking the mean of the rest, $\beta_1 = 296 \pm 19$ M^{-1}

TABLE XI (b)

Reaction medium and temperature	pH	pK_{HL}	β_1 M^{-1}	β_2 M^{-2}	β_3 M^{-3}
0.5M NH_4ClO_4 t = 25°C	3.36	3.46	296 ± 19	6.63×10^4	3×10^6

CHAPTER IV

The Study of Gadolinium (III) Complexes with Sulphate, Oxalate and α-Hydroxyisobutyrate Ligands in Sodium Perchlorate Media at 25°C

Introduction:

The solution-chemistry of gadolinium (III) in respect of its complexing properties with sulphate, oxalate and α-hydroxyisobutyrate ligands in sodium perchlorate media and at 25°C has been studied by a cation-exchange technique. The results obtained are reasonably comparable with those published, recently in respect of these systems and obtained by ion-exchange and other techniques. In the present studies, gadolinium-153 and Zeo-Karb 225 (SRC 15), 8% DVB etc. (vide appendix (i)) have been used as a tracer and a cation-exchanger respectively. The procedures adopted for equilibrations, treatment of radiochemical data and the calculation of the step stability constants are described in appendices (iii) and (iv) and the general introduction (p. 18). The 'concentrations' of the tracer in solutions before and after equilibrations were measured radiometrically by counting of γ-radiations in the energy range of 97 to 103 K.e.v. using a well-type sodium iodide (thallium activated) crystal and a single channel pulse-height analyser (vide appendix (viii)).

Investigation of the Gadolinium (III) Sulphate system in 1M Sodium Perchlorate:

In the investigation of the gadolinium (III)-Sulphate system, the procedure employed for the study of identical systems involving lanthanum (III), cerium (III) and europium (III) and the ligand sulphate, was followed. The $^{V}/m$ ratio ($^{15}/.2$) was maintained throughout. The pH of the equilibrium solutions was kept at nearly 3.80. The essential data and the results of the investigation are collected in Tables XII (a) and XII (b).

TABLE XII (a)

$[L^-]$ mole/litre	ϕ $ml.g^{-1}$	ϕ_1 M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
-	1118	35.50	1.08×10^3	-	-	-	-
0.011	812	34.25	1.33	-	-	-	-
0.020	628	39.01	1.21	0.13	3.51	37.03	9936
-	1046	-	-	-	-	-	-
0.030	476	39.92	1.27	0.19×10^3	4.42	42.99	11117
0.040	384	43.10	1.34	0.26	7.60	34.21	10499
0.050	328	43.78	1.39	0.31	8.28	37.44	11275
0.060	284	44.72	1.44	0.36	9.22	39.04	11755
0.070	241	47.72	1.52	0.44	12.22	36.01	12048
0.080	214	48.60	1.56	0.48	13.10	36.64	12426
-	1118	-	-	-	-	-	-
0.090	185	56.04	1.76	0.68	20.54	33.10	13475
0.100	160	59.87	1.88	0.80	24.37	32.83	14339
0.110	141	63.00	1.99	0.91	27.50	33.09	15125
0.120	131	63.00	2.00	0.92	27.50	33.45	15296
0.130	128	59.50	1.93	0.83	24.00	35.42	14964
0.140	112	64.16	2.07	0.99	28.66	34.54	15992

Mean value of $\beta_1 = 35.83 \pm 2.76\ M^{-1}$

TABLE XII (b)

Reaction medium, pH and temperature	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
1M $NaClO_4$ pH = 3.80 t = 25°C	35.83 ± 2.76	270	1600

Investigation of the Gadolinium-Oxalate System in 0.5 M Sodium Perchlorate at 25°C:

The gadolinium-oxalate system was studied under the same conditions as those used for the identical studies with cerium (III) and europium (III). The $^v/m$ ratio, however, was changed to $^{15}/.1$ in order to obtain a better distribution of the metal between the resin and solution phases in the absence of the ligand. The pH of the equilibrium solutions was maintained at 3.80 ± .01. The essential data and the results of the investigation are given in Tables XIII (a) and XIII (b).

TABLE XIII (a)

$[L^-]$ mole/litre	ϕ $ml.g^{-1}$	ϕ_1 M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
-	7094	0.86×10^5	0.670×10^{10}	-	-	-	-
1.00×10^{-5}	3799	0.87	-	-	-	-	-
2.00	2374	0.99	0.788	0.118×10^{10}	0.13×10^5	0.908×10^5	0.093×10^{15}
3.00	1725	1.04	0.833	0.163	0.18	0.906	0.096
4.25	1252	1.04	0.888	0.218	0.18	$\underline{1.211}$	0.114
5.50	950	1.18	0.954	0.284	0.32	0.887	0.107
7.00	715	1.28	1.044	0.374	0.42	0.890	0.117
8.00	594	1.37	1.113	0.443	0.51	0.869	0.123
9.00	530	1.38	1.126	0.456	0.52	0.877	0.124
1.00×10^{-4}	438	1.52	1.242	0.572	0.66	0.867	0.136
1.20	363	1.54	1.271	0.601	0.68	0.884	0.139
1.40	294	1.65	1.363	0.693	0.79	0.877	0.149

Rejecting the value underlined and taking the mean of the rest, $\beta_1 = 0.885 \pm 0.013 \times 10^5$ M^{-1}

TABLE XIII (b)

Reaction medium, pH and temperature	$pK_{2_{HL}}$	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
0.50M $NaClO_4$ pH = 3.80 ± .01 t = 25°C	3.80 ± .01	$8.85 \pm 0.13 \times 10^4$	9.39×10^8	2×10^{12}

Investigation of the Gadolinium (III)-α-Hydroxyisobutyrate System in 0.50M Sodium Perchlorate at 25°C:

Gadolinium-α-hydroxyisobutyrate equilibria in 0.50M sodium perchlorate were studied in the same manner as employed for the study of the other identical systems involving yttrium (III), lanthanum (III) etc. and α-hydroxyisobutyric acid. The ratio $^{V}/m$, however, was changed to $^{10}/.1$ to have a suitable distribution of the tracer between the resin and the solution phases. The data and the results of the investigation are collected in the Tables XIV (a) and XIV (b).

TABLE XIV (a)

$[L^-]$ mole/litre	ϕ $ml.g^{-1}$	ϕ_1 M^{-1}	f M^{-2}	Δf M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
-	4086	550	2.45×10^5	-	-	-	-
2.356×10^{-3}	1566	683	3.19	0.74×10^5	133	556	0.41×10^8
4.712	857	800	3.87	1.42	250	568	0.49
6.640	586	899	4.42	1.97	349	564	0.54
8.854	411	1010	5.03	2.58	460	561	0.61
1.107×10^{-2}	315	1081	5.47	3.02	531	569	0.65
1.328	234	1239	6.30	3.85	689	559	0.75
1.549	184	1369	7.00	4.55	819	556	0.82
1.771	154	1442	7.43	4.98	892	558	0.87
1.992	128	1552	8.03	5.58	1002	557	0.93
2.214	107	1680	8.73	6.28	1130	556	1.01
2.435	90	1823	9.51	7.06	1273	555	1.09
2.656	61	2484	12.93	10.48	1934	542	1.48
2.878	42	3346	17.43	14.98	2796	536	1.99
3.099	26	5039	26.26	23.81	4489	530	2.99

Mean value of $\beta_1 = 555 \pm 11$ M^{-1}

TABLE XIV (b)

Reaction medium and temperature	pK_{HL}	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
0.50 $NaClO_4$ t = 25°C	3.61	555 ± 11	6.1×10^4	8×10^5

CHAPTER V

Study of the Complexes of Actinium (III) with Sulphate, Oxalate and α-Hydroxyisobutyrate Ligands in Sodium Perchlorate Media at 25°C

Introduction:

Actinium was discovered in 1898 by Debierne[123] and about the same time independently by Giesel[124]. The name 'actinium' is due to Debierne. Boltwood[125] in 1908 demonstrated that the ratio of uranium to actinium in uranium minerals was nearly constant, indicating a genetic relationship between the two. The independent nature of the actinium series originating from some isotope of uranium (uranium-235, discovered in 1935 by Dempster[126]) was established in 1929 by Aston[127]. He found by mass-spectrographic analysis that the ratio of the masses 207 to 208 was much greater in lead from uranium ore than in ordinary lead. Since the end products of the radium and thorium series are lead isotopes of masses 206 and 208, the lead isotope of mass 207 must belong to the actinium series. The isotope actinium-228 was discovered by Hahn[128] in 1908. It is produced by the natural decay of thorium-232.

$$Th^{232} \xrightarrow{\alpha} Ra^{228} \xrightarrow{\beta} Ac^{228} \xrightarrow{\beta} \cdots\cdots$$

It has a half life of 6·13 hours and is a strong β-emitter - the energy of its β-radiation is 2.00 Mev , and has been used considerably as an actinium tracer in the study of actinium chemistry. Because of the characteristic absence of 5f. electrons, actinium is regarded as a homologue of lanthanum which is characterised by the absence of 4f. electrons. The carrying of actinium by lanthanum precipitates, the insolubilities of their hydroxides, fluorides, oxalates, carbonates etc., the identical volatilities of their halides and the constant tervalency of actinium and lanthanum ions in solution establish the homology of the two. The difference in the sizes of their ionic radii can account for the differences in their basicities. Most of the work done on the tracer chemistry of actinium concerns its co-precipitation by inert carriers[129,130] and the x-ray diffraction analysis of its compounds[131]. No information, whatever, is available on the quantitative study of the complexes of actinium. It was, therefore, decided that an effort should be made to study the sulphate, oxalate and α-hydroxyisobutyrate systems of actinium (III) under the same conditions as those used for the study of metal ions previously dealt with so that the results obtained in respect of its behaviour in solution in the presence of these ligands could be compared with lanthanum. Another reason for attempting this tedious study was the unique position of actinium as a precursor of the actinide elements. It might be pointed out here that the interest in the solution chemistry of these elements particularly uranium and the transuranic elements developed mostly from the exigencies of the preparation and subsequent treatment of nuclear fuels and the availability of techniques such as ion-exchange and solvent extraction. In the present work actinium-228 has been used as a tracer and the investigation of the aforementioned systems of actinium (III) has been made by a cation-exchange method using Zeo-Karb 225 (SRC 15), 8% DVB, 100-200 mesh (sodium form). Actinium-228 was separated from an aged sample of thorium nitrate by a solvent-extraction method using a cupferron-chloroform mixture (cf. extraction of lanthanum 140 from barium[140])

Separation of Actinium-228 from Aged Thorium Nitrate:

The conventional methods for the separation of actinium-228 from aged thorium nitrate were abandoned because apart from being lengthy and tedious, they did not give a sufficient yield of the isotope for use in the proposed study. Eventually the cupferron-chloroform extraction was selected for its comparative rapidity and simplicity. The difficulty of low yield and hence also of low initial solution activity was overcome by the simultaneous running of a series of extractions and the subsequent reduction of pH, ~~V/m ratio~~ resin weight and the time allowed for attainment of equilibrium. The method is outlined below:-

(a) Dissolve about 5 gm. of the aged thorium nitrate in a small amount of 60-70% nitric acid. Add 5 mg of barium carrier as barium nitrate solution. Precipitate barium (radium) nitrate with fuming nitric acid - adding a little at a time, stirring and cooling under a running tap of cold water or in well-pounded ice. Separate the precipitate by centrifugation and dissolve in a very small quantity of distilled water. Set aside for a day to let actinium-228 grow in.

(b) Treat the acid solution of barium (radium) nitrate (pH 2) with nearly 3 ml of a 5% aqueous solution of cupferron and 5 ml of chloroform. Shake mechanically for 5 to 10 minutes. Separate the organic phase containing thorium and discard.

(c) Increase the pH of the aqueous phase to 6 by aqueous ammonia. Add ca. 10 ml of 0.9M ammonium acetate. Shake. Add ca. 3 ml of the 5% aqueous cupferron solution. Shake for 2 to 3 minutes. Add 5 ml chloroform. Shake mechanically for 15 minutes. Separate the aqueous phase and re-extract with more cupferron-chloroform mixture (3:5 by volume).

(d) Strip the organic phase with 3N. nitric acid.

(e) Dilute the acid solution containing actinium-228 with distilled water. Add 5 mg of lead carrier as lead nitrate. Pass hydrogen sulphide to remove lead and bismuth.

Filter off the precipitate. Test for lead by dithizone and repeat the hydrogen sulphide treatment if necessary.

(f) Evaporate the solution to near dryness in a china dish. Transfer to a platinum crucible and ignite.

(g) Take up actinium-228 with 1M. perchloric acid. Neutralise to the required pH using standard alkali. Make up the cationic strength by adding the calculated amount of sodium perchlorate.

Radiochemical purity of Actinium-228:

This was checked by following the decay of the isotope over several half-lives by counting of β-particles in a Geiger Müller liquid counting tube. On following the above procedure the half-life obtained from the decay curve agreed well with the literature value (6.13 hours).

Preparation of samples for equilibrations:

10 mg of the resin (Zeo-Karb 225, 8% DVB, 100 to 200 mesh sodium-form) were placed in a 'polythene' capsule along with a known volume of a standard ligand solution. A known volume of the isotope solution was added immediately after preparation. Made up the volume (12 or 14 ml as e.g. in the following investigations) with standard sodium perchlorate (0.500M or 1.00M). Sealed the capsule and placed it in a shaking device (vide appendix (iii), figure 12) for just over an hour~~s~~. An

initial investigation showed that in all the systems in question, the equilibrium is attained in less than an hour.

Radiochemical assay:

The 'concentrations' of actinium-228 in solutions before and after equilibrations were measured radiometrically by counting β-particles in a Geiger Müller counting tube (vide appendix (viii)). Due corrections for background, dead-time and decay of the isotope over the period of the measurement of initial and final activities were made. For decay corrections use was made of the relationship:

$$A_t = A_o \; e^{-\lambda t}$$

where A_t = radioactivity of the solution after time interval t, in counts per minute (c.p.m.) per 10 ml solution.

A_o = radioactivity of the solution at zero time in c.p.m. per 10 ml solution.

λ = decay constant = $\frac{0.693}{t_{\frac{1}{2}}}$ ($t_{\frac{1}{2}}$ = half-life of the isotope).

t = time interval in units used for half-life.

e = exponential constant.

Investigation of the Actinium (III)-Sulphate System in 1M Sodium Perchlorate at 25°C:

This system was studied in the usual way with actinium-228 as a tracer and Zeo-Karb 225 (SRC 15) as a cation-exchanger. The pH of the solutions was kept between 3.20-

3.30, and the $^{v}/m$ ratio at $^{12}/.01$. The pH of the solution was reduced to give a favourable distribution of the tracer between the resin and the solution phases. At the usual pH of 3.70-3.80 used in similar studies with lanthanum and the lanthanides, actinium showed strong sorption on the resin (due to its stronger basic character). This could be tolerated if high initial activities were available. The increase ~~reduction~~ of $^{v}/m$ ratio to ~~sheer~~ $^{12}/.01$ was necessary for the same reason. The essential data and results are given in the following Tables XV (a) and XV (b).

TABLE XV (a)

$[L^-]$ mole/litre	ϕ $ml.\,g^{-1}$	ϕ_1 M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
-	790*	17.25	233	-	-	-	-
0.050	395	20.00	290	57	3.25	17.54	1.49×10^3
0.080	284	22.27	321	88	5.02	17.53	1.46
0.120	197	25.08	367	134	7.83	17.11	1.62
0.160	146	27.57	411	178	10.32	17.25	1.79
0.220	97	32.47	491	258	15.22	16.95	2.09
0.260	82	33.21	511	278	15.96	17.42	2.17
0.300	66	36.56	566	333	19.31	17.24	2.38
0.340	55	39.30	613	380	22.05	17.23	2.55

Mean value of $\beta_1 = 17.28 \pm 0.19\ M^{-1}$

*Mean of six values.

TABLE XV (b)

Reaction medium, temperature and pH	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
1.00M $NaClO_4$ t = 25°C pH = 3.20 - 3.30	17.3 ± 0.2	66	x

Investigation of the Actinium (III)-Oxalate System in 0.50M Sodium Perchlorate at 25°C:

The actinium (III)-oxalate system has been studied in the same way as that employed for the investigations of the identical system of lanthanum (III). The pH of the complexing solutions and the V~~/m ratio~~ resin weight; however, were reduced for reasons already explained (page 110). The essential data and results of the investigation are given in Tables XVI (a) and XVI (b).

TABLE XVI (a)

$^{v}/_{m}$ = $^{14}/_{.01}$
pH = 3.40 ± 0.01
$pK_{2(HL)}$ = 3.80 ± 0.01
$[L^-]$ = 0.29 $[HL]$* (*Calculated in the usual way using Henderson's equation)

$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_1 M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
-	1981†	0.278 x 10^5	0.044 x 10^{10}	-	-	-	-
2.29 x 10^{-5}	1043	0.393	0.059	0.015 x 10^{10}	0.115 x 10^5	0.136 x 10^5	0.005 x 10^{15}
4.58	661	0.436	0.087	0.043	0.158	0.272	0.013
6.35	515	0.483	0.098	0.054	0.205	0.263	0.014
8.54	353	0.540	0.119	0.075	0.262	0.286	0.017
1.145 x 10^{-4}	235	0.649	0.148	0.104	0.371	0.280	0.020
1.374	121	1.119	0.250	0.206	0.841	0.245	0.033
1.603	77	1.543	0.350	0.306	1.265	0.242	0.045
1.832	57	1.842	0.427	0.383	1.463	0.262	0.055
-	2180‡	0.278	0.044	-	-	-	-
4.53 x 10^{-5}	758	0.412	0.085	0.041	0.134	0.306	0.014
7.74	433	0.521	0.114	0.070	0.243	0.288	0.017
9.56	314	0.622	0.133	0.089	0.344	0.259	0.019

Mean value of β_1 = (0.270 ± 0.19) x 10^5 M^{-1}
(1st value rejected)

† Mean of 4 values
‡ Mean of 2 values

TABLE XVI (b)

Results:

Reaction medium, temperature and pH	$pK_{2(HL)}$	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
0.50M $NaClO_4$ t = 25°C pH = 3.40 ± 0.01	3.80 ± 0.01	$(2.7 \pm 0.2) \times 10^4$	3×10^8	x

Investigation of the Actinium (III) α-Hydroxyisobutyrate System in 0.50M Sodium Perchlorate at 25°C:

The system has been investigated by the procedure outlined on page 112 of this text. The pH of the complexing solutions was kept at 3.30 ± 0.01. A $^{v}/m$ ratio of $^{12}/.01$ was used for equilibrations. The time allowed for equilibrations was just over an hour. The essential data and results are given in Tables XVII (a) and XVII (b).

TABLE XVII (a)

$[L^-]$ mole/litre	ϕ ml.g^{-1}	ϕ_1 M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
-	1572	183	0.250×10^5	-	-	-	-
9.9×10^{-3}	443	257	0.396	0.146×10^5	74	197	0.26×10^7
1.65×10^{-2}	273	288	0.464	0.214	105	204	0.29
2.31	162	377	0.606	0.356	194	183	0.36
2.97	105	470	0.764	0.514	287	179	0.45
3.63	95	428	0.716	0.466	245	190	0.42
4.29	74	472	0.796	0.546	289	189	0.46
5.28	56	513	0.876	0.626	330	190	0.52

Mean value of $\beta_1 = 190 \pm 7$ M^{-1}

TABLE XVII (b)

Results:

Reaction medium, temperature and pH	$pK_{(HL)}$	β I M^{-1}	β 2 M^{-2}	β 3 M^{-3}
0.50 $NaClO_4$ t = 25°C pH = 3.30 ± 0.01	3.61 ± 0.01	190 ± 7	1.0×10^4	7×10^4

CHAPTER VI

The Study of Americium (III) Complexes with Sulphate, Oxalate and α-Hydroxyisobutyrate Ligands in Sodium Perchlorate Media at 25°C

Introduction:

Americium belongs to the "actinide" series of elements and contains six electrons in the 5 f. electron shell. It therefore corresponds to europium of the "lanthanide"series of elements (which contains six electron in the 4 f. electron shell). The crystallographic ionic radius of Americium (III) is greater than that of europium (III) by 0.03Å. In the absence of the f-electron participation, therefore, the complexes of americium (III) with a particular ligand would be expected to be weaker than the corresponding complexes of europium (III) with the same ligand under precisely the same environmental conditions. The present investigation was undertaken to check the validity of this assumption. It may be mentioned that the existing evidence[132] to the contrary is derived from a comparison of results obtained on comparable systems by incomparable techniques.

In the present investigation americium-241 has been used as a tracer. The γ-spectrometric examination revealed the presence of less than 1% of protactinium-233 impurity in the isotope. This was ignored. Protactinium-233 is a decay product of americium-241 and a strong γ-emitter (0.31 Mev and 0.09 Mev.)

$$Am^{241} \xrightarrow{\alpha} Np^{237} \xrightarrow{\alpha} Pa^{233} \xrightarrow{\gamma}$$

The 'concentration' of the isotope in solutions was measured radiometrically by γ-scintillation counting in the energy range of 0.03 and 0.06 Mev. using a well-type sodium iodide (thallium) crystal (vide appendix viii). The equilibrations were carried out by the general procedure described in appendix (iii). The data obtained were treated in the usual way (vide appendix (iv) and general introduction page 18) for the calculation of the step stability constants.

Investigation of the Americium (III)-Sulphate System in 1M Sodium Perchlorate at 25°C:

The method and conditions adopted for the investigation of this system were the same as those employed for studying europium (III)-sulphate system. A $^{v}/_{m}$ ratio of $^{10}/.2$ was used throughout. The pH of the complexing solutions was kept around 3.8. The time allowed for equilibrations was over twelve hours. The essential data and results of the investigation are given in Tables XVIII (a) and XVIII (b).

TABLES XVIII (a)

$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_1 M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
-	983‡	30.00	0.69×10^3	-	-	-	-
0.01	821	19.73	1.60	-	-	-	-
0.02	620	29.28	0.93	-	-	-	-
0.03	493	33.13	0.89	0.20×10^3	3.13	63.90	1.43×10^4
0.04	412	34.65	0.93	0.24	4.65	51.61	1.37
0.06	303	37.40	1.00	0.31	7.40	41.89	1.33
0.07	257	40.36	1.06	0.37	10.36	35.71	1.36
0.08	230	40.92	1.09	0.40	10.92	36.63	1.38
-	1080*	30.00	0.69×10^3	-	-	-	-
0.05	375	37.60	0.98	0.29	7.60	38.16	1.41
0.09	205	47.42	1.23	0.54	17.42	31.00	1.54
0.10	178	50.67	1.31	0.62	20.67	30.00	1.62
0.12	145	53.74	1.41	0.72	23.74	30.33	1.74
0.14	119	57.68	1.53	0.84	27.68	30.35	1.87

Mean value of $\beta_1^{@}$ = 34 ± 4 M^{-1}

@First two values rejected.

‡Mean of 2 values.

*Mean of 3 values.

TABLE XVIII (b)

Results:

Reaction medium, temperature and pH	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}
1M $NaClO_4$ t = 25°C pH = 3.80	34 ± 4	360	-

Investigation of the Americium-Oxalate System in 0.5 M Sodium Perchlorate at 25°C:

This system was studied in the usual manner using a $^{v}/m$ ratio of $^{10}/.10$ and at pH 3.62 ± 0.01. The essential data and results are collected in Tables XIX (a) and XIX (b).

TABLE XIX (a)

$[L^-]$ mole/litre	ϕ ml. g^{-1}	ϕ_1 M^{-1}	f M^{-2}	Δ f M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
	5100*	0.64×10^5	0.37×10^{10}	-	-	-	-
2.19×10^{-5}	1943	0.74	0.43	0.06×10^{10}	0.10×10^5	0.60×10^5	0.022×10^{15}
2.79	1710	0.71	0.43	0.06	0.07	0.86	0.028
3.18	1460	0.78	0.46	0.09	0.14	0.64	0.027
3.98	1280	0.75	0.45	0.08	0.11	0.73	0.028
4.38	1130	0.80	0.48	0.11	0.16	0.69	0.030
4.78	1050	0.81	0.48	0.11	0.17	0.65	0.027
5.57	840	0.91	0.53	0.16	0.27	0.59	0.029
5.97	830	0.86	0.51	0.14	0.22	0.64	0.029
6.37	740	0.93	0.55	0.18	0.29	0.62	0.029
7.16	630	0.99	0.59	0.22	0.35	0.63	0.033
7.56	630	0.94	0.56	0.19	0.30	0.63	0.031

*Mean of six values.

Mean value of $\beta_1 = (0.66 \pm .07) \times 10^5 M^{-1}$

TABLE XIX (b)

Reaction medium, temperature and pH	pK_2 (HL)	β I M^{-1}	β 2 M^{-2}	β 3 M^{-3}
0.50M $NaClO_4$ t = 25°C pH = 3.62 ± 0.01	3.80 ± 0.01	$(0.66 \pm 0.07) \times 10^5$	2.0×10^8	1.2×10^{12}

Investigation of the Americium-α-Hydroxyisobutyrate System in 0.50M Sodium Perchlorate at 25°C:

This system has been studied in the usual way employed for the investigation of the identical systems involving the rare-earths and α-hydroxyisobutyric acid. A $^V/m$ ratio of $^{10}/.10$ has been used throughout. The pH of the complexing solutions was kept the same as that used in the study of the analogous europium-α-hydroxyisobutyrate system. The essential data and results are given in Tables XX (a) and XX (b).

TABLE XX (a)

$[L^-]$ mole/litre	ϕ ml g^{-1}	ϕ_1 M^{-1}	f M^{-2}	Δf M^{-2}	$\Delta\phi_1$ M^{-1}	β_1 M^{-1}	g M^{-3}
-	5613*	487	1.83×10^5	-	-	-	-
1.8×10^{-3}	2961	498	2.36	-	-	-	0.57×10^8
2.3	2357	601	2.43	0.06×10^5	114	526	0.38
3.4	1729	661	2.71	0.88	174	506	0.41
4.7	1273	725	3.02	1.19	238	500	0.44
6.0	929	840	3.50	1.67	353	473	0.50
7.3	814	808	3.49	1.66	321	517	0.50
9.0	593	941	4.08	2.25	454	496	0.57
1.07×10^{-2}	471	1020	4.47	2.64	533	495	0.62
1.27	369	1119	4.95	3.12	632	494	0.68
1.50	287	1237	5.52	3.69	750	492	0.75
1.75	209	1478	6.63	-	-	-	0.89
2.00	160	1704	7.69	-	-	-	1.03
2.25	118	2070	9.37	-	-	-	1.25

*Mean of six values.

Mean value of $\beta_1 = 500 \pm 14$ M^{-1}

TABLE XX (b)

Reaction medium and temperature	$pK_{(HL)}$	β I M^{-1}	β 2 M^{-2}	β 3 M^{-3}
0.50M $NaClO_4$ t = 25°C	3.61 ± 0.01	500 ± 14	6.1×10^4	x

2

CHAPTER VII

DISCUSSION OF RESULTS

As stated already in the 'Outline of the present work' (page 23), part II of this work deals mainly with a study of the complexes of some trivalent ions of elements of the rare-earth and actinium series with fluoride, chloride, sulphate, oxalate, α-hydroxyisobutyrate and glycollate ligands. Since it had been planned to study these systems in sodium perchlorate media chiefly for reasons of conformity to the common practice of other workers, it was decided to study the sorption of lanthanum (III) and cerium (III) with respect to pH on Zeo-Karb 225 (SRC 15) and De-acidite FF from sodium perchlorate solutions in order to obtain a general idea of the sorption behaviour of the elements in question on these resins from sodium perchlorate solutions. The results obtained are shown in figures 9 and 10. It is evident from these figures that the sorption of lanthanum (III) and cerium (III) follows the same pattern as that of yttrium (III) from ammonium perchlorate solutions. It follows that the change of medium is not of any consequence in the sorption of the elements in question on the said resins, and that the explanation given already for the sorption pattern of yttrium (III) may also be applied to that of lanthanum (III) and cerium (III).

The results obtained from the present investigation of the aforementioned systems are discussed hereafter individually and in relation to each other.

Fluoride

The study of the lanthanum (III)-fluoride system revealed the formation of only one complex in the ligand concentration range of 3.65×10^{-5} to 7×10^{-3} mole $.l^{-1}$ (vide table 1 p.69). The equilibria involved in the system are:-

$$(1) \quad M^{3+} + F \rightleftharpoons MF^{2+} \; ; \quad K_I = \frac{[MF^{2+}]}{[M^{3+}]\,[F^-]}$$

$$(2) \quad HF \rightleftharpoons H^+ + F \; ; \quad K_{HF} = \frac{[H^+]\,[F^-]}{[HF]}$$

Multiplying K_1 by K_{HF}, the following expression is obtained:

$$K_1 K_{HF} = \frac{[MF^{2+}]\,[H^+]}{[M^{3+}]\,[HF]} = K_1^{*}$$

(K_1^{*} is the equilibrium quotient for the reaction:

$$M^{3+} + HF \rightleftharpoons MF^{2+} + H)$$

Using 1.23×10^{-3} for K_{HF} (vide R. E. Connick et. al.)[148] and the value 465 obtained in the present work for K_1, the following K_1^{*} value is obtained:

$$K_1^{*} = \frac{465 \times (1.23 \times 10^{-3})}{} = 0.57$$

This value of K_1^* is in very good agreement with that reported by J. W. Kury et. al.[145] (namely, $K_1^* = 0.59$) (vide table XXI) who obtained it by the so-called 'ferri method' which is essentially a potentiometric method based on competition between lanthanum (III) and iron (III) for the fluoride ions in a ferrous-ferric concentration cell. Regarding the validity of the K_{HF} value[148] used for the calculation of the results in the present investigation it may be mentioned that J. W. Kury et. al. also used the same K_{HF} value in the calculation of their results and that more recently Farrer and Rossotti[149] assuming the validity of this value for 0.5M sodium perchlorate have used it for the interpretation of their own results derived from the study of the 'Proton-Fluoride Association'. It may further be observed that in the present investigation ϕ_I values showed a sudden drop beyond 7×10^{-3} mole l^{-1} concentration of the fluoride ions suggesting the probable precipitation of some lanthanum fluoride species (compare a value of 484 for ϕ_I at 5.39×10^{-3} mole l^{-1} concentration of the fluoride ions with a ϕ_I value of 139 obtained at 7.37×10^{-3} mole l^{-1} concentration of the ligand). No attempt was made to explore the effect of increasing metal ion concentration in solution on the system in question.

TABLE XXI

Ligand	M^{3+}	Method	Medium	Temp.	K_I^*	K_I	Ref.
F^-	La(III)	i. ex.	0.50M $NaClO_4$	25°C	0.57	493 ± 28	P.W.
		Pot.	- do -	- do -	0.59	478	145

i. ex. = ion-exchange.
solv. ext. = solvent-extraction.
P.W. = Results from the present work.

Chloride

A β_I value of 1.73 for the cerium (III)-chloride system on comparison with those reported in the literature for cerium (III) and the other trivalent rare-earth ions (vide table XI) seems plausible in view of the difference of the ionic strengths of the media used.

Sulphate

The β_n values obtained for the systems involving sulphate as ligand and the trivalent rare-earth ions, namely, lanthanum (III), cerium (III), europium (III) and gadolinium (III) have been observed to follow the trend suggested by the relative sizes of the crystal ionic radii (vide table XXIV page 139), i.e., the increasing stabilities of the complex with decreasing ionic radii. The sizes of β_n values for the sulphate complexes of actinium (III) and americium (III) relative to those pertaining to the identical complexes of lanthanum (III) and europium (III) indicate the mutually exclusive dependence of their chemistries on the sizes of their ionic radii as well as the homologous relationship existing between the two series of elements (vide table XXII). It may further be added that the β_n values obtained for the various systems involving the cations in question and the ligand sulphate have been observed to be in fairly good agreement with those reported in the literature for the same systems in recent years (vide table XXII).

TABLE XXII

Ligand	M^{3+}	Method	Medium	Temp.	β_{I} M^{-1}	β_2 M^{-2}	β_3 M^{-3}	Ref.
SO_4^{--}	La(III)	i. ex.	1M $NaClO_4$	25°C	24 ± 3	- -	- -	P.W.
		solv.ext.	"	"	28	288	. .	141
		- -	. .	. .	25	. .	- -	150
	Ce(III)	i. ex.	1M $NaClO_4$	25°C	34 ± 1	271	800	P.W.
		i. ex.	"	"	43 ± 3	220 ± 50	1200 ± 300	152
	Eu(III)	i. ex.	"	"	37 ± 4	354	1200	P.W.
		solv.ext.	"	"	35	490	- -	141
		i. ex.	- -	- -	37 ± 2	250 ± 30	- -	153
	Gd(III)	i. ex.	1M $NaClO_4$	25°C	36 ± 3	270	1600	P.W.
	Ac(III)	i. ex.	1M $NaClO_4$	25°C	17	66	- -	P.W.
	Am(III)	i. ex.	1M $NaClO_4$	25°C	34 ± 4	360	. .	P.W.
		solv.ext.	"	"	37.15	457.09	--	141
		solv. ext.	μ = 1-1.3M	"	30	390	--	153
		i. ex.	"	- -	31	300	. .	153
		i. ex.	μ = 0.75	..	60	- -	. .	158
			μ = 1.75	- -	58	130	. .	158

i. ex. = ion-exchange
solv. ext. = solvent-extraction

P.W. = Results from the present work.

Oxalates

The β_n values obtained from the present investigation of the systems involving the oxalate ligand and the trivalent rare-earth ions show a regular increase from lanthanum (III) to gadolinium (III) (vide table XXIII). This is consistent with the expected trend of these values in view of the diminishing sizes of the crystal ionic radii from lanthanum (III) to gadolinium (III) (vide table XXIV). The similar values obtained for the systems involving the oxalate ligand and actinium (III) and americium (III) appear to follow the same trend as the trivalent rare-earth ions relative to one another and to the corresponding rare-earths, namely, lanthanum (III) and europium (III) respectively (vide table XXIII). Recently T. Sekine[141] has reported results for the oxalate systems involving trivalent lanthanum, europium and americium ions for μ = 1M and t = 25°C (vide table XXIII, page 138). A comparison of his results with those obtained from the present investigation would show the latter to be consistently higher (except the β_2 value for the americium (III)-oxalate system) and this is what would be expected bearing in mind that ionic strength of the medium used in the present investigation was 0.50M. The general trend of the relative β_2

and β_3 values reported by T. Sekine and those from the present work suggests that the β_2 value reported by the former for americium (III)-oxalate system is presumably slightly higher than it should have been. The β_I value obtained from the present investigation for the europium-oxalate system for $\mu = 0.50$ is almost in complete agreement with a similar value reported by Kerechuk and Paramanova[155] for the same system and for the same ionic strength of the medium. The discrepancies in the β_2 and β_3 values though apparently large are not out of the order commonly observed in the reported values.

TABLE XXIII

Ligand	M^{3+}	Method	Medium	Temp.	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}	Ref.
COO_2^{--}	La(III)	i. ex.	0.50M $NaClO_4$	25°C	$(2.88 \pm 0.10) \times 10^4$	1.25×10^8	3.3×10^{10}	P.W.
		solv.ext.	1M $NaClO_4$	25°C	1.82×10^4	7.08×10^7	1.86×10^{10}	141
	Ce(III)	i. ex.	0.50M $NaClO_4$	25°C	$(3.03 \pm 0.02) \times 10^4$	1.87×10^8	4×10^{11}	P.W.
	Eu(III)	i. ex.	〃	〃	6.52×10^4	6.27×10^8	1.5×10^{12}	P.W.
		〃	〃	〃	6.4×10^4	3.7×10^8	3×10^{11}	155
		solv.ext.	1M $NaClO_4$	〃	5.89×10^4	5.25×10^8	2.46×10^{11}	141
	Gd(III)	i. ex.	0.50M $NaClO_4$	〃	$(8.81 \pm 0.13) \times 10^4$	9.39×10^8	2×10^{12}	P.W.
	Ac(III)	i. ex.	〃	〃	$(2.7 \pm 0.2) \times 10^4$	3×10^8		P.W.
	Am(III)	i. ex.	〃	〃	$(6.6 \pm 0.7) \times 10^4$	2×10^8	1.2×10^{12}	P.W.
		solv.ext.	1M $NaClO_4$	25°C	4.27×10^4	2.24×10^8	1.41×10^{11}	141

i. ex. = ion-exchange. P.W. = Results from the present work.

solv. ext. = solvent-extraction.

TABLE XXIV

Ion	Radius
Y^{3+}	0.98 Å
La^{3+}	1.061
Ce^{3+}	1.034
Eu^{3+}	0.950
Gd^{3+}	0.938
Ac^{3+}	1.11
Am^{3+}	0.99

The above values for the ionic radii of the trivalent ions listed in column I of the above table are taken from the 'Advanced Inorganic Chemistry' by Cotton and Wilkinson Interscience Publishers 1962, pages 877 and 891.

α-hydroxyisobutyrate

The relative sizes of the β_n values obtained from the present investigation for the systems involving α-hydroxyisobutyrate ligand and the trivalent rare-earth ions (excluding yttrium (III)) appear to follow the trend expected of the sizes of their ionic radii (vide tables XXIV and XXV). The β_n values obtained for the actinium (III) and americium (III)-α-hydroxyisobutyrate systems (vide table XXIV) also fit in nicely with the concept of the ionic-radium-dependence of their solution chemistries relative to one another and to the corresponding rare-earths, namely, lanthanum (III) and europium (III). The β_n values obtained from the present investigation for lanthanum (III) and europium (III) are in very good agreement with those reported by Stagg and Powell[151] for the same systems and ionic strength of the medium, namely, for 0.5M sodium perchlorate (vide table XXV). The β_n values reported by Choppin and Chopoorian[135] for the cerium (III), europium (III) and gadolinium (III) α-hydroxyisobutyrate systems for $\mu = 2M$ appear to be out of tune with those reported by other workers[101, 151] and the ones obtained from the present investigation for $\mu = .5M$, especially when the agreement of these latter results is taken into consideration. The higher β_n values for the yttrium (III)-α-hydroxyisobutyrate system than those reported for a corresponding system involving europium (III) under comparable conditions (vide table XXVI) could be, according to Choppin and Chopoorian[135], due to the inductive influence of the methyl groups in the α-hydroxyisobutyrate ion and the absence of a crystal field stabilization in yttrium (III). The absence of a similar trend in the glycollate systems involving yttrium

(III) and europium (III) (vide table XXVII p. 146) may then be explained by the absence of the methyl groups in the glycollate ion.

TABLE XXV

Ligand	M^{3+}	Method	Medium	Temp.	β_{I} M^{-1}	β_{2} M^{-2}	β_{3} M^{-3}	Ref.
α-hydroxyisobutyrate	La(III)	i. ex.	0.50M $NaClO_4$	25°C	181 ± 4	7.8×10^{3}	7.5×10^{4}	P.W.
		pH	″	″	166	4.7×10^{3}	--	151
	Ce(III)	i. ex.	″	″	229	1.8×10^{4}	--	101
		pH	″	″	234.4	1.02×10^{4}	--	151
		Pot.	μ = 2M	″	270	2.08×10^{4}	2.08×10^{5}	135
	Eu(III)	i. ex.	0.50 $NaClO_4$	25°C	516 ± 13	7.67×10^{4}	10^{6}	P.W.
		pH	″	″	513	8.32×10^{4}	8.13×10^{5}	151
		Pot.	μ = 2M	″	503	8.75×10^{4}	3.33×10^{6}	135
	Gd(III)	i. ex.	0.50 $NaClO_4$	25°C	555 ± 11	6.1×10^{4}	8×10^{5}	P.W.
		pH	″	″	513	9.33×10^{4}	1.02×10^{6}	151
		Pot.	μ = 2M	″	503	8.75×10^{4}	3.33×10^{6}	135
	Ac(III)	i. ex.	0.50 $NaClO_4$	25°C	190 ± 7	1×10^{4}	7×10^{4}	P.W.
	Am(III)	i. ex.	″	″	500 ± 14	6.1×10^{4}	--	P.W.

TABLE XXVI

Yttrium-α-hydroxyisobutyrate

Method	Medium	Temp.	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}	Ref.
i. ex.	0.50M NH_4ClO_4	25°C	750 ± 30	2.1×10^5	..	P.W.
i. ex.	0.50M NH_4Cl	25°C	661	2.34×10^5	1.6×10^6	101
i. ex.	..	..	1300	4×10^4	2×10^7	136
Pot.	μ = 2M	25°C	730	2.8×10^5	2.0×10^7	135

i. ex. = ion-exchange

Pot. = Potentiometric

P.W. = Results from the present work

Glycollate

The investigation of the europium (III)-glycollate system in 0.5M ammonium perchlorate revealed the formation of three complexes. The values for the step-stability constants calculated from the experimental data are given in table XXVI along with those reported by other workers for the same system. A comparison of the β_n values obtained from the present work with those reported by I. Grenthe[156] shows the two to be related as follows:

$$\frac{\beta_n(\text{P.W.})}{\beta_n(\text{I.G.})} = 0.80 : 1.61 : 3.70$$

It is evident that the ratios of the corresponding β_n values are approximately related to each other as the terms of a geometrical progression. This is indicative of the presence of a systematic error in the measurement of one or the other set of the quoted values. The β_1 value, namely, 285 from the present work is in complete agreement with that reported by Choppin and Chopoorian[135] for the system in question for μ = 2M, provided a due adjustment as suggested by I. Grenthe[156] for comparison of results in the concentration range of 0.5M and 2M, is made. It may be mentioned that the adjustment suggested by I. Grenthe is based on his computation of the probable differences of

β_n values between the said ionic strengths of the media from the results reported by A. Sonesson[157] for the gadolinium (III)-glycollate system for μ = 2M and μ = 1M, derived from the potentiometric and ion-exchange studies of the system in question. According to I. Grenthe a β_1 value valid for 0.5M ionic strength should be reduced by 10% of its nominal value for comparison with a similar value obtained at 2M ionic-strength; for β_2 and β_3 the suggested reduction is 20% of their nominal values. The agreement between the β_I values for the yttrium (III) and europium (III)-glycollate systems is consistent with the concept of the ionic-radius-dependence of their chemistry.

TABLE XXVII

Ligand	M^{3+}	Method	Medium	Tem.	β_I M^{-1}	β_2 M^{-2}	β_3 M^{-3}	Ref.
Glycollate	Eu(III)	i.ex.	0.50 NH_4ClO_4	25°C	296 ± 19	6.63×10^4	3×10^6	P.W.
		Pot.	〃	20°C	369 ± 3	$(4.1 \pm 0.3) \times 10^4$	$(8.1 \pm 0.7) \times 10^5$	156
		Pot.	= 2M	25°C	285	2.62×10^4	6×10^5	135
	Y(III)	i.ex.	0.50 NH_4ClO_4	25°C	297.10	2.40×10^4		P.W.
				〃	302.28	2.57×10^4	5×10^5	P.W.
		i.ex.	0.50 NH_4Cl	〃	290	1.6×10^4	1.45×10^4	101
		i.ex.	..	..	600	5.1×10^4	1×10^6	136
		Pot.	μ = 2M	20°C	295	2.5×10^4	5×10^5	137
		Pot.	μ = 2M	25°C	239	2.30×10^4	4×10^5	135

i. ex. = ion-exchange

Pot. = Potentiometric

P.W. = Results from the present work

Comparison of the lanthanum (III) and actinium (III) results:-

The ratios β_I La (III)/β_I Ac (III) for each of the ligand used have been calculated and found to be nearly the same size. It follows that the chemistry of the two elements is a function of their ionic-radii rather than any other factor.

(a)

Ligand	β_I La (III)/β_I Ac (III)
Sulphate	1.41
Oxalate	1.07
α-hydroxyisobutyrate	0.95

Comparison of the europium (III) and americium (III) results:-

The ratios β_I Eu (III)/β_I Am (III) calculated from the corresponding results of the systems investigated are found to be nearly the same size (vide table below). It follows that the relative chemistry of these ions is a function of the relative sizes of their ionic-radii.

(b)

Ligand	β_I Eu (III)/β_I Am (III)
Sulphate	1.09
Oxalate	0.99
α-hydroxyisobutyrate	1.03

The ratios of the β_I values for the pairs Ce (III)/ Ac (III) and Gd (III)/Am (III) for the ligands in question are as follows:

(c)

Ligand	β_I Ce (III)/β_I Ac (III)
Sulphate	2.00
Oxalate	1.12
α-hydroxyisobutyrate	1.21

(d)

Ligand	β_I Gd (III)/β_I Am (III)
Sulphate	1.06
Oxalate	1.34
α-hydroxyisobutyrate	1.11

Comparison of the ratios given in tables (a) and (c) for the pairs La (III)/ Ac (III) and Ce (III)/ Ac (III) show an increase commensurate to the decrease of ionic radius from lanthanum (III) to cerium (III). Likewise the ratios given in tables (b) and (d) for the pairs Eu (III)/ Am (III) and Gd (III)/ Am (III) show the same trend. The higher ratios of the β_1 values for the sulphate systems of the La (III)/Ac (III) and Ce (III)/ Ac (III) pairs appear to be exceptional, presumably due to the differences of pH involved in the study of the respective systems.

APPENDICES

The general information on the materials used, the procedures adopted for the conversion of resins to an appropriate salt-form and equilibration, the preparation of the essential stock-solutions, the counting devices employed for the quantitative determination of the tracers in solution and the other relevant experimental asides are laid down in the appendices in the following order:-

APPENDIX (i)

Materials used

Reagents - Chemicals of 'Analar' quality were used unless otherwise specified.

Ion-exchangers - ZeoKarb 225 series of chromatographic grade ion-exchangers of 2% (SRC 7), 4-5% (SRC 12), 8% (SRC 15), 20% (SRC 23), cross-linking were used.

Ammonium perchlorate - B.D.H. 'Laboratory Reagent Grade' was used. In some experiment , the reagent used was prepared by neutralising perchloric acid with ammonia.

Glycollic acid - (Judex Laboratory Reagent, from the General Chemical and Pharmaceutical Co. Ltd., Sudbury, Middlesex, England). The acid was recrystallised from water and dried in vacuum over sulphuric acid. The purity was checked by alkalimetric litration.

α-Hydroxyisobutyric acid - (kindly supplied by A.E.R.E., Harwell) was recrystallised from benzene and stored in a vacuum dessicator.

Chromotropic acid - (B.D.H. Laboratory Reagent Grade and 'for formaldehyde determination').

Isotopes used: All the isotopes used were carrier-free and obtained from The Radiochemical Centre, Amersham, Bucks., England. These are:-

(1) Yttrium - 91. The isotope solution was IN in HCl and contained less than 1.8 mg. of solids per 2.25 ml. of the solution.

(2) Cerium 144 - Pr144. The amount of solids in the isotope solution was about 0.7 mg./2 ml.

(3) Barium - 140. Contained no solids.

(4) Europium - 152, 154. The isotope solution contained carrier. The total amount of Europium per ml. of the solution being 3 mg.

(5) Gadolinium - 153. The isotope solution contained 19 ug. of Gadolinium/ml.

(6) Americium - 241.

APPENDIX (ii)

A. Conversion of a resin to an appropriate salt-form

A batch of about 100 g. of a resin in the sodium-form was taken in a large beaker and washed free of 'fines' with 2N. hydrochloric acid. It was then transferred to a large column and washed with nearly 10 to 12 column-volumes of 2N. hydrochloric acid to remove iron completely and convert it to the hydrogen-form. The excess of the acid was washed out with distilled water. The resin was then treated with 0.5M ammonium or sodium chloride solution (depending on the desired salt-form of the resin), till the effluent was neutral to litmus paper. The excess of the chloride was removed by washing with distilled water. Finally the resin was dried in flat petri-dishes in an electric oven at 90°C, till the grains just separated, and stored in dry, clean screw-capped glass bottle. Samples for use were kept in petri-dishes in silica-gel dessicators.

B. Preparation of stock-solutions:

(a) Medium solution: Appropriate weight of ammonium perchlorate or anhydrous sodium perchlorate to give 0.5M or IM strength was dissolved in distilled water in a standard flask and its pH adjusted to the required using aqueous ammonia or perchloric acid. Volume was made up to the mark with distilled water and the pH of the solution rechecked.

(b) Tracer solution: An adequate volume of the tracer solution was taken and diluted with distilled water so that one or two mililitres on further dilution to 25 ml. gave an activity of 10^4 counts per minute per 10 ml. in a G.M. liquid counter or per 2 to 5 ml. in a scintillation counter using a well-type Sodium Iodide (Thallium) crystal as a scintillator. The pH of the solution was adjusted to the required by standard ammonia or sodium hydroxide and perchloric acid solutions. Appropriate amount of ammonium or sodium perchlorate was then added to give the required cationic strength and the volume made up to the mark with distilled water in a standard flask. The solution was stored in a polythene bottle with a screw top.

(c) α- Hydroxyisobutyric acid - ligand solution: An appropriate amount of the recrystallised acid to give 0.5M solution was dissolved in air-free distilled water and neutralised to the desired pH with standard ammonia or sodium hydroxide solutions - the amount of alkali required was calculated from the proper pK value of the acid in the given medium and at the given temperature using the Henderson's equation, viz.

$$pH = pK + \log \frac{\text{Salt}}{\text{Acid}}$$

Appropriate amount of ammonium or sodium perchlorate was then added to give the desired cationic strength, and the volume of the solution made up to the mark with air-free distilled water in a standard flask.

(d) Glycollic acid - ligand solution: The solution was prepared in exactly the same manner as employed for the preparation of α-hydroxyisobutyric acid solution.

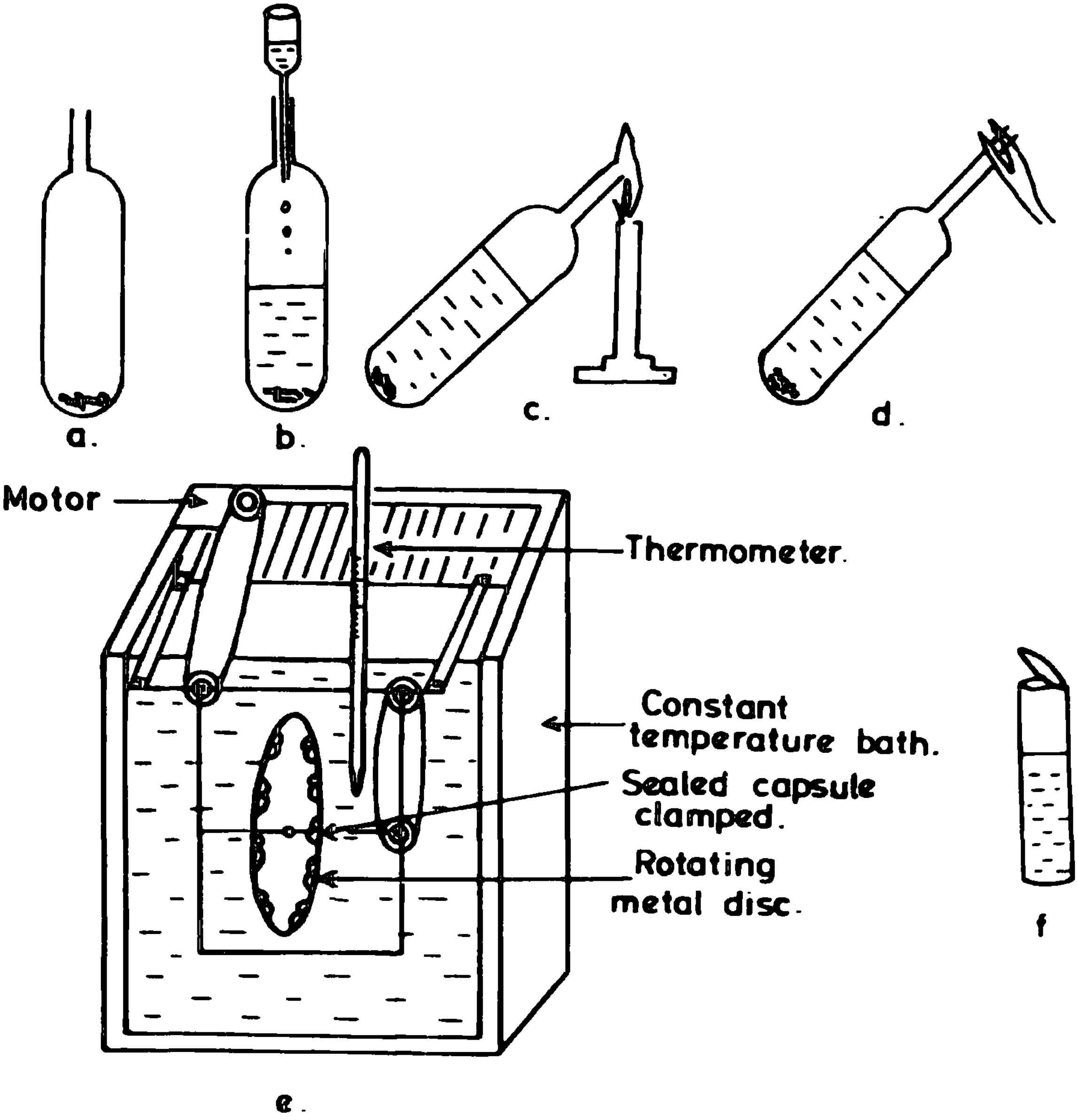
(e) Sodium oxalate - ligand solution: The solution was obtained by dissolving appropriate amounts of sodium oxalate, sodium perchlorate and perchloric acid in water to give 0.IM oxalate, 0.3M sodium perchlorate and $I.6 \times IO^{-4}$M hydrogen ion concentrations. Further dilutions were made with 0.5M sodium perchlorate solution adjusted to the same pH.

(f) Sodium sulphate - ligand solution: Appropriate amounts of sodium sulphate and sodium perchlorate were taken and dissolved in water to give 0.3M and 0.4M concentrations of the respective salt. Enough of pure perchloric acid was added to give pH of 3.80 and the volume made up to the mark with distilled water in a standard flask.

(g) Sodium fluoride - ligand solution: (a) 0.IM sodium fluoride solution was obtained by mutual neutralisation of standard sodium hydroxide and hydrofluoric acid solutions. The cationic strength was made to 0.5M by the addition of anhydrous sodium perchlorate. Solution obtained showed strong buffering and had a pH of 4.57. No salting out took place. (b) Alternative solution was prepared by mixing sodium fluoride and hydrofluoric acid in such proportions as to give 0.45M concentration with respect to sodium fluoride and 0.05M concentration with respect to hydrofluoric acid. The total cationic concentration viz. $Na^+ + H^+$, being 0.5M. For further dilutions, a medium solution containing 0.45M sodium perchlorate and 0.05M perchloric acid mixture was used.

(h) Ammonium chloride - ligand solution: 0.5M ammonium chloride solution in water was prepared by dissolving an appropriate amount of the salt in water. The pH was adjusted to the required with aqueous ammonia and perchloric acid solutions.

Figure 12.


a.
b.
c.
d.
Motor
Thermometer.
Constant temperature bath.
Sealed capsule clamped.
Rotating metal disc.
f
e.

APPENDIX (iii)

General Procedure for equilibrations

A known weight of resin was taken in a polythene capsule (see attached ~~diagram~~ fig. 12 a.) and secured at the top with a cap.

I ml. of the tracer solution (or 2 ml., depending on the activity of the stock) was placed in a 25 ml. standard flask and a known volume of a standard ligand solution added to it. Finally the volume was made to the mark with the stock ammonium or sodium perchlorate of predetermined strength. The contents of the flask were vigorously shaken to ensure thorough mixing.

A known aliquot of this solution was transferred to the capsule containing the resin (see attached ~~diagram~~ fig 12 b.). The capsule was then sealed at the top by softening in the flame of the bunsen burner and pressing between the tweezers.

A series of solutions were similarly prepared with varying amount of the ligand solution and sealed up in order in numbered capsules. In each run, a number of blanks (minimum of two) were also prepared and sealed up with the same weight of resin in marked polythene capsules.

The capsules were then clamped onto a rotating wheel in a constant temperature water bath (see attached ~~diagram~~ fig 12 e.) and allowed enough time (over 12 hours generally) so that an equilibrium got established.

At the end of the equilibration, the capsules were taken out of the bath, two at a time, unsealed and their contents squeezed into centrifuge tubes (polythene) and centrifuged to separate resin. The clear supernate was transferred to snap top polythene bottles (see attached diagram fig 12 f.).

Activities of the solutions were measured before and after equilibration. The pH values of the individual solutions were also measured after equilibration.

APPENDIX (iv)

Treatment of Radiochemical data for the calculation of the distribution co-efficients

The values of the distribution co-efficients between the resin and the aqueous phases were obtained from the initial and final (after equilibration and separation from the resin) solution activities with the help of the relationship:

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

where C_I = Initial solution activity (expressed as counts per minute)

C_2 = Final solution activity

v = Volume complexing solution (in mililitres)

m = Weight of resin (in gramme)

For solutions which do not contain any ligand,

$$\phi = l_o$$

Knowing l_o and ϕ, the successive stability constant are worked out by Fronaeus treatment[78] as outlined in Chap. 1 p.18. In the same run, it is desirable to keep $\frac{v}{m}$ constant.

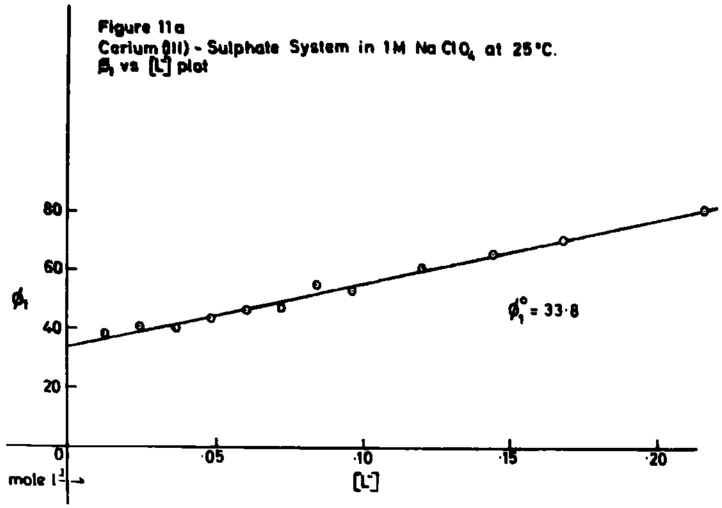


Figure 11a

Cerium (III) - Sulphate System in 1M $NaClO_4$ at 25°C.

ϕ_1 vs $[L^-]$ plot

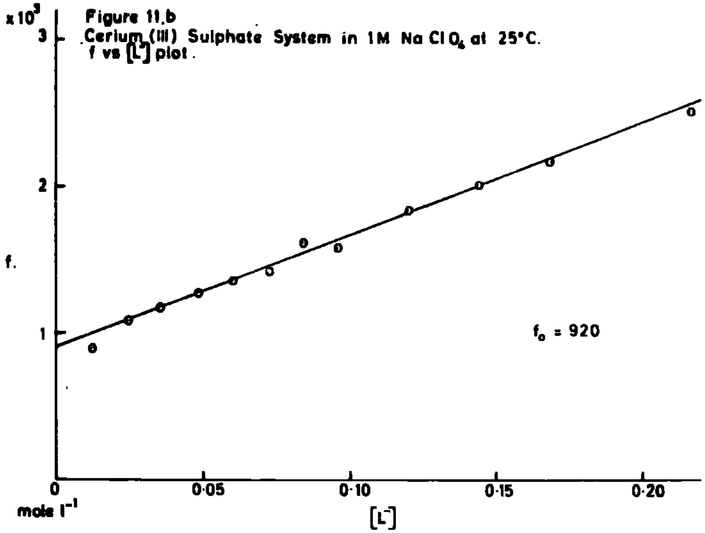


Figure 11.b

Cerium (III) Sulphate System in 1M $NaClO_4$ at 25°C.

f vs $[L^-]$ plot.

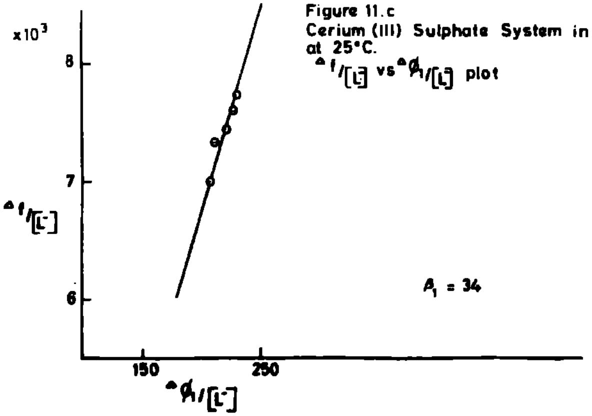


Figure 11.c

Cerium (III) Sulphate System in 1M $NaClO_4$ at 25°C.

$^{\Delta}f/[L^-]$ vs $^{\Delta}\phi_1/[L^-]$ plot

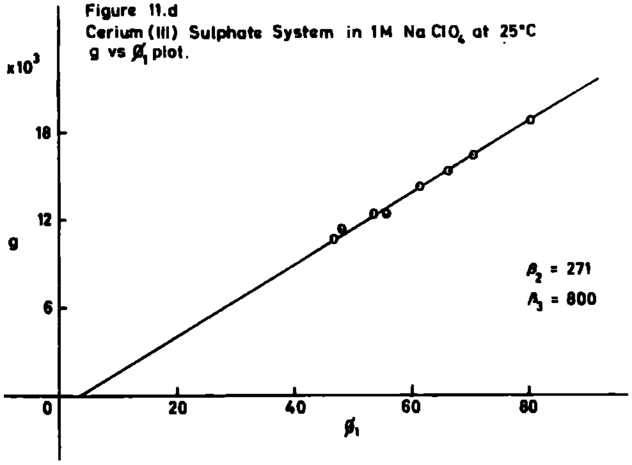


Figure 11.d

Cerium (III) Sulphate System in 1M $NaClO_4$ at 25°C

g vs ϕ_1 plot.

A resume of the same, particularly with respect to the mode of computing β_n values in the present work, is given below:

(1) From 1_o and a series of ϕ values, ϕ_1 values are obtained using the relationship:

$$\phi_1 = \frac{1_o \phi^{-1} - 1}{[L]}$$

(2) ϕ_I values obtained are plotted against corresponding $[L]$ values on linear graph paper. A straight line is drawn through the points corresponding to reasonably low ligand concentrations. Points corresponding to very low concentrations are rejected because they tend to be erratic due to the fact that definite complex formation giving a reproducible and consistently tendentious ϕ_1 values appears to begin at definite minimal ligand concentration. Points corresponding to higher concentrations of the ligand are rejected because as soon as the 3rd and higher complexes begin to be formed the assumption that ϕ_I vs $[L]$ plot should be linear is no more valid (vide page 22 of the present text). It may be observed that if the standard deviation of ϕ_1 values is not far outside the expected limits of experimental errors in ϕ and $[L]$ values, a best straight line can easily be drawn through the given points by visual inspection (vide figure 11a). Alterna-

tively the method of least squares should be employed to obtain the best straight line fit for the points.

(3) The straight line obtained above is then extrapolated to zero concentration of the ligand (X-axis, fig. 11a). A value of $\phi_I{}^o$ is thus obtained.

(4) From the values of the known quantities like l_o, ϕ_2, $\phi_I{}^o$, and $[L]$ another function f is calculated using the relationship:

$$f = \frac{\left[l_D \, \phi^{-I} \, (\beta_I - l'_I) - 1 \right] + 1}{[L]^2}$$

A series of values obtained for the function f are then plotted against $[L]$ values using the same range of $[L]$ values as employed for obtaining ϕ_I vs $[L]$ graph at (2) above.

(5) The straight line obtained above is extrapolated to zero concentration of $[L]$ to obtain f_o value.

(6) Knowing ϕ_I, $\phi_I{}^o$, f, f_o, the following quantities are found out:

$$\Delta f = f - f_o$$

$$\Delta \phi_I = \phi_I - \phi_I{}^o$$

(7) β_I is computed from Δf and $\Delta \phi_I$ either by plotting $\Delta f/[L]$ against $\Delta \phi_I/[L]$ (vide fig. 11c) or by taking the ratio of $\Delta f/\Delta \phi_I$, followed by taking the mean of the individual ratios; the latter expedience is resorted to

when the quantities $\Delta f/[L]$ and $\Delta\phi_I/[L]$ are tending to be constant as they do quite often and assumes the linearity of the $\Delta f/[L]$ vs $\Delta\phi_I/[L]$ plot, the slope of which according to Fronaeous should give β_I. It may be pointed out that the linearity of this plot is based on the assumption that within the concentration range of the ligand used for obtaining ϕ_I and f values, higher complexes are not being formed. β_I as shown on page 22a, is related to Δf and $\Delta\phi_I$ as follows:

$$\beta_I = \frac{\Delta f}{\Delta\phi I} + \beta_3\frac{[L]}{\Delta\phi I} + \beta_4\frac{[L]}{\Delta\phi I} - \frac{l_2'\phi_I[L]}{\Delta\phi I}$$

While it seems reasonable to assume that in the ligand concentration range selected, β_3 and β_4 will not be formed and hence the quantities $\frac{\beta 3[L]}{\Delta\phi I}$ and $\frac{\beta 4[L]}{\Delta\phi I}$ may be neglected, the term $\frac{l_2'\phi_I[L]}{\Delta\phi I}$ is still bound to make its contribution unless the ratio $\frac{\phi I}{\Delta\phi I}$ is very close to unity and l_2' is negligible.

(8) Knowing β_I, the quantity $(\beta_2 - l_2')$ is calculated as follows:

$$(\beta_1\phi_1^0 - f_0) = (\beta_2 - l_2')$$

This is followed by a calculation of another function g using the relationship:

$$g = \frac{l_0 \; \phi^{-1} (\beta_2 - l'_2) \; + \; (f \; - \beta_I \; \phi_I)}{[L]}$$

$$= \beta_2 \, \phi_I \; - \; \beta_3 \; - \; X_4 \; [L]$$

It is evident from the above equation that a plot of g against ϕ_I will be linear provided no fourth or higher complex is formed (vide fig. 11d). It may be pointed out that in the present investigations no evidence for the formation of the 4th complex was observed in the ligand concentration ranges employed in these investigations. It should further be noted that as one function is calculated from its predecessor it will naturally include the errors involved in the latter and its precursors. Evidently error limits for β_2 and β_3 will increase. This explains why the greatest possible care should be taken to obtain as accurate values for the basic functions like l_0, ϕ, and $[L]$.

APPENDIX (v)

Calculation of the ligand concentration

(a) α - hydroxyisobutyric, glycollic and oxalic acids: The values of $[L^-]$ were calculated from the stoichiometric concentrations of the acids in the solution, and the equilibrium pH values of the solutions by making use of the Henderson's equation, viz.,

$$pH = pK + \log \frac{[L^-]}{[HL] - [L]}$$

where HL = Total stoichiometric concentration of the acid.

$[L^-]$ = Ligand concentration, i.e. the concentration available at equilibrium for complex formation

pK = Log K*.

*K = Dissociation constant of the acid.

(b) Chloride and Sulphate: In all the calculations given in this text, the stoichiometric concentrations have been used for L^- values, assuming that under the given conditions, the acids are completely dissociated.

(c) Fluoride: In order to calculate $[F]$ values, use was made of the relationships:

$$K_{HF} = \frac{[H^+]\ [F^-]}{[HF]}$$

where K_{HF} = Dissociation constant of hydrofluoric acid $= 1.23 \times 10^{-3}$

The value of $[H^+]$ was computed from the pH value of the respective solution.

APPENDIX (vi)

Determination of the dissociation constants of the acids

Such determinations became necessary because the pK values of α-hydroxyisobutyric, glycollic and oxalic acids in the proper medium were not available in the literature.

A. General Procedure

A series of solutions covering the entire range of concentration likely to be used in the equilibrium studies were prepared by dissolving known weights of the acids in water in standard flasks or by dilution of a stock solution. These were then partially neutralised by standard ammonium or sodium hydroxide. The cationic strength was made to 0.5M by further addition of solid ammonium or sodium perchlorate. After the volumes had been made up to the mark, the solutions were placed in a constant temperature (25°C.) water bath for several hours. The pH values of the solutions were then carefully measured using a Doran'Universal'pH meter and saturated, calomel/glass electrode system having saturated sodium chloride as a salt bridge. The pK values of the acids were then calculated by the Henderson's equations, viz.,

$$pK = pH - \log \frac{\text{Salt}}{\text{Acid}}$$

and

$$pK = pH - \log \frac{\text{Salt} + C_{H^+}}{\text{Acid} - C_{H^+}}$$

where C_{H^+} = concentration of the hydrogen ions.

B. Data and Results

(a) α-Hydroxyisobutyric Acid:

Solution No.	Weight of acid g.	Vol. .5545N NH_4OH added ml.	Vol. 0.8M NH_4ClO_4 used to make = .5M	Total volume of solution ml.	pH	pK by Henderson's equation	pK by modified Henderson's equation
1.	0.6528	5.74	11.65	25.00	3.635	3.62	-
2.	0.6523	2.80	13.68	"	3.125	3.61	-
3.	0.2608	2.25	14.08	"	3.610	3.61	-
4.	0.2614	1.05	14.89	"	3.110	3.62	-
5.	0.1035	0.90	31.00	50.00	3.620	3.61	-
6.	0.1022	0.90	312.00	500	3.810	3.80	3.65
7.	0.1035	0.90	solid added	100	3.650	3.64	3.61
8.	0.1022	0.90	"	1000	3.860	3.84	3.59

pK (α-hydroxyisobutyric acid) = 3.61

(b) Glycollic acid:

No.	$[\mathrm{HL}]$ m/l.	$[\mathrm{L}^-]$ m/l.	pH	pK^{x}	pK*
1.	3.74×10^{-3}	1.88×10^{-3}	3.68	3.67	3.60
2.	8.89	4.44	3.51	3.51	3.45
3.	2.22×10^{-2}	1.12×10^{-2}	3.51	3.51	3.48
4.	9.77	2.55	3.01	3.46	
5.	1.01×10^{-1}	4.99	3.46	3.46	
6.	2.45	4.54	2.92	3.46	
7.	2.49	1.11×10^{-1}	3.35	3.46	

^{x}pK values calculated from Henderson's equation

*pK values calculated from the modified Henderson's equation

(c) Oxalic Acid:

Total acid mole/litre	Total salt mole/litre	pH	pK
5×10^{-5}	2.5×10^{-5}	3.65	3.82
5×10^{-4}	3.4×10^{-4}	3.81	3.80
5×10^{-3}	4.3×10^{-3}	3.98	3.79

$\mathrm{p}K_2$ Oxalic acid = 3.797 = 3.80 ± .01

APPENDIX (vii)

Determination of the resin swelling correction for 4.5% cross-linked resin

$$\sigma = \frac{\text{Concentration (m/l) after equilibration}}{\text{Concentration (m/l) before equilibration}}$$

10 ml. of the ammonium perchlorate solution (0.5M) were equilibrated with 1g. of the resin at 25°C for nearly the same length of time as used in the actual study of the Yttrium (III)-Glycollate system. The concentrations before and after were determined by passing known eliquots of the ammonium perchlorate down a column of Zeo-Karb 225 of 8% cross-linking in Hydrogen form and titrating the effluent against standard alkali.

Changes of concentration corresponding to 20 ml. of the equilibrated solution were calculated mathematically. The results of a duplicate determination are given in the following table:

No.	Concentration before C_I	Concentration after C_2	$\sigma = C_2/C_I$
1.	0.4973	0.5217	1.0492
2.	0.4973	0.5217	1.0492

APPENDIX (viii)

Instrumental measurements:

Measurement of pH

All measurements of pH were made with a Doran 'Universal' pH meter, using a saturated Calomel glass electrode system. A saturated solution of sodium chloride was used as a salt-bridge, unless otherwise mentioned. The change of the conventional Potassium chloride salt-bridge became necessary due to the use of sodium and ammonium perchlorates as back-ground salts. Potassium perchlorate, being sparingly soluble in water, tends to precipitate in the presence of high concentration of perchlorate ions causing fluctuations of pH. The change of the salt-bridge introduced a constant difference of -0.19 pH units in all measurements relative to the values obtained with the conventional salt-bridge, namely saturated potassium chloride.

Spectrophotometric measurements

These were made with a Unicam-500 spectrophotometer.

Infra-red spectrophotometric Examination of resin samples

In these investigations a Grubb Parsons GS-2A double beam grating spectrophotometer was used. The samples for examination were prepared as follows:-

The resin was dried at nearly 120°C in an electric oven and ground to a fine powder in an agate mortar. The powder was placed in a clean dry sample tube and further dried under a vacuum for several hours. A miligramme of the dry resin was then mixed with nearly 200 mg. of finely powdered potassium bromide and subjected to a pressure of 3000 lbs. per square inch under vacuum.

Radiochemical Measurements

(1) Yttrium-91, Lanthanum-140, Cerium-144, -Pr^{144} and Actinium-228 activities in solution were measured by β-counting using a 20th Century Electronics 'Annular liquid Geiger counter-tube - Type M_6H'. The working voltage selected being in the plateau region, the counter-tubes could be easily checked by counting a standard source before actual measurements. A deviation of 1% in the counting rate (counts per minute - c.p.m.) was condoned as a statistical variation. Solutions with low activities were counted for a sufficiently long time to give a total count of ten thousand or so to minimise statistical errors. The same scaling and probe units were used throughout a series of measurements.

(2) Europium-152, 154, Gadolinium-153 and Americium-241 activities were measured by γ-scintillation counting of solution samples placed in 2-4" snap-top polythene capsules using NaI (Tl) well-type crystal manufactured by the 'Nuclear

Enterprises (G.B.) Ltd., Sight Hill, Edinburgh 11' - Type $7F_8$; diameter 1¾", height 2", and a single channel Pulse height analyser - Type N/101 manufactured by Dynatron Radio Ltd., St. Peter's Road, Furze Platt, Maidenhead, Berks., and the wide-band amplifier - Type 652 manufactured by the 'Isotope Development Ltd., Beenham Grange Aldermaston Wharf, Reading, Berks. Prior to actual counting, comparable γ-spectra of the specific isotope were obtained on a multichannel pulse-height analyser (Hutchinson-Scarrat pulse height analyser (100-channel) - Type 1363D, made by Clifford and Snell, Sutton, Surrey) and the single channel pulse height analyser used in actual measurements. Suitable instrumental settings were then made on the single channel pulse height analyser to count γ's of the given isotope in a specified energy range. Since drifting may occur the settings were checked periodically by counting standard sources prepared from the particular isotope and altered, if necessary, to give reproducible counting rates. The linearity check was also frequently made on the instrument by counting a series of sources prepared from the isotope by known dilution of the original and plotting the counting rate against the dilution. The plot should preferably be a straight line passing through the origin. In all radiochemical measurements, due account was taken of the dead-time and back-ground corrections. In the case of short-lived isotopes viz., Lanthanum-140 and Actinium-228, corrections due to the decay of the isotope over the period of equilibration and measurements of initial and final solution-activities were also made.

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