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The stability constants of rare-earths with some carboxylic acids

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THE STABILITY CONSTANTS OF RARE-EARTHS
WITH SOME CARBOXYLIC ACIDS

by

Virginia Rowland Schoeb

A Dissertation Submitted to the
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INTRODUCTION

There are fifteen elements between barium and hafnium that are commonly called rare earths. Their chemistry is predominantly that of the trivalent ion. The trivalent ions of the fifteen elements have the electron configuration $[\text{Xe}] 4f^n$, where n runs from 0 to 14. The chemistry of these highly electropositive elements is largely ionic and is determined by the size of the M^{+3} ion. Yttrium is usually placed with the rare earths since its trivalent ion also has an inert gas core $[\text{Kr}]$, and its ionic and atomic radii lie within the range of the rare-earths' radii. Because of this, yttrium is found associated with the rare earths in nature.

Since there is only one space between barium and hafnium on the periodic chart for the fifteen elements, it comes as no surprise that their chemistries are quite similar. In fact they are so similar, they are very difficult to separate. The first means of separating the rare earths were fractional crystallization and precipitation. These processes are based on slight differences in solubilities of salts and are extremely tedious and time consuming. Coordinating ligands have been useful in such separations both individually and in conjunction with the precipitation of simple salts.

Mandelic acid, for example, precipitates rare earths, but the solubilities are pH dependent. Thus rare-earth mandelates

may be continuously fractionated by varying the pH by addition of ammonia or hydrochloric acid (1).

Solvent extraction is another method of separating the rare earths. This method can be operated continuously and when using an adequate countercurrent arrangement amounts to the application of a great number of batchwise separations. Phosphorus containing acids and esters have been the most widely investigated solvents in the countercurrent extraction of rare earths. Tri-n-butylphosphate (TBP) has been widely studied both by itself and in conjunction with complexing agents. For example, EDTA increases the separation of the heavy rare earth ions but not those of the light rare earth ions. In the series holmium to ytterbium, the separation factor increases 2.5 to 3 times (2).

The most widely investigated method of separation is that of ion exchange. For small amounts of rare earths, elution chromatography is used. That is, the rare earths are placed on a column and then eluted off by a solution of some complexing agents (the classical reagent being citric acid buffered with ammonium citrate). The rare earths progress down the ion-exchange column at different rates under the influence of the eluant.

For large quantities of rare earths, displacement chromatography is used. That is, the resin bed system contains an additional cation that is more strongly complexed by the elut-

ing agent than the rare earths. This additional cation will permit resorption of the rare-earth ions on the exchanger only after the additional cation has been removed from the resin. The sharpened band fronts that result permit infinite equilibration of each rare-earth ion between solution and resin phases and thus take full advantage of differences in chelate stability.

To determine whether a given chelating agent will separate individual rare earths on an ion-exchange system, one could, of course, test it experimentally. However, in the case of a powerful multidentate chelating agent where it is only necessary to consider the predominant 1:1 complex species, the separation factor is essentially the ratio of the two stability constants. The separation factor, α , is

$$\alpha = K_{ACh}/K_{BCh} \quad (1)$$

where K_{ACh} = the stability constant of A, and

K_{BCh} = the stability constant of B.

Therefore, if one knows the stability constants of the rare-earth chelate species formed with a promising chelating agent, one could easily ascertain whether it had any potential as an eluant.

The above-mentioned is not the only reason for determining stability constants. Since rare earths are so much alike

chemically, one can gain a better understanding of the influence of various minor properties, e.g. ionic radii, on coordination chemistry. Therefore, the present study was undertaken for both practical and theoretical reasons.

REVIEW OF LITERATURE ON THE RARE-EARTH COMPLEXES

Stability constants for rare-earth ions with inorganic ligands have been determined for chloride (3-7), bromide (3-5), iodide (4, 5), nitrate (6), carbonate (8), sulfate (9), and perchlorate (4). The decreasing order of affinity of these ions for rare-earth cations is $\text{SO}_4^- > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{ClO}_4^-$. The hydrolysis constants have been reported for some of the rare earths and appear to range from 10^{-8} to 10^{-10} for the 1:1 complexes (10, 11).

Stability constants have been determined in the case of many rare-earth combinations with organic ligands. Stability constant sequences have been reported for acetate (12-16), glycolate (14, 15, 17-21), methoxyacetate (17, 22), thioglycolate (17, 22-24), and aminoacetate (17). As one replaces a hydrogen next to the carboxylate group, one finds that the order of stability enhancement is $\text{NH}_2 > \text{OH} > \text{OCH}_3 \gg \text{SH}$. There seems to be a discrepancy in the aminoacetate data as compared to what others have found for NH_2 versus OH . All of the ligands except glycolate exhibit heavy-rare-earth chelates that are less stable than the corresponding chelates of the light rare earths. (There are data for only four rare-earth aminoacetates; therefore, the trend in the case of this ligand can not be stated.) If one compares the stability constants

for β -mercaptopropionate (17), β -aminopropionate (17), and β -hydroxypropionate (17), one finds that $\text{OH} > \text{NH}_2 > \text{SH}$. Beta substitution of the donor groups is not as favorable for complexation as substitution in the alpha position. The placement of a methyl group on the acetate giving propionate (22) decreases the stability constants.

Let us consider the glycolate homologous series to see what various alkyl substituents do to the α -hydroxycarboxylated ligands' affinity for rare-earth cations. Those ligands that have been studied so far are lactate (MG) (18, 19, 21, 25, 26), ethylglycolate (EG) (27), iso-propylglycolate (IG) (28), tertiarybutylglycolate (t-BG) (28), hydroxyisobutyrate (MMG) (19, 21, 25, 26, 29, 30), methylethylglycolate (EMG) (27, 31), methylpropylglycolate (MPG) (31), methylisopropylglycolate (IMG) (28), methyltertiarybutylglycolate (t-BMG) (28), diethylglycolate (EEG) (27), 1-hydroxycyclopentanecarboxylate (HCP) (32), and 1-hydroxycyclohexanecarboxylate (HCH) (33). If one refers to the ligands as substituted glycolates, the stability sequence with the light rare earths is:

dimethyl- \cong methyl- \cong unsubstituted $>$ methylethyl- \cong tetramethylene- \cong ethyl- $>$ isopropyl- $>$ methylisopropyl- $>$ diethyl- $>$ t-butylmethyl- $>$ t-butyl- $>$ pentamethylene $>$ ethylisopropyl- glycolate. However, the same sequence is not followed with the heavy rare earths. For the yttrium-group rare earths the sequence is instead dimethyl- $>$ ethylmethyl- $>$

diethyl- > methyl- > unsubstituted \cong tetramethylene- \cong ethyl- > isopropylmethyl- > ethylisopropyl- > t-butylmethyl- > t-butyl- > pentamethylene- glycolate. The change in the stability trend (when this change occurs) usually takes place at europium. In general, the more alkyl groups the higher the stability constant until steric hindrance enters into the picture. Thus dimethylglycolate chelates are more stable than methylglycolate chelates. However, the ethyl group is bulky enough that steric hindrance is beginning to take its toll.

Other monobasic acids which have been studied as complexants for rare earths are salicylate (17), anthranilate (17), and glyoxylate (34).

Some dibasic acids which have been reported are malonate (35), thiomalate (17), malate (17, 36, 37), aminosuccinate (17), oxaloacetate (35), and diglycolate (38). They are listed according to their stability constants, the lowest first.

There is another series of compounds which shows how dentate character affects stability constants. As we go through the series, the dentate character increases from three on up, thus the $\log \beta_1$ varies from four to twenty. They are iminodiacetate (IMDA) (39, 40), ethylenediamine-N-N'-diacetate (EDDA) (41), N-hydroxyethyliminodiacetate (HIMDA) (42), nitrilotriacetate (NTA) (43-45), N-hydroxyethylethylenediamine-N,N',N'-triacetate (HEDTA) (46-48), 1,2-bis[2-di(carboxy-

methyl)aminoethoxy]ethane (ME) (49), 2,2'-bis[di(carboxymethyl)amino] diethylether (DE) (49), 1,2-diaminocyclohexane-N,N,N',N'-tetraacetate (DCTA) (50), propylenediaminetetraacetate (51), ethylenediaminetetraacetate (EDTA) (52, 53), diethylenetriamine-N,N,N',N',N'-pentaacetate (DTPA) (39, 54). It is very difficult to compare them in any other way than just dentate character because the ionic strength is not the same.

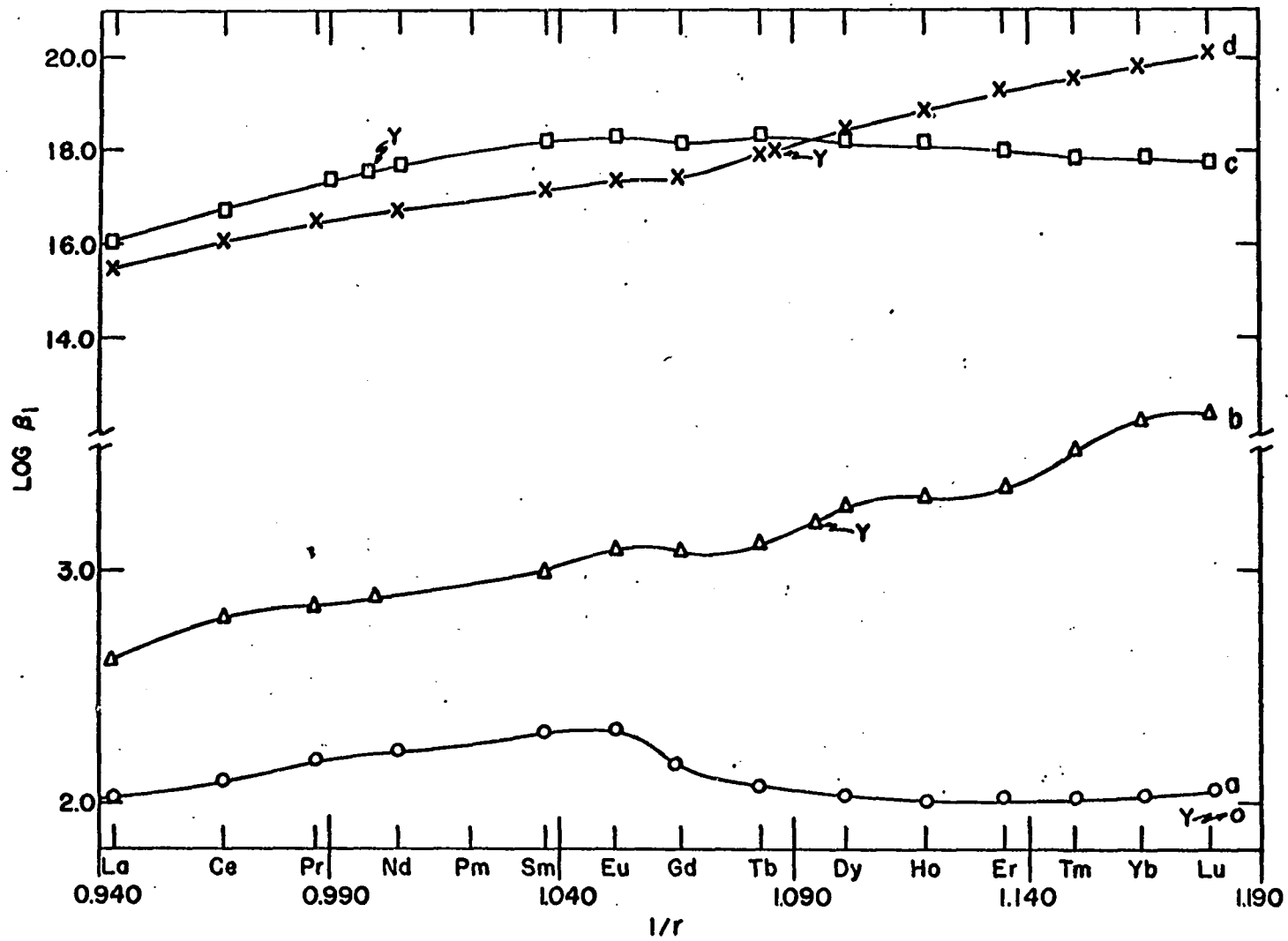
Another series which is in the literature is ligands which have nitrogen in the ring. They are in order of their stability α -picolinate-N-oxide (55), picolinate (55, 56), 6-methyl-2-picolyliminodiacetate (57), 2-picolyliminodiacetate (57), and 2,6-pyridinedicarboxylate (58).

Others have been done such as acetylacetonate (59, 60) as well as mixed complexes of HEDTA with IMDA, HIMDA, EDDA (61). There are complexes that have been studied in other than aqueous media, and many ligands that have been studied in conjunction with only one or two rare earths which are not mentioned in this review.

In Figure 1 there are several examples of stability constants plotted against $1/r$. This graph illustrates the difficulty in making generalizations about the stability constants. For all complexes studied so far, the gadolinium complex is less stable than would be expected from the electrostatic model. There is no single position for yttrium. On the basis of a simple electrostatic model, yttrium should

Figure 1. One over the ionic radius in angstroms versus the logarithm of the first stability constants of the rare-earth

- a acetate
- b α -hydroxyisobutyrate
- c EEDTA
- d EDTA



fall between holmium and thulium. However, yttrium sometimes seems similar to the heavy rare earths, at other times it is found to compare with the light rare earths. With three ligands, acetic acid, methoxyacetic acid, and mercaptoacetic acid, yttrium has the smallest stability constant of any of the rare earths.

Although it is difficult to make generalizations about rare-earth stability constants, it is even more difficult to interpret them. There are four considerations to explain the trends. The first, historically, is crystal field effect. This states that the gadolinium complex has no crystal field stabilization; thus its lower value. It also states that the yttrium complex does not fall where it is supposed to because it has no crystal field stabilization. However, the yttrium complex should always be more stable than the gadolinium complex. This is not always the case. For all complexes studied there is a regular change in $\log \beta_1$ with increasing atomic number for the light rare earths. However, if there is a regular change in $\log \beta_1$ for the heavy rare earths, it is not the same as the change for the light rare earths with the same ligand. In many cases there is no regular change in $\log \beta_1$ for the heavy rare earths.

The second consideration is steric factors. Either the ligand is too large to let another group come in easily or the ligand cannot adapt to the smaller metal ions.

The third consideration is a coordination number larger

than six. In the past the coordination number of six has been assumed by many authors. However, there is an increasing impressive array of evidence that the true coordination number is larger than six. The following experimental observations are significant.

1. Many solid salts contain more than six solvate molecules or donor groups per cation. The crystal structure of $\text{Ln}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ (62), $\text{Ln}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (63), $\text{Ln}(\text{C}_2\text{H}_5\text{OSO}_3)_3 \cdot 9\text{H}_2\text{O}$ (64), and $\text{Ln}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ (65) have been determined. All contain the grouping $\text{Ln}(\text{H}_2\text{O})_9^{+3}$ which has a trigonal prismatic geometry with three water molecules opposite the rectangular faces. A second form of $\text{Ln}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (66) contains the grouping $\text{Ln}(\text{H}_2\text{O})_6\text{O}_6^{-9}$, which is two interpenetrating trigonal prisms and requires a coordination number of twelve.

2. The crystals of some 6-hydrates do not contain the grouping $\text{Ln}(\text{H}_2\text{O})_6^{+3}$ (67). The compound $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, and presumably other isomorphous salts of this composition, has the grouping $\text{Gd}(\text{H}_2\text{O})_6\text{Cl}_2^+$, a square antiprismatic arrangement of coordination number eight.

3. The formation of complex ions such as $\text{Ln}(\text{RCHOHCO}_2)_4$ (18, 19), $\text{Ln}(\text{cit})_n^{(3-3n)}$ (68, 69), $\text{Ln}(\text{NTA})_2^{-3}$ (45, 70), $\text{Ln}(\text{DTPA})^{-2}$ (39, 54), $\text{Ln}(\text{HEDTA})(\text{IMDA})^{-2}$ (61), $\text{Ln}(\text{gluc.})^{+2}$ (71, 72), and $\text{Ln}(\text{HCP})_4^{-5}$ (32), where more than six donors exist for each Ln^{+3} ion, probably requires coordination numbers in excess of six.

4. The ability of certain complex species to add additional ligands, e.g., to form $\text{Ln}(\text{HEDTA})(\text{IMDA})$ (61), $\text{Ln}(\text{NTA})_2^-$ (45, 70), or $\text{Ln}(\text{HEDTA})(\text{OH})^-$ (73, 74) again indicates coordination numbers larger than six.

5. The existence of the species $\text{HLn}(\text{EDTA})(\text{H}_2\text{O})_n$ (16, 75, 76), $\text{Ln}(\text{EDTA})(\text{H}_2\text{O})_m^-$ (16, 75, 76), $\text{Ln}(\text{glycolate})_3(\text{H}_2\text{O})_8$ (21), and $\text{Ln}(\text{lactate})_3(\text{H}_2\text{O})_r$ (21) and the commonness with which water appears in the derivatives of other complexes require a larger coordination number than six.

6. The crystal structure of a number of compounds that are not complexes indicate clearly that, irrespective of oxidation state, these cations are most commonly associated with 7-12 nearest donor neighbors.

The problem of coordination number can best be solved by determination of the crystal structures of representative complex species. A promising beginning shows a ten-coordination in the compound $\text{HLa}(\text{EDTA})(\text{H}_2\text{O})_4 \cdot 3\text{H}_2\text{O}$ and nine coordination in the $\text{La}(\text{EDTA})(\text{H}_2\text{O})_3^-$ (77).

The fourth consideration is the change in coordination number of the solvent layer in contact with the metal ion. This seems to be one possible explanation for the double series observed with the variation of properties such as activity coefficients, transference numbers, heats of dilution, partial molar volumes, and partial molar compressibilities for a number of rare-earth salts (78) as well as the

double series found in the ΔH° , $T\Delta S^\circ$ data reported for EDTA (79), NTA (80), diglycolate (81), dipicolinate (81), acetate (82), glycolate (82) and thioglycolate (82). The trends in ΔH° and $T\Delta S^\circ$ for all ligands are very much the same. The rare-earth diglycolates are used as an example see Figures 2 and 3. This indicates that the variation is caused mainly by some property of the metal ion itself. The ordered water structure around the metal ions serves as an entropy source, and the magnitude of the entropy change depends mainly on the number of water molecules replaced by the ligand. An increase in the number of water molecules replaced will result in an increase of entropy accompanied by a change in enthalpy. Thus, this could be the cause of the double series.

Figure 2. ΔH_1^0 for the formation of rare-earth diglycolates

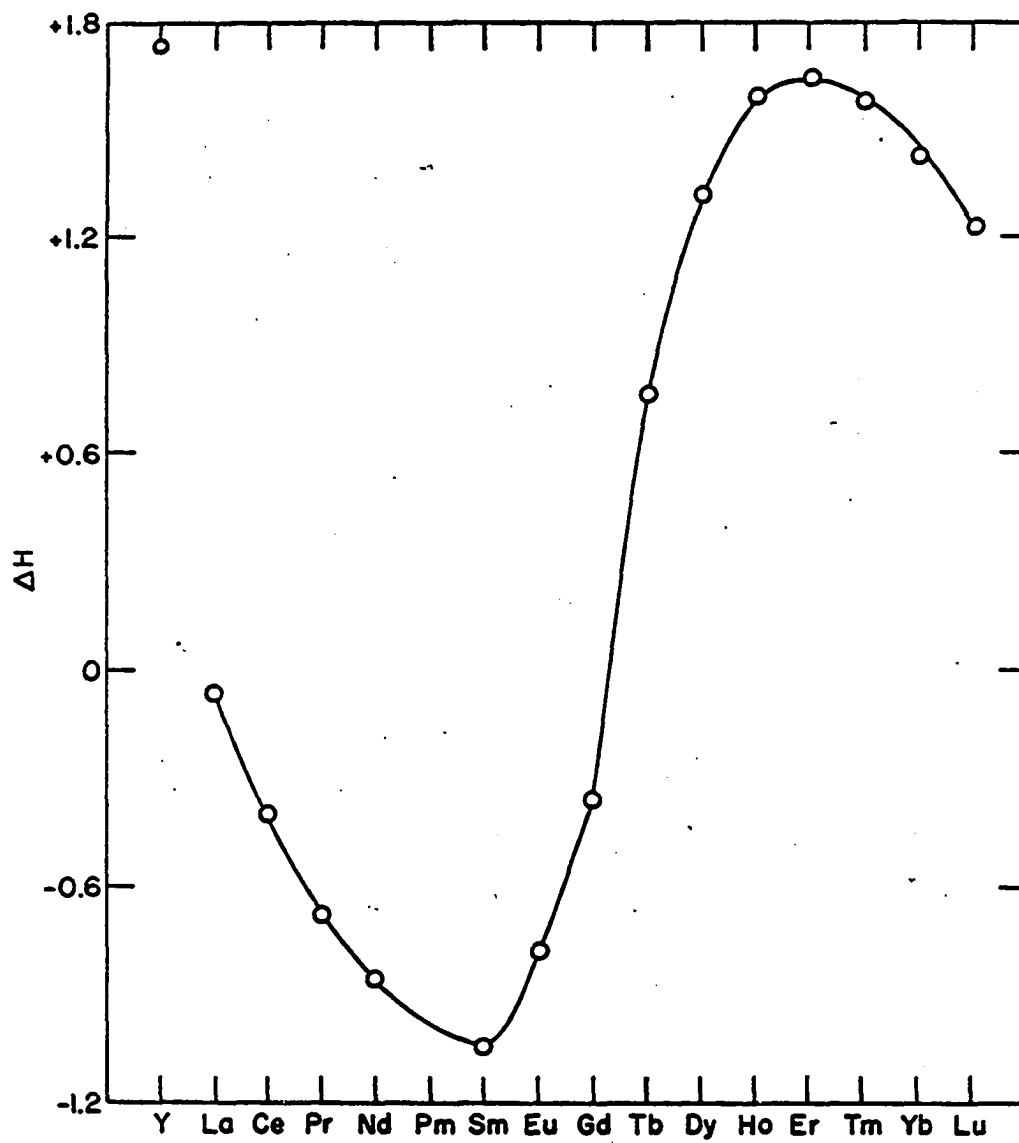
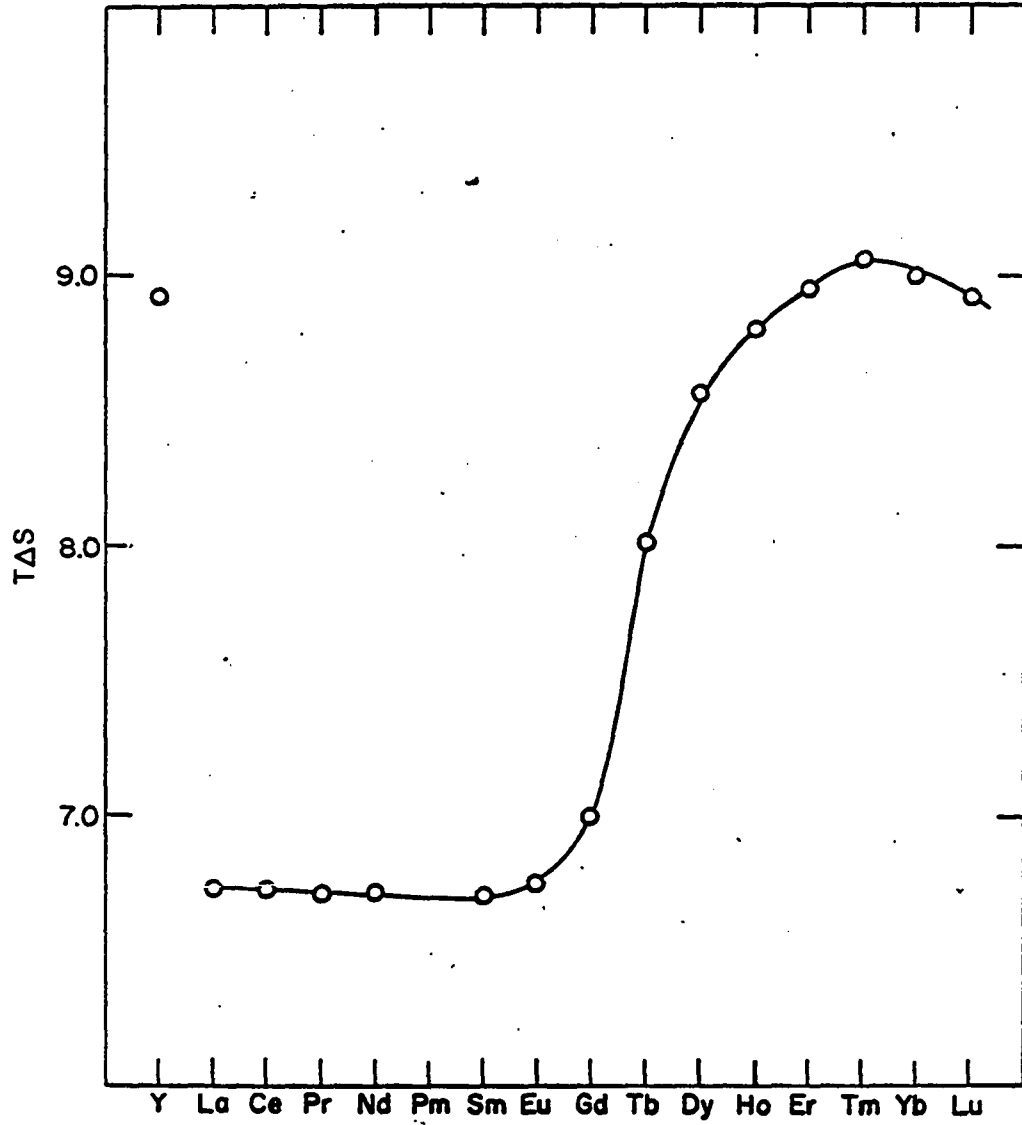


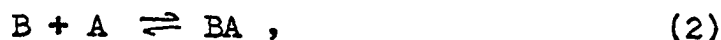
Figure 3. TAS_1^0 for the formation of rare-earth diglycolates



MATHEMATICAL COMPUTATION OF STABILITY CONSTANTS

General Approach

What is going on chemically in solution when complexes are formed? A solvated ligand approaches a solvated cation and replaces some of the water molecules around the metal ion. Since an investigator cannot determine the exact number of waters, hydration will not be taken into account in expressing the following equilibria. Neither will this author show the charge of the species in the following equilibria, since the reaction is not a redox reaction. The various equilibria between the metal ion, B, and the ligand, A, can be represented as follows:



. . . ,



for mononuclear complexes, and



for polynuclear complexes. However, polynuclear complexes have been shown not to exist in any appreciable quantity for acetate (12, 13), glycolate (20), isobutyrate (30), α -hydroxyisobutyrate (30), trihydroxyisobutyrate (30), methylethylglycolate (31), methylpropylglycolate (31), propylglycolate (31), and diglycolate (38).

According to the Debye-Hückel theory, the activities of ionic species in a solution are primarily a function of the ionic strength of the solution. The work in this dissertation was done at a constant high concentration of non-participating background electrolyte, and consequently concentrations based on stoichiometry will be used instead of activities.

The equilibrium constants representing equations 2 through 4 can be written

$$b_1 = \frac{(BA)}{(B)(A)} , \quad (6)$$

$$b_2 = \frac{(BA_2)}{(BA)(A)} , \quad (7)$$

• • • ,

$$b_N = \frac{(BA_N)}{(BA_{N-1})(A)} , \quad (8)$$

where the parentheses represent the concentration of the species contained therein. The constants b_n are referred to as stepwise formation constants. The overall constants may also be written for the reactions



• • • ,



These constants are

$$\beta_1 = \frac{(BA)}{(B)(A)}, \quad (12)$$

$$\beta_2 = \frac{(BA_2)}{(B)(A)^2}, \quad (13)$$

. . . ,

$$\beta_N = \frac{(BA)_N}{(B)(A)^N}. \quad (14)$$

Obviously,

$$\beta_n = \prod_{i=1}^n \beta_i \quad (15)$$

where β_0 is defined as unity.

The following definitions must be made:

C_A = total ligand concentration in solution

a = free (uncomplexed) ligand concentration

C_B = total metal concentration in solution

C_b = free (uncomplexed) metal concentration.

The quantities C_A and C_B are very easy to come by; however, one must determine either a or C_b . The quantity a is determined in this research. Bjerrum defines the mean ligand number \bar{n} as the concentration of the complexed ligand divided by the total concentration of metal or

$$\bar{n} = \frac{C_A - a}{C_B}. \quad (16)$$

From material balance,

$$C_A = a + (BA) + 2(BA_2) + 3(BA_3) + \dots + N(BA_N) \quad (17)$$

$$C_B = (B) + (BA) + (BA_2) + (BA_3) + \dots + (BA_N) . \quad (18)$$

It is readily seen that

$$C_A = a + C_b \sum_{n=0}^N n \beta_n a^n , \quad (19)$$

$$C_B = C_b \sum_{n=0}^N \beta_n a^n . \quad (20)$$

Equation 16 then becomes

$$\bar{n} = \frac{\sum_{n=0}^N n \beta_n a^n}{\sum_{n=0}^N \beta_n a^n} = \frac{C_A - a}{C_B} . \quad (21)$$

Equation 21 must be solved in order to find the stability constants.

Calculation of Ionization Constants

In order to solve equation 21, we must know \bar{n} and a . When working with carboxylic acids as ligands, we use hydrogen ion concentration to determine a . Hydrolysis is assumed not to occur since solutions in this work were between pH 2 and pH 4; and at such low pH values, hydrolysis is negligible (10, 11). The possibility of hydrolysis was studied for acetate and glycolate and was not found to occur (12, 13, 21). It also has been shown that rare-earth ion does not complex with undissociated carboxylic acid (12, 13, 19). Thus knowing

the ionization constant, one can determine α .

The following definitions must now be introduced:

α_j = the ionization constant of the j th proton

$$\alpha_j = \frac{(H^+)^j (A)}{(H_j A)}$$

K_j = the j th stepwise ionization constant

$$K_j = \frac{(H^+) (H_{(j-1)} A)}{(H_j A)}$$

thus

$$\alpha_j = \prod_{n=1}^j K_n$$

C_A = total ligand concentration

C_H = total hydrogen concentration

C_{Na} = all sodium ion concentration except sodium ion
from $NaClO_4$

(H^+) = the concentration of free hydrogen.

For a monobasic acid, one has

$$\alpha_1 = K_1 = \frac{(H^+) (A^-)}{(HA)} , \quad (22)$$

$$C_A = (HA) + (A^-) , \quad (23)$$

$$C_H = (HA) + (H^+) . \quad (24)$$

Thus we have three equations and three unknowns, which is easy to solve. Here is equation 22 with experimentally determined quantities

$$\alpha_1 = K_1 = \frac{(H^+)(C_{Na} + (H^+))}{(C_H - (H^+))} . \quad (25)$$

For a dibasic acid, one has

$$\alpha_1 = K_1 = \frac{(H^+)(A^-)}{(HA^-)} , \quad (22)$$

$$\alpha_2 = K_1 K_2 = \frac{(H^+)^2 (A^{2-})}{(H_2A)} , \quad (26)$$

$$C_A = (H_2A) + (HA^-) + (A^-) , \quad (27)$$

$$C_H = 2(H_2A) + (HA^-) + (H^+) . \quad (28)$$

Thus we have five unknowns and four equations. After the proper substitutions of one equation into another, one obtains the equation

$$\frac{(H^+)^2 (C_{Na} + (H^+))}{(2C_A - C_{Na} - (H^+))} = \frac{K_2 (H^+) (C_A - C_{Na} - (H^+))}{(2C_A - C_{Na} - (H^+))} + K_1 K_2 \quad (29)$$

which is an equation of a straight line with slope of K_2 and intercept of $K_1 K_2$. This equation was solved by an unweighted least square method using a digital computer.

Calculation of \bar{n} and a from Potentiometric Data

For a monobasic acid, we have

$$K_1 = \frac{(H^+)(C_{Na} + (H^+))}{(C_H - (H^+))} ; \quad (25)$$

thus

$$(A^-) = a = \frac{K_1 (C_H - (H^+))}{(H^+)} \quad (30)$$

and

$$\bar{n} = \frac{C_{Na} + (H^+) - a}{C_B} \quad (31)$$

If there is excess acid, C_p , in the metal perchlorate solution, it is accounted for in equations 30 and 31 as follows:

$$a = \frac{K_1(C_H + C_p - (H^+))}{(H^+)} \quad (32)$$

$$\bar{n} = \frac{C_{Na} - C_p + (H^+) - a}{C_B} \quad (33)$$

For a dibasic acid, we have

$$\alpha_1 = K_1 = \frac{(H^+)(A^-)}{(HA)} \quad (22)$$

$$\alpha_2 = K_1 K_2 = \frac{(H^+)^2 (A^{2-})}{(H_2A)} \quad (26)$$

$$(H_2A) = C_H/2 - (HA^-)/2 - (H^+)/2 \quad (28)$$

With the proper substitution of one equation into another, one obtains the following equation

$$(A^-) = a = \frac{\alpha_1 \alpha_2 (C_H - (H^+))}{2\alpha_1 (H^+)^2 + \alpha_2 (H^+)} \quad (34)$$

The total amount of ligand in solution available for complexing is

$$(A^-) = C_A - C_H/2 + (H^+)/2 - 1/2(HA^-) \quad (35)$$

$$(A^-) = C_A - C_H/2 + (H^+)/2 - \frac{(H^+)(A^-)}{2\alpha_1} \quad (36)$$

Since total ligand minus free ligand equals complexed ligand,

$$\bar{n} = \frac{C_A - C_H/2 + (H^+)/2 - (H^+)(A^-)/2\alpha_1 - (A^-)}{C_B} \quad (37)$$

Substituting from equation 34 for $C_H/2 + (H^+)/2$

$$\bar{n} = \frac{C_A - (A^-)/2 \left(\frac{\alpha_2(H^+) + 2\alpha_1(H^+)^2}{\alpha_1\alpha_2} \right) + \frac{(H^+)(A^-)}{2\alpha_1} - (A^-)}{C_B}, \quad (38)$$

and collecting like terms and putting over a common denominator

$$\bar{n} = \frac{C_A - \frac{(A^-)}{2} \left(\frac{2\alpha_2(H^+) + 2\alpha_1(H^+)^2}{\alpha_1\alpha_2} \right) - (A^-)}{C_B}, \quad (39)$$

and again collecting like terms, \bar{n} finally is

$$\bar{n} = \frac{C_A - (A^-) \left(1 + \frac{\alpha_2(H^+) + \alpha_1(H^+)^2}{\alpha_1\alpha_2} \right)}{C_B} \quad (40)$$

For both monobasic and dibasic acids, \bar{n} and a were calculated using a digital computer.

Calculation of the Stability Constants from \bar{n} and a

There are many methods of calculating stability constants. In this dissertation two will be discussed: 1) Fronaeus' method (83) as an example of graphical technique, and 2) the least squares method (84) used in this research as an example of the computer technique. In Fronaeus' method, we define

$$X = \sum_{n=0}^N \beta_n a^n, \quad (41)$$

$$X' = \frac{dX}{da} = \sum_{n=0}^N n \beta_n a^{n-1}. \quad (42)$$

Then inserting these into equation 21

$$\bar{n} = \frac{\sum_{n=0}^N n \beta_n a^n}{\sum_{n=0}^N \beta_n a^n} = \frac{C_A - a}{C_B}, \quad (21)$$

we have

$$\bar{n} = aX' / X. \quad (43)$$

This may be solved to give

$$nX = \int_0^{a_1} (\bar{n}/a) da. \quad (44)$$

The integral in equation 44 may be evaluated graphically or numerically to give sets of data (X_1, a_1) . The stability constants β_1, β_2 , etc. can now be calculated by successive extrapolation to $a = 0$ of the function X_1, X_2 , etc..

$$X_1 = \frac{X - 1}{a} = \beta_1 + \beta_2 a + \beta_3 a^2 + \dots \quad (45)$$

$$X_2 = \frac{X_1 - 1}{a} = \beta_2 + \beta_3 a + \dots \quad (46)$$

The least squares method used in this research was developed by W. R. Stagg (84) using the weighting factor which was described by Sullivan et al. (85) and Rydberg (86).

If we take equation 21

$$\bar{n} = \frac{\sum_{n=0}^N n\beta_n a^n}{\sum_{n=0}^N \beta_n a^n} = \frac{C_A - a}{C_B} \quad (21)$$

and crossmultiply

$$\sum_{n=0}^N nC_B\beta_n a^n = \sum_{n=0}^N (C_A - a)\beta_n a^n \quad (47)$$

and then subtract $\sum_{n=0}^N nC_B\beta_n a^n$ from both sides and combine like terms, we get

$$\sum_{n=0}^N (C_{A_1} - a_1 - nC_{B_1})\beta_n a_1^n = 0 \quad (48)$$

The i was inserted to denote that for every experimental point there is a discrete C_A , a , and C_B . Because of experimental error, in practice, equation 48 does not exactly equal zero. The residual of a given set of data $(C_{A_1} - a_1 - nC_{B_1})$ is given by

$$U_1 = \sum_{n=0}^N (C_{A_1} - a_1 - nC_{B_1})\beta_n a_1^n \quad (49)$$

The weighted sum of the squares of these residuals is then

$$S = \sum_{i=1}^I W_i U_i^2 \quad (50)$$

where the summation is carried over I sets of data. If we minimize this sum with respect to each of the parameters,

that is,

$$\partial S / \partial \beta_n = 0 , \quad (51)$$

we have N equations in the β_n which then may be solved using Cramer's rule of matrix algebra. In the matrix technique, the standard deviation of each of the parameters may be calculated from the diagonal elements of the inverse of the matrix of the coefficients of the β_n 's. This deviation is given by

$$\beta_n = \sqrt{\frac{r_{nn}S}{I - N}} \quad (52)$$

where r_{nn} is the diagonal element of the inverse coefficient. These deviations are the errors of internal consistency of the data points used to compute each parameter and are considerably smaller than the more realistic maximum possible error. The systematic error, which may have occurred in determining acid dissociation constants, concentrations of metal perchlorate, ligand buffer solutions, and so forth, are not reflected in these deviations. When computations were made in which the input data were varied within their estimated maximum limits of error, it was found that the relative errors in β_1 , β_2 , β_3 could be as great as $\pm 10\%$, $\pm 25\%$, and $\pm 50\%$, respectively for a three parameter system (85). For a two parameter system, the relative errors could be as great as $\pm 25\%$ and $\pm 50\%$ for β_1 and β_2 respectively (84).

The choice of weighting factor is arbitrary. The

weighting factor used in this research is

$$w_i = 1/\delta U_i^2 \quad (53)$$

where

$$\delta U_i = (\partial U_i / \partial a_1) a_1 p, \quad (54)$$

p being the estimated relative probable error in the free ligand concentration. Thus each point is weighted with respect to the variance of the residual with free ligand concentration. Consequently, the first data points are weighed more heavily than the later.

In practice, after the \bar{n} 's and a 's are calculated, they are looked over to detect any discrepancies. If there are any, these points are removed. Then the value of the total ligand concentration, the free ligand concentration, and the total metal concentration and estimated β_n 's are fed into the computer. The IBM 7074 calculates β_n 's until the β_n 's differ from each other by less than one part per thousand and until the standard deviation in each parameter was of smaller magnitude than the given parameter. The limit on the number of iterations is 50; however, it was found that if these conditions were to be found they were found in no more than 10 iterations. The program then was called upon to calculate \bar{n} from the β_n 's it had calculated. The experimenter then compares the calculated \bar{n} to the experimental \bar{n} to see if the β_n 's calculated correspond to the experimental conditions.

EXPERIMENTAL DETAILS

Preparation of Reagents

Rare earth perchlorate solutions

The stock solutions of approximately 0.5 M, which were the same solutions used by Stagg and Powell (84) in the determination of the rare-earth isobutyrate, α -hydroxyisobutyrate, and α, β, β' -trihydroxyisobutyrate stability constants, were diluted to 0.1000 M. The cerium solution had excess perchloric acid to stabilize the trivalent state. Promethium was not done.

Sodium hydroxide solution

An approximately 1 M carbonate-free sodium hydroxide solution was prepared by the method of Powell and Hiller (87) and standardized against potassium acid phthalate.

Sodium perchlorate solution

An approximate 1 M sodium perchlorate was prepared by neutralizing to a pH 6 perchloric acid with sodium hydroxide. This solution was then run through ion-exchange column which had Dowex-50 resin in the sodium form. This was done to insure there were no hydrogen ions as well as other metal ions in the solution. The solution was analyzed by passing aliquots through a hydrogen-form Dowex-50 bed and titrating the eluate with standard KOH.

Perchloric acid reference solution

Approximately 0.1 M perchloric acid was prepared by dilution of the 70% acid and standardized against sodium carbonate. An exactly 0.001 M solution of this was prepared by dilution with distilled water and sufficient sodium perchlorate to give an ionic strength of 0.1 M.

Mandelate buffer

Mandelic acid (Eastman Organic Chemicals) was recrystallized three times from acetone-petroleum ether mixture. The equivalent weight was determined by titration with a standard KOH. It was found to be 151.2 (calc. 151.9). Two buffers were made up. Both had the same ratio of NaA/HA which was one. One buffer was 0.5 M while the other was 0.05 M. It was made up by weighing the mandelic acid, neutralizing it partially with standard sodium hydroxide. The excess acid was then titrated with standard KOH.

Quinic acid

The equivalent weight of quinic acid (K & K Chemicals) was determined by titration with standard KOH to be 194.8 (calc. 192.2). A 0.2 M solution of quinic acid with a ratio of NaA/HA of one was made up by weighing the quinic acid, neutralizing it partially with standard sodium hydroxide. The excess acid was then titrated with standard KOH.

Dilactic acid

The diethyl lactate (88) was prepared from ethyl lactate, sodium, and ethyl α -bromopropionate by Dr. Jack E. Powell. The diethyl lactate fraction collected at 20 mm from 115-125°C had three impurities when checked by GPC. The ester was redistilled and the 103-104°/7 mm fraction was collected. It was greater than 99% pure by GPC. Infra-red and NMR were also done on the ester. The ester was then dissolved in 500 ml absolute ethanol. Eighty g of NaOH were dissolved in 1500 ml hot absolute ethanol. While the ester was refluxing, the NaOH solution was filtered directly into it. The sodium dilactate precipitate was filtered and washed. The sodium dilactate was dissolved in 2 l. of water and passed through a four equivalent Dowex-50 bed in the hydrogen form. Approximately 5.5 l. of dilactic acid were obtained. Since the dilactic acid is very hydroscopic, and water could not be removed, it was assumed no impurities were added in converting the ester to the acid. A 0.1 M solution of dilactic acid with the ratio of $\text{Na}_2\text{A}/\text{H}_2\text{A}$ of one by partially neutralizing a solution of dilactic acid with standard sodium hydroxide. The excess acid was titrated with standard KOH.

Technique

The ionization constants of the ligand must first be determined under the same conditions as one is going to deter-

mine the stability constants. Twelve to eighteen solutions, whose total volume was 50.0 ml, were prepared varying the C_A concentration from 0.1 mmoles to 5.0 mmoles, except for dilactic acid where C_A varied from 0.05 to 2.0 mmoles. In the case of dilactic acid, there were also six solutions with the ratio Na_2A/H_2A varying from 0 to 4. All these buffer solutions had the same total concentration $C_A = 0.5$ mmoles. The solutions to determine the stability constants had the same varying C_A ; however, the C_B was kept constant at 0.2 mmoles. For quinic acid, dysprosium was also run where $C_B = 0.3$ mmoles. Both ionization and stability constants were first determined roughly, and then new solutions were prepared in which the amount of sodium perchlorate added was varied slightly to compensate for the expected change in ionic strength.

The hydrogen concentration was determined using a Beckman Research pH Meter whose relative accuracy is 0.001 pH and its repeatability is 0.0005 pH. Glass and calomel electrodes were used. To avoid activity coefficient corrections, standardization was done frequently with a perchloric acid solution of known pH adjusted to $\mu = 0.1000$ with sodium perchlorate.

Solid Chelates

The method of preparation used was to stir stoichiometric (3:1) quantities of the sodium salt of quinic acid with rare-

earth chlorides. The solid was filtered under vacuum and washed with acetone until chloride-free. They were allowed to air dry before determining the water of hydration using the thermobalance technique. The temperature range was from room temperature up to 500°C. The solid was then placed in a muffle furnace and ignited to the oxide.

EXPERIMENTAL RESULTS

The Mandelate Complexes

The results obtained for the rare-earth mandelates are shown in Table 1 and Table 2. The difference in the two tables is that the results in Table 1 are calculated by using a constant K_1 while the results in Table 2 are calculated using a variable K_1 .

Table 1. Stability constants of the rare-earth mandelate complexes ($T = 25.0^\circ\text{C}$; $\mu = 0.1$ (NaClO_4); $K_1 = 6.110 \times 10^{-4}$)

Metal	$\beta_1 \times 10^{-2}$	$\beta_2 \times 10^{-4}$	$b_2 \times 10^{-2}$	$\beta_1 \times 10^{-2}{}^a$
La	1.84 \pm 0.06	0.97 \pm 0.06	52 \pm 4	2.16
Ce	2.24 \pm 0.04	1.97 \pm 0.05	88 \pm 3	2.67
Pr	2.90 \pm 0.05	2.99 \pm 0.07	103 \pm 3	3.70
Nd	3.19 \pm 0.03	3.92 \pm 0.05	123 \pm 2	4.20
Sm	3.56 \pm 0.06	6.35 \pm 0.11	178 \pm 4	4.58
Eu	3.45 \pm 0.20	7.23 \pm 0.70	209 \pm 24	4.97
Gd	3.38 \pm 0.12	6.96 \pm 0.44	206 \pm 15	4.88
Tb	3.92 \pm 0.18	8.72 \pm 0.96	223 \pm 27	5.51
Dy	4.02 \pm 0.07	11.7 \pm 0.7	290 \pm 18	5.95
Ho	4.30 \pm 0.14	13.9 \pm 0.4	325 \pm 11	6.49
Er	4.61 \pm 0.14	18.2 \pm 0.8	396 \pm 21	7.07
Tm	4.52 \pm 0.45	28.1 \pm 3.4	621 \pm 97	7.90
Yb	7.04 \pm 0.49	28.4 \pm 4.4	403 \pm 68	9.65
Lu	6.69 \pm 0.24	36.9 \pm 2.3	551 \pm 39	10.00
Y	3.64 \pm 0.12	10.8 \pm 0.5	298 \pm 16	5.43

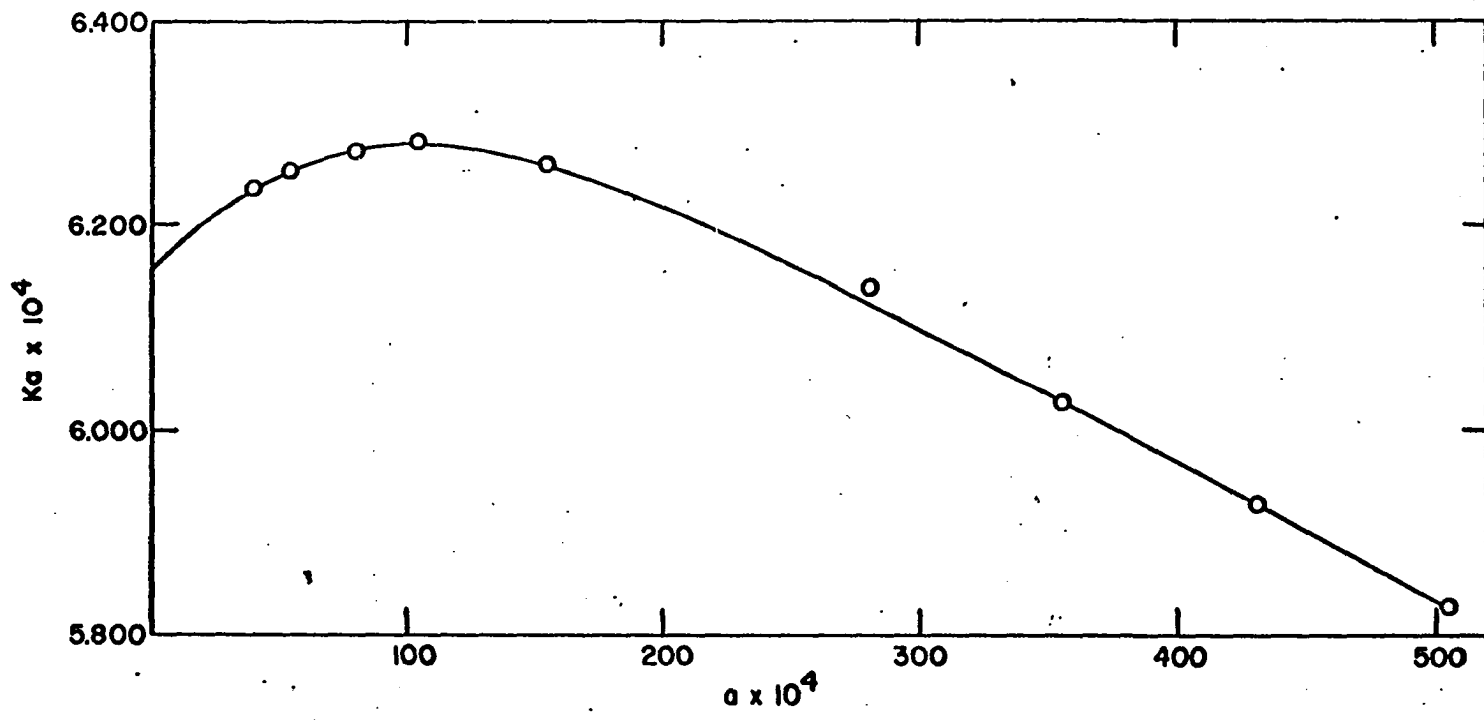
^aCalculated as if only one complex present.

Table 2. Stability constants of the rare-earth mandelate complexes ($T = 25^{\circ}\text{C}$; $\mu = 0.1$ (NaClO_4))

Metal	$\beta_1 \times 10^{-2}$	$\beta_2 \times 10^{-4}$	$b_2 \times 10^{-2}$
La	1.91 \pm 0.07	0.64 \pm 0.06	34 \pm 4
Ce	2.32 \pm 0.06	1.52 \pm 0.08	66 \pm 4
Pr	2.98 \pm 0.03	2.45 \pm 0.04	82 \pm 2
Nd	3.30 \pm 0.03	3.25 \pm 0.05	99 \pm 2
Sm	3.62 \pm 0.04	5.65 \pm 0.08	156 \pm 3
Eu	3.44 \pm 0.19	6.65 \pm 0.66	193 \pm 22
Gd	3.36 \pm 0.12	6.49 \pm 0.43	193 \pm 16
Tb	3.93 \pm 0.24	7.95 \pm 1.28	202 \pm 35
Dy	3.99 \pm 0.11	11.1 \pm 0.6	278 \pm 18
Ho	4.28 \pm 0.07	13.3 \pm 0.4	311 \pm 11
Er	4.58 \pm 0.13	17.4 \pm 0.8	380 \pm 21
Tm	4.48 \pm 0.44	27.2 \pm 3.3	606 \pm 95
Yb	6.99 \pm 0.48	27.4 \pm 4.3	392 \pm 67
Lu	6.66 \pm 0.23	35.6 \pm 2.2	535 \pm 38
Y	3.63 \pm 0.12	10.3 \pm 0.5	282 \pm 16

This was done because it was noticed that there was a regular variation in the ionization constant as determined experimentally which can be seen in Figures 4 and 6. This trend has been found in all the ionization constants determined in this laboratory. To vary the ionization constant one used the a calculated with constant K_1 and read off the figure the appropriate K_1 corresponding to that a . The \bar{n} and a values were next recalculated using the variable K_1 , and then the β values were recalculated. In most instances the variable K_1 method has provided a better fit of the β 's to the experimental results. That is, \bar{n} and a calculated are

Figure 4. K_a versus a for mandelic acid



closer to \bar{n} and a experimental.

For mandelate complexes, using a variable K_1 does not improve the precision, but the fit is better. The precision is probably not improved because the maximum \bar{n} , for europium through lutetium, is no higher than 0.7. For lanthanum through samarium the maximum \bar{n} is 1.5. That is for europium through lutetium, the data do not warrant calculating a second stability constant. The maximum obtainable \bar{n} is low because of precipitation of the chelate with samarium through lutetium.

Because of this equation 21 was rewritten

$$\frac{\bar{n}}{(1 - \bar{n})a} = \beta_1 + \beta_2 \frac{(2 - \bar{n})a}{(1 - \bar{n})} + \sum_{n=3}^N \frac{n - \bar{n}}{1 - n} \beta_n a^{n-1} . \quad (55)$$

It has been found experimentally that only after \bar{n} of 0.4 does β_2 influence the calculations. Therefore, it was assumed that β_2 was negligible up to \bar{n} equal 0.4. Equation 55 for data up to $\bar{n} = 0.4$ then reduces to

$$\frac{\bar{n}}{(1 - \bar{n})} = \beta_1 . \quad (56)$$

Values of β_1 were recalculated using equation 56. These β_1 values are shown in Table 1 and Figure 5.

Polynuclear complexes were assumed to be absent, since they were not present in other glycolate systems (20, 30, 31).

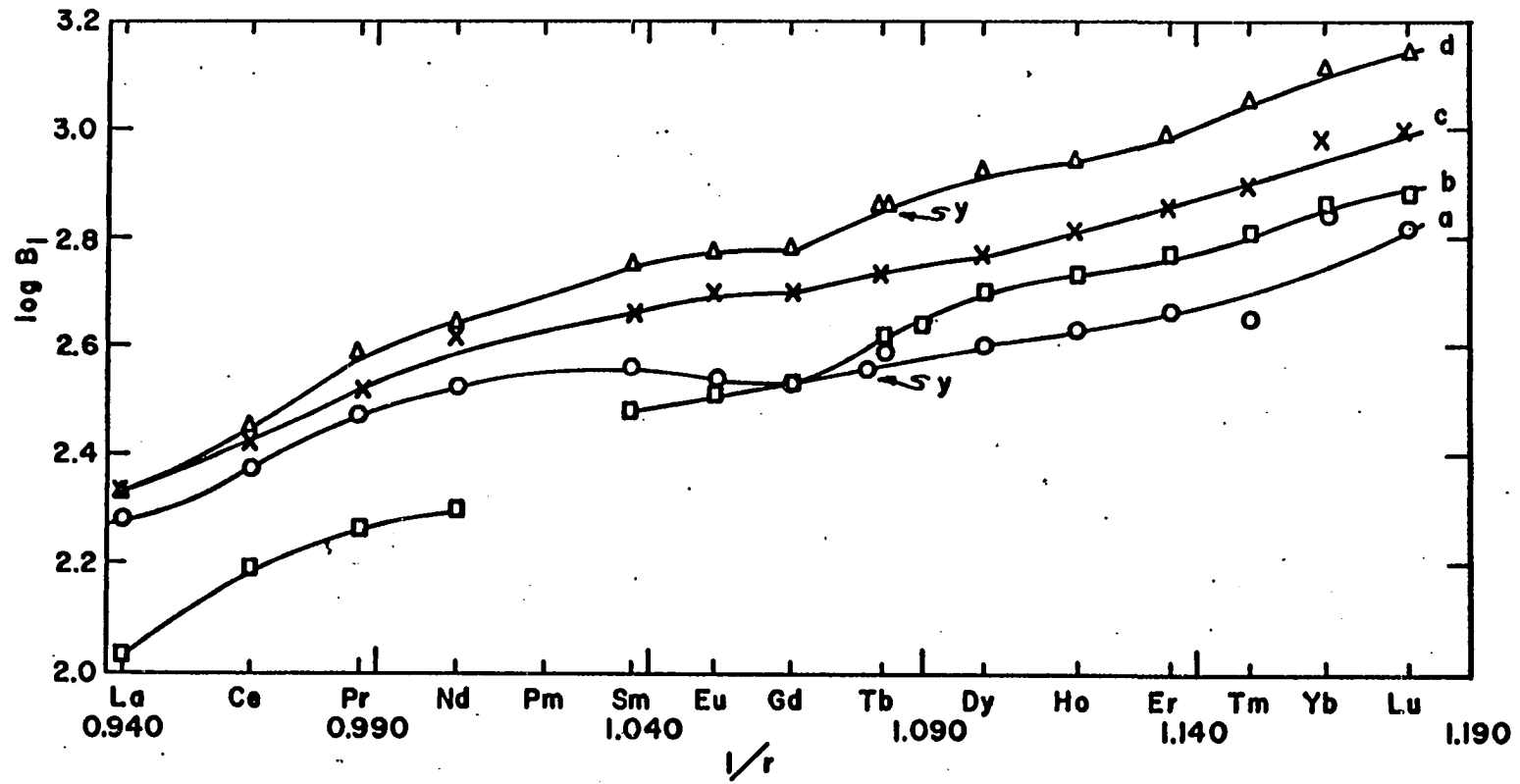
Figure 5. One over the ionic radius in angstroms versus the logarithm of the first stability constants of the rare-earth

a) mandelate (calculated assuming two complexes)

b) tertiarybutylglycolate

c) mandelate (calculated assuming one complex)

d) ethylglycolate



The Quinate Complexes

Again the stability constants were calculated using both constant K_1 as listed in Table 3 and variable K_1 as listed in Table 4. A four parameter program was tried on the heavy rare-earths' data, since \bar{n} went up to 2.8-2.9, to see if this would provide a better fit. Since the four parameter program did not improve matters, only the β values calculated using the three parameter program are reported.

Because of the hydroxyl groups on the 3,4,5 positions, it was thought quinic acid might possibly form polynuclear complexes. If a system is mononuclear, \bar{n} is a function of a alone; but, if polynuclear complexes are present, \bar{n} is a function of the metal ion concentration as well as a . Consequently, dysprosium was studied at two concentrations. A plot of \bar{n} versus a shows no appreciable difference between the data for the two metal concentrations. See Figure 8. Therefore, it was assumed that no polynuclear complexes were formed.

From the thermal decomposition data for the heavy-rare-earth quinates, it appears that there are no water coordinated to the metal. See Table 5. The light-rare-earth quinates were not studied because only jelly-like substances could be obtained.

Table 3. Stability constants of the rare-earth quininate complexes (T = 25°C;
 $\mu = 0.1$ (NaClO₄); K = 4.35x10⁻⁴)

Metal	$\beta_1 \times 10^{-2}$	$\beta_2 \times 10^{-4}$	$\beta_3 \times 10^{-6}$	b ₂	b ₃
La	2.22 ± 0.06	2.14 ± 0.13	0.52 ± 0.06	96 ± 6	24 ± 3
Ce	3.22 ± 0.11	3.82 ± 0.79	1.31 ± 0.16	118 ± 10	34 ± 5
Pr	3.65 ± 0.09	6.09 ± 0.29	1.88 ± 0.17	167 ± 9	31 ± 3
Nd	4.15 ± 0.12	7.41 ± 0.36	2.14 ± 0.22	178 ± 10	28 ± 3
Sm	5.30 ± 0.12	9.93 ± 0.44	4.56 ± 0.32	187 ± 9	45 ± 4
Eu	4.89 ± 0.09	9.59 ± 0.33	4.85 ± 0.24	196 ± 7	51 ± 3
Gd	4.55 ± 0.14	9.18 ± 0.52	4.34 ± 0.37	202 ± 13	47 ± 5
Tb	4.74 ± 0.12	12.4 ± 0.5	4.59 ± 0.34	261 ± 12	37 ± 3
Dy	5.81 ± 0.16	16.6 ± 0.8	7.27 ± 0.68	284 ± 14	44 ± 5
Ho	6.53 ± 0.18	17.5 ± 0.8	10.7 ± 0.7	268 ± 14	61 ± 5
Er	6.63 ± 0.14	21.4 ± 0.5	11.9 ± 0.5	322 ± 10	55 ± 3
Tm	7.56 ± 0.25	27.3 ± 1.2	19.4 ± 1.2	359 ± 20	71 ± 6
Yb	8.77 ± 0.25	36.2 ± 1.3	32.5 ± 1.5	413 ± 20	89 ± 5
Lu	9.42 ± 0.44	44.3 ± 2.5	45.2 ± 3.4	471 ± 35	101 ± 9
Y	4.89 ± 0.17	12.4 ± 0.6	4.56 ± 0.45	254 ± 16	37 ± 4

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Table 4. Stability constants of the rare-earth quinate complexes (T = 25°C;
 $\mu = 0.1$ (NaClO₄))

Metal	$\beta_1 \times 10^{-2}$	$\beta_2 \times 10^{-4}$	$\beta_3 \times 10^{-6}$	b ₂	b ₃
La	2.24 ± 0.04	1.83 ± 0.07	0.37 ± 0.03	81 ± 3	20 ± 2
Ce	3.32 ± 0.08	3.35 ± 0.16	0.97 ± 0.08	101 ± 5	29 ± 3
Pr	3.58 ± 0.12	5.64 ± 0.27	1.29 ± 0.14	157 ± 8	23 ± 3
Nd	4.07 ± 0.12	7.14 ± 0.32	1.45 ± 0.16	175 ± 9	20 ± 2
Sm	5.04 ± 0.09	9.61 ± 0.33	3.35 ± 0.21	191 ± 7	35 ± 2
Eu	4.67 ± 0.07	9.17 ± 0.25	3.51 ± 0.17	196 ± 6	38 ± 2
Gd	4.65 ± 0.13	8.44 ± 0.34	3.37 ± 0.23	182 ± 9	40 ± 3
Tb	5.13 ± 0.13	11.6 ± 0.4	3.40 ± 0.30	226 ± 12	29 ± 3
Dy	5.52 ± 0.09	15.6 ± 0.5	5.38 ± 0.30	282 ± 8	35 ± 2
Ho	6.25 ± 0.15	16.8 ± 0.6	7.98 ± 0.50	269 ± 12	47 ± 3
Er	6.33 ± 0.13	20.5 ± 0.5	8.78 ± 0.36	325 ± 9	42 ± 2
Tm	7.85 ± 0.19	25.8 ± 0.7	15.8 ± 0.6	329 ± 11	61 ± 3
Yb	8.93 ± 0.16	34.7 ± 0.6	26.7 ± 0.7	388 ± 9	77 ± 3
Lu	9.00 ± 0.44	43.0 ± 2.4	35.8 ± 3.0	478 ± 35	83 ± 8
Y	4.67 ± 0.22	11.8 ± 0.6	3.15 ± 0.42	253 ± 18	26 ± 4

Figure 6. K_a versus a for quinic acid

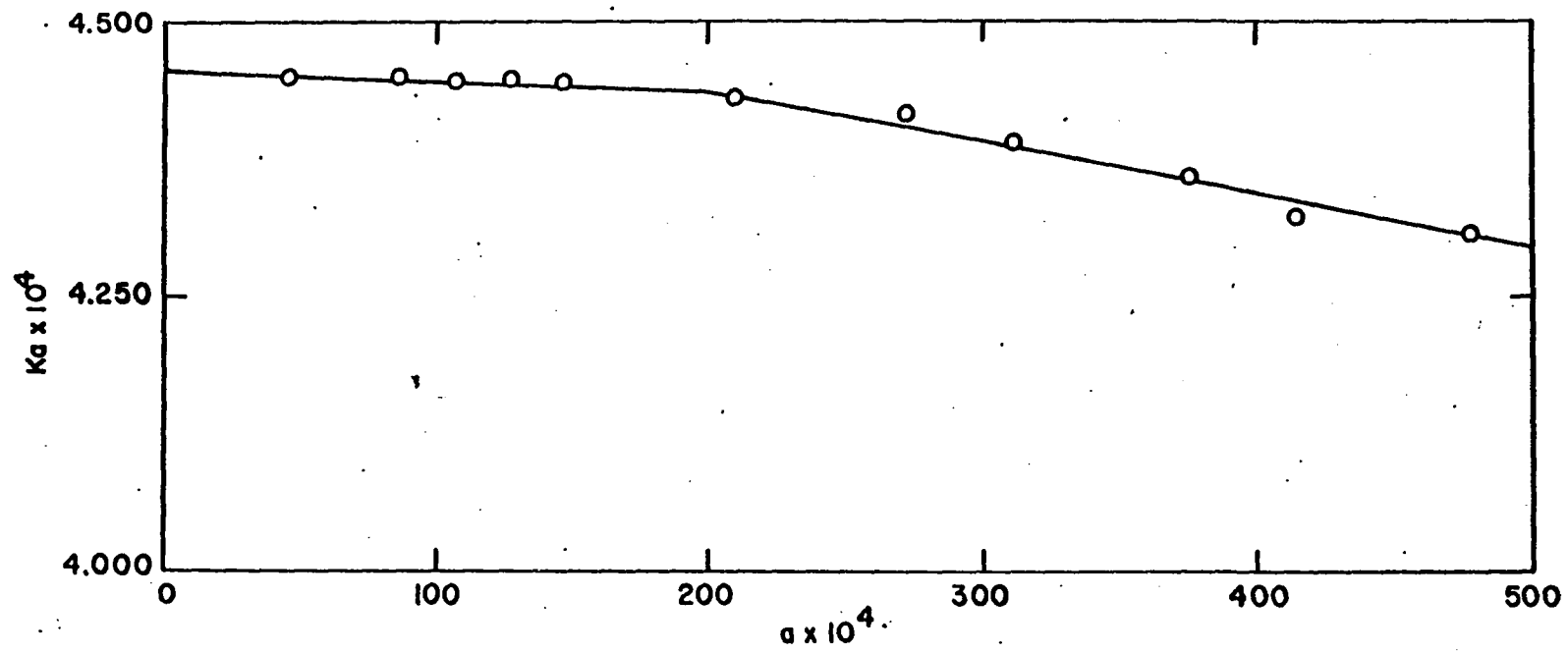


Figure 7. One over the ionic radius in angstroms versus the logarithm of the first stability constants of the rare-earth

- a) 1-hydroxycyclohexanecarboxylate
- b) quinate
- c) 1-hydroxycyclopentanecarboxylate
- d) diethylglycolate

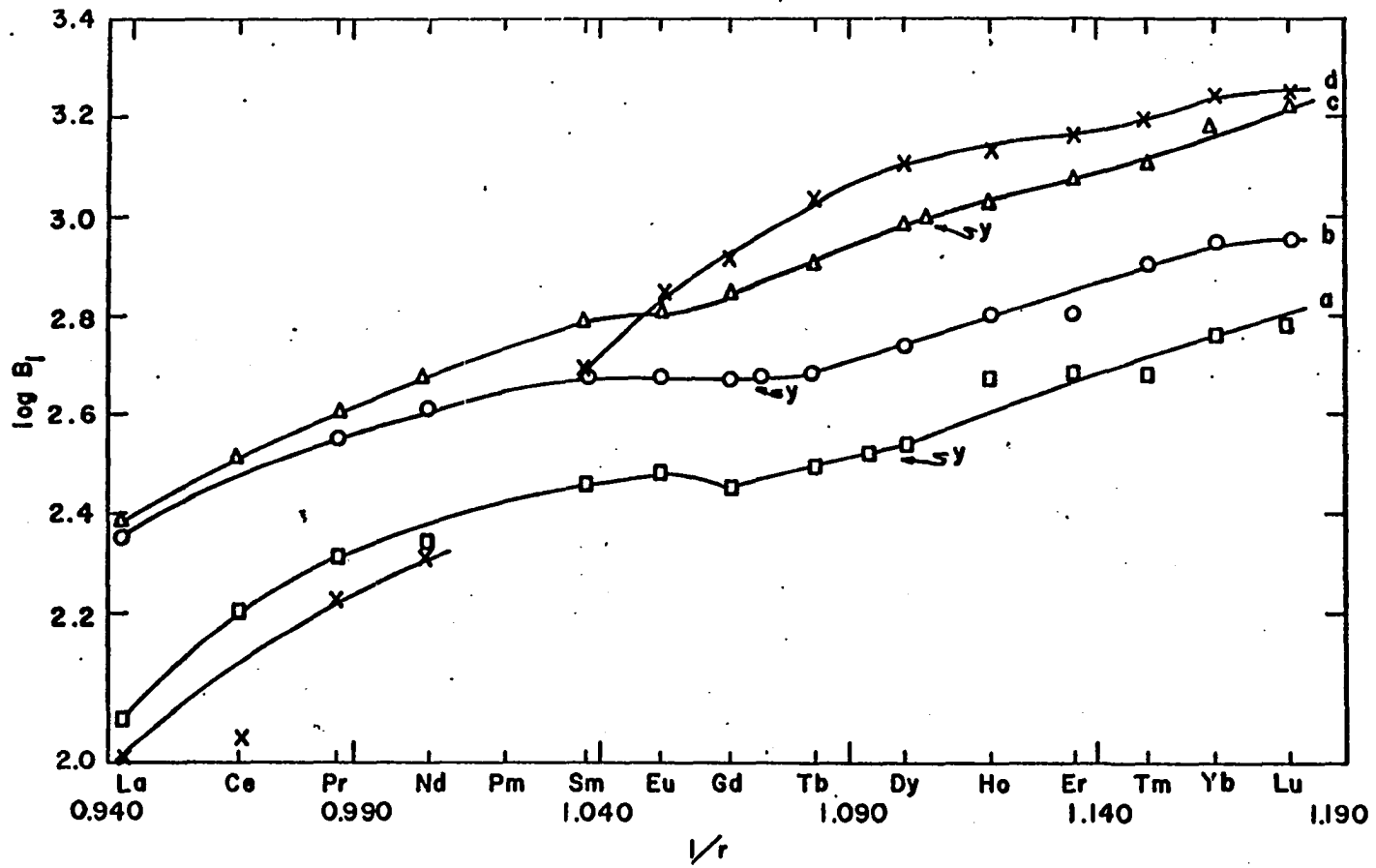


Figure 8. \bar{n} versus a for dysprosium quinate

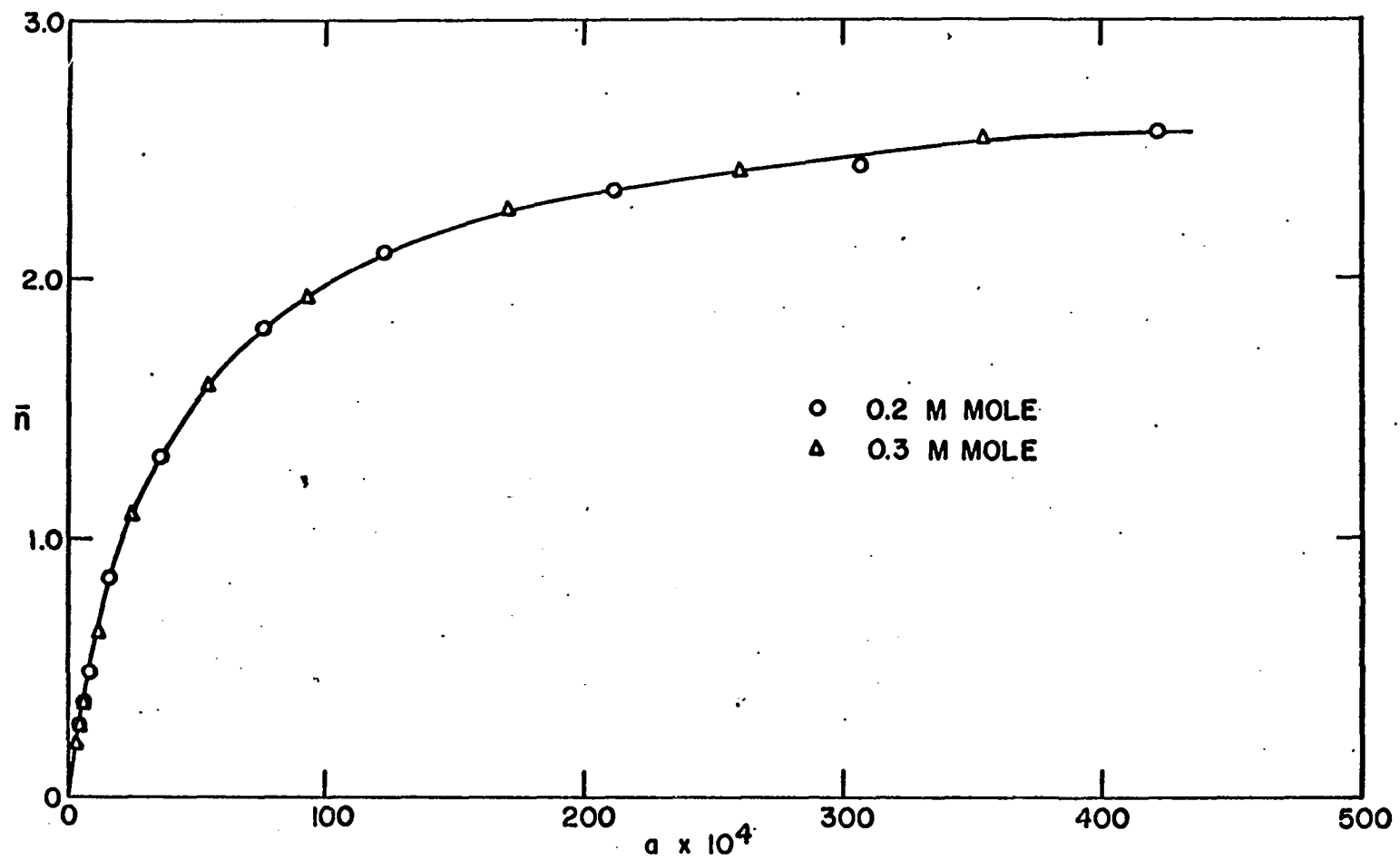


Table 5. Data from thermal decomposition of rare-earth quinates

Metal	Total number of H ₂ O	Molecular weight lost	Temperature (°C)	Onset of degradation
Dy	3	55.4 (3H ₂ O) 65.2	54 140	222
Ho	6	52.1 (3H ₂ O) 56.4	52 150	212
Er	1	12.4 (1H ₂ O) 64.8	52 162	224
Tm	1	24.0 (1 1/2 H ₂ O) 71.8	37 164	224
Yb	3	74.1 (4H ₂ O)	162	222
Lu	2	39.2 (2H ₂ O) 71.1	47 165	225
Y	3	40.8 (3H ₂ O) 62.9	40 156	219

The Dilactate Complexes

An unsuccessful attempt was made to find a way to vary α_1 (or both α_1 and α_2). The experimenters who determined the stability constants for the diglycolates at $\mu = 1.0$ also tried to improve their results in this manner, but met with little success.

In calculating the β values, the first point was dropped systematically because it was impossible to determine a with

Table 6. Stability constants of the rare-earth dilactate complexes ($T = 25^{\circ}\text{C}$; $\mu = 0.1$ (NaClO₄); $\alpha_1 = 7.71 \times 10^{-5}$, $\alpha_2 = 1.19 \times 10^{-7}$)

Metal	$\beta_1 \times 10^{-5}$	$\beta_2 \times 10^{-8}$	$b_2 \times 10^{-4}$
La	0.69 \pm 0.03	0.75 \pm 0.05	0.11 \pm 0.01
Ce	1.24 \pm 0.06	3.09 \pm 0.20	0.25 \pm 0.02
Pr	1.78 \pm 0.09	7.05 \pm 0.49	0.40 \pm 0.03
Nd	2.25 \pm 0.12	14.1 \pm 0.9	0.63 \pm 0.05
Sm	3.09 \pm 0.20	37.5 \pm 2.7	1.21 \pm 0.11
Eu	2.85 \pm 0.23	46.7 \pm 3.9	1.64 \pm 0.19
Gd	2.42 \pm 0.16	44.7 \pm 2.9	1.85 \pm 0.17
Tb	2.96 \pm 0.13	71.0 \pm 2.7	2.40 \pm 0.14
Dy	3.69 \pm 0.25	111 \pm 6	3.01 \pm 0.26
Ho	3.89 \pm 0.34	144 \pm 11	3.72 \pm 0.43
Er	3.87 \pm 0.61	207 \pm 26	5.34 \pm 1.08
Tm	4.77 \pm 0.72	328 \pm 40	6.88 \pm 1.34
Yb	4.71 \pm 0.97	451 \pm 69	9.57 \pm 2.45
Lu	4.20 \pm 1.01	556 \pm 86	13.2 \pm 3.8
Y	2.74 \pm 0.31	79.8 \pm 8.3	2.91 \pm 0.45

sufficient accuracy for low values of \bar{n} , since $C_H - (H^+) \ll C_H$. The difficulty is that β_1 is approximately two powers of ten larger than $1/\alpha_1$ and α_1/α_2 . A case can be made for dropping the first three points in each case; however, since this procedure did not appreciably change the β_n values, the second and third points were retained in the calculations.

The β_n values were calculated using both the two and three parameter programs. Positive β_3 values were obtained for samarium, europium, gadolinium, and terbium. However, the errors were as large as the β_3 values themselves. For

the other rare earths, the β_3 values came out negative. Thus it is only reasonable to respect values for β_1 and β_2 .

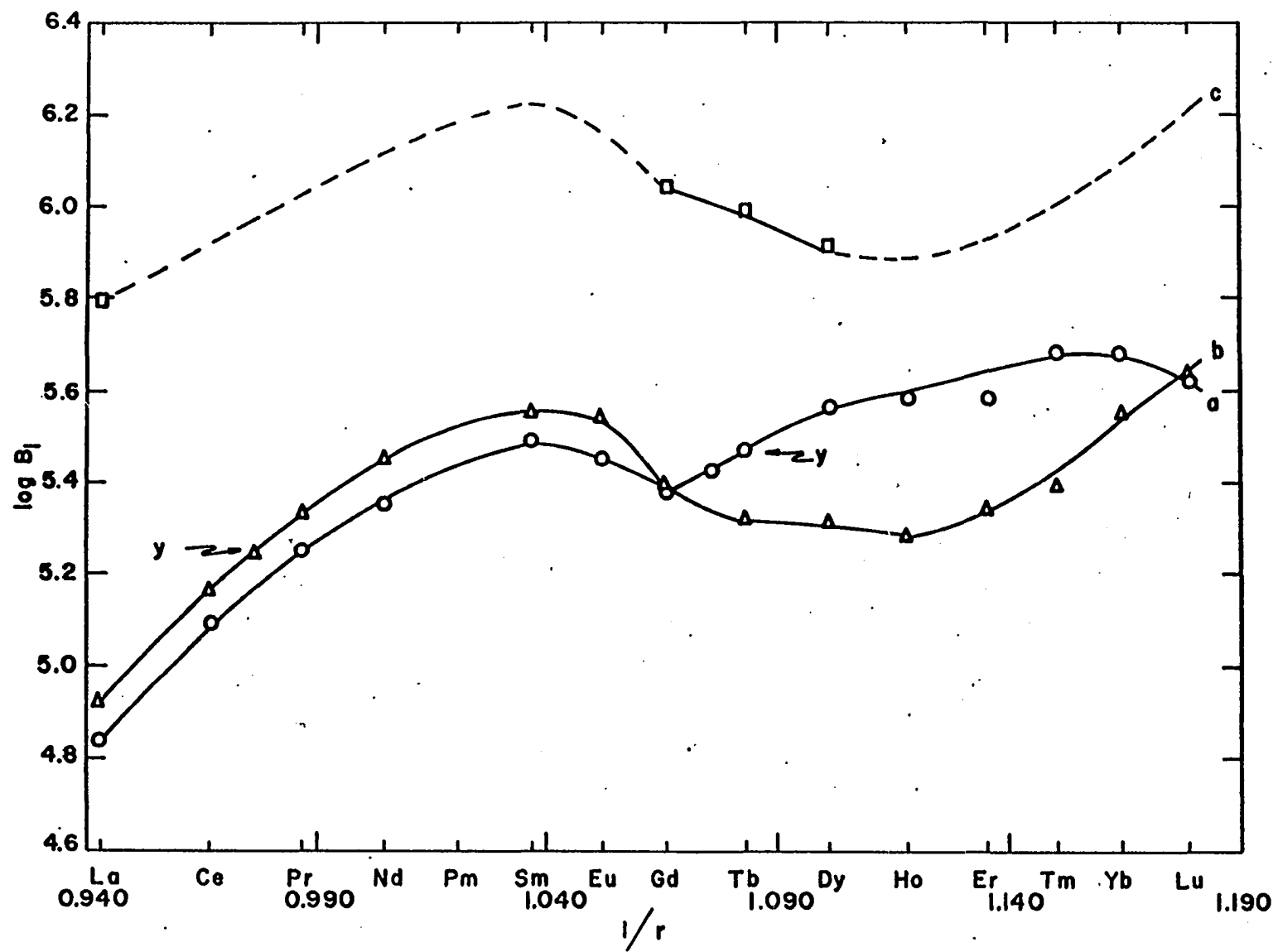
Polynuclear complexes were assumed to be absent since it has been shown that they do not form in the case of diglycolic acid, even at much higher concentrations.

Figure 9. One over the ionic radius in angstroms versus the logarithm of the first stability constants of the rare-earth

a) dilactate at $\mu = 0.1$ M

b) diglycolate at $\mu = 1.0$ M

c) diglycolate at $\mu = 0.1$ M



DISCUSSION

It was noticed, as a general rule, that the calculated value of \bar{n} would pass through a maximum and then decrease with increased concentrations of buffer when a constant mean value of K_a was used, in spite of the fact that the pH trend was apparently normal. In series of similar buffer solutions containing no rare-earth ion, it was found that the variation in the calculated K_a was not random but systematic, i.e., the computed K_a decreased slightly as the 1:1 salt acid buffer concentrations increased, in spite of the fact that the ionic strength was held precisely constant by addition of the required amount of NaClO_4 . Similar "salt effects" have been observed by others. In the case of acetic acid in a perchlorate supporting electrolyte, the effect was observed to be seven times as great as with other common anions (89).

In spite of this minor difficulty NaClO_4 was retained as the supporting electrolyte, due to the fact that it shows the least tendency to form complexes with metal ions. What was done to avoid errors, was to use a set of K_a values corresponding to the particular ligand anion concentrations present in a series of buffers containing a rare earth. Using a variable K_a set had very little effect on the calculated values for β_1 . The effect became much more apparent with β_2 and β_3 . The calculated \bar{n} increased with increasing a as predicted by

theory and for the most part negative values of even β_4 were avoided.

Mandelic acid is an analogue of the homologous series of monosubstituted glycolic acids which include methylglycolic, ethylglycolic, isopropylglycolic and tertiarybutylglycolic. Mandelate complexes for the light rare earths are stronger than the corresponding isopropylglycolate and tertiarybutylglycolate species. However, the mandelate complexes of the heavy rare earths are the weakest if one uses the β_1 calculated assuming formation of both 1:1 and 1:2 complex species; but, if one uses the β_1 calculated assuming just one complexed form, the mandelate complexes for the heavy rare earths are about the same stability as the isopropylglycolates, but more stable than the corresponding tertiarybutylglycolates.

Quinic acid is essentially one of the analogues of the series of disubstituted glycolic acids. However, it makes more sense to compare it to other cyclicglycolates instead of the acyclicglycolates.

Since the ligands are part of a series where the amount of alkyl substitution on the alpha carbon varies, there are two different effects that should be taken into account. The first is the basicity of the donor oxygen atoms. The inductive effect of an alkyl group alpha to the carboxylate is to increase the basicity. Thus alkyl substitution decreases the

acid ionization constant. This can be seen in Table 7. This electron-releasing contribution causes the basicity of the hydroxyl oxygen and, to a lesser extent, the carboxylate oxygens to increase, thus increasing the strength of the complex. This can be seen by the fact that glycolate < methylglycolate < dimethylglycolate in its affinity for rare-earth cations. In contrast to alkyl substitution, replacement of an α -hydrogen by a phenyl group increases the acidity by a factor of about two. This can be seen in Table 7. Thus mandelate ought to be the weakest, which it nearly is.

Table 7. Ionization constants of some substituted glycolic acids

Acid	Temperature (°C)	μ	$K_1 \times 10^{-4}$
Glycolic	20	0.1	2.72
Methylglycolic	20	0.1	2.33
Dimethylglycolic	20	0.1	1.61
Ethylglycolic	25	0.1	2.13
Methylethylglycolic	25	0.1	1.77
Diethylglycolic	25	0.1	2.38
Isopropylglycolic	25	0.1	2.03
Methylisopropylglycolic	25	0.1	1.71
Tertiarybutylglycolic	25	0.1	1.34
Methyltertiarybutylglycolic	25	0.1	1.14
Ethylisopropylglycolic	25	0.1	2.27
Tetramethyleneglycolic	25	0.1	1.10
Pentamethyleneglycolic	25	0.1	1.02
Phenylglycolic	25	0.1	6.11

The second factor is the steric factor. That is, the least alkylated group ought to be the most stable especially for the second and third groups entering. However, even for the first group entering there is steric hindrance because its added bulk disrupts more of the oriented water molecules around the rare-earth ion aside from those in the primary coordination sphere. This can be illustrated by the fact that the quinate with all the hydroxyl groups around the cyclohexane ring disrupts less of the oriented water around it than does plain 1-hydroxycyclohexanecarboxylate. This is because the hydroxyl groups themselves hydrogen bond to the water. Because of this quinates are more stable than the corresponding 1-hydroxycyclohexanecarboxylate. Nonetheless, the ability of quinate to hydrogen bond to the water does not make its chelates as stable as those of the 1-hydroxycyclopentanecarboxylate anion.

When the size of the substituent groups is increased the non-bonded interaction between groups is one of increased repulsion which results in an increase in the bond angle between alkyl groups and a decrease in the HO-C-COOH bond angle. Thus dimethylglycolate chelates are more stable than the corresponding methylglycolate species because the donor groups are closer together and are more readily accommodated by the rare-earth cations, particularly by the smaller heavy rare-earth cations. However, the angle can become too small.

Nevertheless, one should generally see a greater enhancement of the stability of the heavy rare earths compared to the light rare earths with bulkier groups. This is seen, especially in the case of the diethylglycolate series in Figure 7. The HO-C-COOH bond angle should not be diminished greatly by groups more bulky than ethyl groups (isopropyl and t-butyl) because it can readily be seen that ethyl groups require approximately the same space for full rotation as do the isopropyl and t-butyl groups.

In summary, increasing basicity and reduction of the bond angle between donor groups increases the stability of the complexes formed with rare-earth cations, although bond angle shrinkage can proceed too far for optimum bonding to the larger light rare-earth cations. Steric hindrance, on the other hand, decreases the stabilities of all the chelate species. Steric hindrance is manifested by abnormal lowering of the b_2 and b_3 values and results in increased ratios of b_1 to b_2 and b_2 to b_3 . It is obvious that steric hindrance and excessive shrinkage of the bond angle between donor groups will eventually negate the beneficial effect of increased basicity.

It is interesting to compare the ratios of the successive stepwise formation constants. From these one may be able to tell something about steric hindrance, coordination number, configuration and dentate character. It has been

suggested by Bjerrum (90) that the statistical effect related to the b_n values should be proportional to the number of ways of forming the ML_n species from the ML_{n-1} species, divided by the number of ways that ML_{n-1} can be formed from ML_n by splitting off a complete ligand.

Since the rare earths probably have a coordination number greater than six as shown in the review of the literature, the statistical effect has been calculated for various eight- and nine-coordinated structures. The carboxyl group has been actually observed to act as a bidentate coordinating group in several transition metal acetate complexes (91, 92). Consequently, the mandelate and quinate ligands could function tridentately as well as bidentately. For the light rare earths, other than lanthanum, mandelate appears (from b_1/b_2 ratios) to behave purely as a bidentate ligand. In the case of the heavy rare earths, the limited solubility of the chelates precludes an accurate determination of β_2 so that no conclusions should be drawn from the latter b_1/b_2 ratios. For the heavy rare earths, mandelate is probably still bidentate, although the observed b_1/b_2 ratios are nearer to the monodentate than the bidentate value. The stability constants are too high for chelation (bidentate behavior) not to be involved. The rare-earth trimandelates, from lanthanum through samarium, separate from aqueous solution with three waters of hydration; for the rare earths heavier than samarium, the

Table 8. Statistical factors in the ratios of the stepwise formation constants for various configurations

Configuration	b_1	:	b_2	b_1/b_2
Bidentate ligand				
Cubic (8)	12/1	:	7/2	3.43
Archimedean antiprism (8)	16/1	:	9/2	3.56
Dodecahedron (8)	18/1	:	89/18	3.64
Trigonal prism with ends (8)	15/1	:	21/5	3.57
Trigonal prism +3 (9)	18/1	:	11/2	3.27
Tridentate ligand				
Cubic (8)	24/1	:	6/2	7.33
Archimedean antiprism (8)	8/1 ^a	:	3/2 ^a	5.33
	16/1	:	9/4	7.11
Dodecahedron (8)	12/1	:	10/6	7.2
Trigonal prism with ends (8)	6/1 ^a	:	3/2 ^a	4.00
	16/1	:	19/16	13.5
Trigonal prism +3 (9)	8/1	:	13/8	4.92
Tetradentate ligand				
Cubic (8)	6/1	:	1/2	12
Archimedean antiprism (8)	2/1 ^b	:	1/2 ^b	4.0
Dodecahedron (8)	4/1		(blocks 5 positions)	
Trigonal prism with ends (8)	3/1		(blocks 5 positions)	
Trigonal prism +3 (9)	3/1		(blocks 5 positions)	
Pentadentate ligand				
Dodecahedron (8)	4/1			
Trigonal prism with ends (8)	3/1			
Trigonal prism +3 (9)	3/1			

^aAssumed could only form on triangular faces.

^bAssumed could only form on rectangular faces.

Table 9. Ratios of successive formation constants of some rare-earth complexes

Metal	b_1/b_2 mandelate	b_1/b_2 IG	b_1/b_2 t-BG
La	5.7(?)	2.5	3.4
Ce	3.5	2.6	2.4
Pr	3.6	2.7	2.8
Nd	3.3	2.9	3.1
Sm	2.3	3.6	8.4(?)
Eu	1.8	3.7	3.5
Gd	1.7	3.5	3.7
Tb	1.9	3.4	4.8
Dy	1.4	3.7	4.3
Ho	1.4	3.6	4.4
Er	1.2	3.7	4.7
Tm	0.74	3.8	4.7
Yb	1.8	3.8	4.9
Lu	1.2	4.0	4.8
Y	1.3	3.5	4.6

trimandelates are dihydrated. Mandelates in solution could be nine-coordinated in the case of light rare earths, and either eight- or nine-coordinated in the case of the heavy rare earths, with mandelate behaving bidentately throughout the entire series. One can not rule out loss of a coordinated water as the complex species in solution condense to form the solid compounds.

It is interesting to note that the b_1/b_2 ratio is too low in the case of the heavy-rare-earth mandelates where precipitation occurred. It could be that β_1 was simply lowered

Table 10. Ratios of successive formation constants of some rare-earth complexes

Metal	b_1/b_2	b_2/b_3	b_1/b_2	b_2/b_3	b_1/b_2	b_2/b_3	b_1/b_2	b_2/b_3
	quinates		HCP		HCH		EEG	
La	2.7	4.0	5.01	5.28	2.9	--	3.4	--
Ce	3.3	3.5	4.82	5.60	4.5	--	2.5	--
Pr	2.3	6.9	4.83	5.67	4.1	--	3.1	--
Nd	2.3	8.6	5.08	7.59	2.8	--	3.1	--
Sm	2.6	5.5	4.39	4.37	3.0	9.4	4.9	8.2
Eu	2.4	5.1	4.05	4.24	2.2	6.3	6.2	9.2
Gd	2.6	4.6	4.18	3.71	2.0	3.8	7.5	7.9
Tb	2.3	8.6	3.44	4.26	1.5	5.4	7.6	9.9
Dy	2.0	7.4	3.27	4.97	1.3	6.5	8.4	8.7
Ho	2.3	5.7	3.48	4.08	2.5	1.1	8.4	8.0
Er	2.0	7.6	3.05	5.77	1.8	-1.7	7.9	9.1
Tm	2.4	5.4	3.15	4.17	1.4	2.2	7.8	8.9
Yb	2.3	5.0	3.16	4.23	1.3	2.8	8.5	7.9
Lu	1.9	5.8	3.15	3.77	1.2	2.5	8.0	8.3
Y	1.8	9.5	3.64	3.96	1.8		7.9	9.3

too much by calculating two stability constants in the region where the \bar{n} was too low to warrant the second constant. However, this does not explain the generally low b_1/b_2 ratios for the quinates. The 1-hydroxycyclohexanecarboxylate series also exhibits the same low b_1/b_2 ratios. Thus it seems for quinate that the low b_1/b_2 ratio is somehow related to the cyclohexane ring being present. Curiously, data for the 1-hydroxycyclopentanecarboxylate does not exhibit this effect. In the case of the 1-hydroxycyclopentanecarboxylate, it appears that the light rare earths are nine-coordinated

and are coupled to a tridentate ligand in a trigonal prism +3 configuration. The heavier rare earths appear to be nine-coordinated, as well, but are coupled to three bidentate 1-hydroxycyclopentanecarboxylate ligands and three molecules of water (32).

Thermogravimetric data reveal no clue regarding the structure of the quinate since in most cases all water is lost below 50°C. It may be assumed that this loosely bound water is simply contained in the crystal lattice and is not coordinated with the rare-earth cation. It may be presumed that the substance lost by the anhydrous solids at around 160°C is also water, formed by bimolecular coupling through hydroxyl groups of the quinate groups.

Although dilactic acid is not a substituted glycolic acid, it is a substituted diglycolic acid. It can be seen in Figure 9 that dilactic acid does not form chelates with the individual rare earths as stable as the diglycolates. Consequently, the addition of methyl groups did not increase the chelate stability as observed in the glycolate homologous series. However, it did increase the spread in stability between the lanthanum chelate species and the lutetium chelate species. If the tetramethyl compound could be made, it might be interesting to see whether a further general decrease in stability and increase in spread occurred. From molecular models it would appear that tetramethyl substitution would

lock the coordinating groups into a possible pentacoordinating position.

Comparing the b_1/b_2 ratios for rare-earth dilactates, one is led to speculate that the lactate ligand behaves either pentadentately or pseudopentadentately (actually tetradentately) in bonding to a nine-coordinated (trigonal prism +3) configuration of coordination sites in the case of the 1:1 species formed with the light rare earths, lanthanum through samarium. In the case of pentadentate bonding one would have to assume that the four carboxyl oxygens were

Table 11. Ratios of successive formation constants of some rare-earth complexes

Metal	b_1/b_2	b_1/b_2	b_2/b_3
	dilactate	diglycolate ($\mu = 1.0$)	
La	65	28	45
Ce	50	25	28
Pr	45	28	31
Nd	36	25	25
Sm	26	16	27
Eu	17	10	22
Gd	13	7.5	26
Tb	12	4.7	23
Dy	12	4.4	20
Ho	10	4.0	21
Er	7.2	4.7	29
Tm	6.9	5.8	46
Yb	4.9	5.5	100
Lu	3.2	5.3	200
Y	9.4	5.3	18

rectangularly arrayed and that the ether oxygen was in the right position to occupy the coordination site lying outside the rectangular face of the trigonal prism +3. In the case of pseudopentadentate bonding, the carboxylate oxygens would occupy the same positions, but the ether oxygen would not be bonded to a coordination site. Instead the fifth coordination site above the face of the rectangular face of the trigonal prism +3 would simply be blocked by the connecting -C-C-O-C-C-chain. That is to say, the entering four oxygen donor groups would actually displace five of the nine water molecules but would not greatly change the non-planar distribution of the remaining four. If the natural arrangement of the carboxylate oxygens of dilactic acid is planar and rectangular, it is obvious that a second ligand could not bond either pentadentately or tetradentately. The high b_1/b_2 ratios for the light-rare-earth chelates would, therefore, be readily explained. The somewhat lower b_1/b_2 ratios observed with the diglycolates could be explained by the fact that the diglycolate ligand is less restrained from twisting and so it can be distorted sufficiently to allow tetradentate bonding to take place in the case of the second ligand which attaches. Nevertheless, in the case of the lanthanum through samarium diglycolates, an unusually high b_1/b_2 ratio is still noted (assuming three positions available to the first ligand and only one for the second would lead to a b_1/b_2 ratio of 6.0,

provided one could disregard the fact that b_1 would be low due to the fact that bonding was pseudopentadentate or higher if it were actually pentadentate, and that b_2 would be lowered by the necessity of distorting the ligand).

The b_1/b_2 ratios for europium through erbium (and yttrium) dilactates and for samarium through gadolinium diglycolates are not far from the value of 12 required for tetradentate bonding on an eight-coordinate cubic configuration of coordination sites, while the b_1/b_2 ratios for thulium through lutetium (and yttrium) diglycolates are closer to the value of four required for tetradentate bonding to the square faces of the eight-coordinate Archimedes' antiprism. In the case of the heavier diglycolates and dilactates, of course, a case could also be made for tridentate bonding on the nine-coordinate trigonal prism +3 configuration of sites. In any event, one is led to hypothesize a dentate character greater than two, if either eight or nine coordination is assumed.

SUMMARY

The stepwise formation constants for complexes between yttrium, lanthanum, and the rare earths, except promethium, and the ligands quinate, mandelate, and dilactate were measured at 25°C and the ionic strength of 0.1 M (NaClO₄). They were determined potentiometrically using a Beckman Research pH meter. Optimum values of the successive equilibrium constants were computed via a least squares technique using an IBM 7074 computer.

The presence of hydroxyl groups enhances the stability of rare-earth quinates over rare-earth 1-hydroxycyclohexanecarboxylates. The mandelates in solution could be nine-coordinated in the case of the light rare earths and either eight- or nine-coordinated in the case of the heavy rare earths, with mandelate acting bidentately throughout. Dilactic acid seems to be at least a tridentate ligand if not a pentadentate ligand.

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APPENDIX A: EXPERIMENTAL DATA FOR THE
RARE-EARTH MANDELATES

Buffer solution: a) 0.2495 M mandelic acid
0.2501 M sodium mandelate

b) 0.02495 M mandelic acid
0.02501 M sodium mandelate

Rare-earth solutions: 0.1000 M rare-earth perchlorate

Ce⁺³ solution: 0.100 M Ce⁺³
0.002605 M HClO₄

Sample: V_b ml. of buffer, 2.00 ml. of 0.1 M rare-earth perchlorate plus sufficient sodium perchlorate and water to make 50.00 ml. total volume at an ionic strength of 0.1 M.

Lanthanum		Cerium		Praseodymium	
V _b ml.(a)	pH	V _b ml.(a)	pH	V _b ml.(a)	pH
1.000 b	3.5750	1.000 b	3.4662	1.000 b	3.5322
3.000 b	3.3005	3.000 b	3.2379	3.000 b	3.2460
5.000 b	3.2141	5.000 b	3.1619	5.000 b	3.1615
7.000 b	3.1741	7.000 b	3.1275	7.000 b	3.1180
1.000	3.1440	1.000	3.0960	1.000	3.0866
1.500	3.1206	1.500	3.0825	1.480	3.0719
2.000	3.1180	2.000	3.0820	2.000	3.0721
3.000	3.1238	3.000	3.0940	3.000	3.0841
5.500	3.1499	5.500	3.1310	5.500	3.1279
7.000	3.1650	7.000	3.1520	7.000	3.1468
8.500	3.1805	8.500	3.1685	8.750	3.1655
10.00	3.1961	10.00	3.1855	10.00	3.1830

Neodymium		Samarium		Europium	
V _b ml.(a)	pH	V _b ml.(a)	pH	V _b ml.(b)	pH
1.000 b	3.5338	1.000 b	3.5120	1.000	3.5080
3.000 b	3.2345	2.000 b	3.3080	1.500	3.3841
5.000 b	3.1455	3.000 b	3.2123	2.000	3.3013
7.000 b	3.1021	4.000 b	3.1552	2.500	3.2485
1.000	3.0728	5.000 b	3.1199	3.000	3.2301
1.500	3.0580	8.000 b	3.0622	3.500	3.1768
2.000	3.0585	1.000	3.0449	4.000	3.1502
3.000	3.0770	1.250	3.0330	4.500	3.1360
5.500	3.1205	1.500	3.0300	5.000	3.1139
7.000	3.1420	1.750	3.0280	6.000	3.0896
8.500	3.1626	2.000	3.0335	8.000	3.0563
10.00	3.1778	2.500	3.0419	1.000 a	3.0379

Gadolinium	
V_b ml.(b)	pH
1.200	3.4510
1.500	3.3790
1.700	3.3484
2.000	3.3040
2.500	3.2556
3.000	3.2101
3.500	3.1815
4.500	3.1387
5.000	3.1221
6.000	3.0982
8.000	3.0580
1.000 a	3.0415

Terbium	
V_b ml.(b)	pH
1.000	3.4800
1.200	3.4332
1.500	3.3730
2.000	3.2821
2.200	3.2680
2.500	3.2382
2.700	3.2232
3.000	3.2003
3.200	3.1848
3.500	3.1710
3.700	3.1630
5.000	3.0979
7.000	3.0535

Dysprosium	
V_b ml.(b)	pH
1.000	3.4935
1.200	3.4285
1.500	3.3620
1.700	3.3220
2.000	3.2860
2.200	3.2585
2.500	3.2292
2.700	3.2130
3.000	3.1922
3.200	3.1775
3.500	3.1560
3.700	3.1446
5.000	3.0830
7.000	3.0370

Holmium	
V_b ml.(b)	pH
1.000	3.4880
1.200	3.4278
1.500	3.3540
1.700	3.3185
2.000	3.2770
2.200	3.2523
2.500	3.2239
2.700	3.2000
3.000	3.1781
3.200	3.1621
3.500	3.1457
3.700	3.1328
5.000	3.0758
7.000	3.0220

Erbium	
V_b ml.(b)	pH
1.000	3.4859
1.200	3.4141
1.500	3.3445
1.700	3.3100
2.000	3.2662
2.200	3.2400
2.500	3.2100
2.700	3.1890
3.000	3.1620
3.200	3.1485
3.500	3.1278
3.700	3.1182
5.000	3.0500
7.000	3.0117

Thulium	
V_b ml.(b)	pH
1.000	3.4780
1.100	3.4385
1.200	3.4110
1.400	3.3658
1.800	3.2778
2.000	3.2545
2.200	3.2240
2.400	3.1950
2.600	3.1780
2.800	3.1605
3.000	3.1420
4.000	3.0821
6.000	3.0118

Ytterbium	
V_b ml.(b)	pH
1.000	3.4580
1.100	3.4182
1.200	3.3895
1.300	3.3619
1.400	3.3340
1.700	3.2685
1.900	3.2405
2.100	3.2079
2.300	3.1859
2.500	3.1620
2.700	3.1427
4.000	3.0704
6.000	2.9930

Lutetium	
V_b ml.(b)	pH
1.000	3.4490
1.100	3.4199
1.200	3.3840
1.300	3.3538
1.400	3.3305
1.500	3.3075
1.700	3.2700
1.900	3.2378
2.100	3.2070
2.300	3.1823
2.500	3.1618
2.700	3.1361
4.000	3.0518
6.000	2.9744

Yttrium	
V_b ml.(b)	pH
1.000	3.5005
1.200	3.4445
1.500	3.3761
1.700	3.3371
2.000	3.2934
2.500	3.2350
3.000	3.1945
3.500	3.1619
4.000	3.1330
4.500	3.1138
5.400	3.0820
6.000	3.0670
8.000	3.6330
1.000 a	3.0140

<u>Ionization constant</u>	
<u>V_b ml.(a)</u>	<u>pH</u>
1.000 b	3.7280
3.000 b	3.4370
5.000 b	3.3740
7.000 b	3.3249
1.000	3.2940
1.500	3.2666
2.000	3.2520
3.000	3.2383
5.500	3.2320
7.000	3.2358
8.500	3.2403
10.00	3.2460

APPENDIX B: EXPERIMENTAL DATA FOR THE
RARE-EARTH QUINATES

Buffer solution: a) 0.1003 M quinic acid
0.1030 M sodium quinate

b) 0.1006 M quinic acid
0.1030 M sodium quinate

c) 0.10004 M quinic acid
0.09998 M sodium quinate

Rare-earth solutions: 0.1000 M rare-earth perchlorate

Ce⁺³ solution: 0.1000 M Ce⁺³
0.002605 M HClO₄

Sample: V_b ml. of buffer, 2.00 ml. of 0.1 M rare-earth perchlorate plus sufficient sodium perchlorate and water to make 50.00 ml. total volume at an ionic strength of 0.1 M.

(d) 3.00 ml. of 0.1 rare-earth perchlorate.

Lanthanum		Cerium		Praseodymium	
V _b ml.(a)	pH	V _b ml.(a)	pH	V _b ml.(a)	pH
0.500	3.4404	0.500	3.3490	0.500	3.3785
0.750	3.3579	0.750	3.2765	0.750	3.2930
1.000	3.3148	1.000	3.2350	1.000	3.2460
2.000	3.2379	2.000	3.1790	2.000	3.1642
3.000	3.2205	3.000	3.1605	3.000	3.1505
4.000	3.2128	4.000	3.1570	4.000	3.1495
5.000	3.2140	5.000	3.1730	5.000	3.1545
6.000	3.2140	6.000	3.1815	6.000	3.1540
7.000	3.2219	7.000	3.1887	7.000	3.1690
8.000	3.2219	8.000	3.1975	8.000	3.1854
10.00	3.2318	9.000	3.2060	9.000	3.1950
13.00	3.2520	10.00	3.2095	10.00	3.2105
15.00	3.2611	13.00	3.2358	13.00	3.2400
18.00	3.2765	15.00	3.2425	15.00	3.2497
20.00	3.2845	18.00	3.2613	18.00	3.2677
23.00	3.2905	20.00	3.2720	20.00	3.2731
25.00	3.2941	23.00	3.2860	23.00	3.2782
		25.10	3.2940	25.00	3.2910

Neodymium	
V_b ml.(b)	pH
0.500	3.3621
0.750	3.2720
1.000	3.2270
2.000	3.1510
3.000	3.1379
4.000	3.1293
5.000	3.1395
6.000	3.1495
7.000	3.1678
8.000	3.1788
9.000	3.1922
10.00	3.2005
13.00 a	3.2369
15.00	3.2442
18.00 a	3.2680
20.00	3.2770
23.00 a	3.2920
25.00	3.2970

Samarium	
V_b ml.(b)	pH
0.500	3.3315
0.750	3.2496
1.000	3.1990
2.000	3.1135
3.000	3.1021
4.000	3.1019
5.000	3.1260
6.000	3.1375
7.000	3.1450
8.000	3.1635
9.000	3.1698
10.00	3.1835
13.00 a	3.2150
15.00	3.2325
18.00 a	3.2585
20.00	3.2650
23.00 a	3.2835
25.00	3.2915

Europium	
V_b ml.(b)	pH
0.500	3.3392
0.750	3.2562
1.000	3.2060
2.000	3.1200
3.000	3.1032
4.000	3.1019
5.000	3.1168
6.050	3.1349
7.000	3.1371
8.000	3.1599
9.000	3.1720
10.00	3.1847
13.00 a	3.2133
15.00	3.2262
18.00 a	3.2525
20.00	3.2615
23.00 a	3.2816
25.00	3.2845

Gadolinium	
V_b ml.(b)	pH
0.500	3.3522
0.750	3.2626
1.000	3.2035
2.000	3.1278
3.000	3.1050
4.000	3.1127
5.000	3.1215
6.000	3.1342
7.000	3.1462
8.000	3.1560
9.000	3.1680
10.00	3.1808
13.00	3.2116
15.00	3.2321
18.00	3.2384
20.00	3.2650
23.00	3.2782
25.00	3.2919

Terbium	
V_b ml.(b)	pH
0.500	3.3360
0.750	3.2530
1.000	3.1960
2.000	3.1008
3.000	3.0912
4.000	3.0999
5.000	3.1014
6.000	3.1219
7.000	3.1408
8.000	3.1530
9.000	3.1070
10.00	3.1818
13.00	3.2168
15.00 a	3.2399
18.00 a	3.2585
20.00	3.2648
23.00 a	3.2839
25.00	3.2875

Dysprosium	
V_b ml.(c)	pH
0.510 d	3.2410
0.750 d	3.1530
1.000 d	3.0900
2.000 d	2.9862
4.000 d	2.9375
7.000 d	2.9892
10.00 d	3.0540
15.00 d	3.1300
20.00 d	3.1837
25.00 d	3.2165
0.500	3.2962
0.750	3.2145
1.000	3.1560
2.000	3.0620
4.000	3.0665
7.000	3.1183
10.00	3.1657
15.00	3.2200
20.00	3.2534
25.00	3.2715

Holmium	
V_b ml.(b)	pH
0.500	3.3042
0.750	3.2122
1.000	3.1558
2.000	3.0700
3.000	3.0515
4.000	3.0597
5.000	3.0850
6.000	3.1010
7.000	3.1208
8.000	3.1382
9.000	3.1498
10.00	3.1618
13.00	3.2000
15.00	3.2179
18.00	3.2440
23.00	3.2682

Erbium	
V_b ml.(b)	pH
0.500	3.3040
0.750	3.2050
1.000	3.1482
2.000	3.0580
3.000	3.0358
4.000	3.0518
5.000	3.0720
6.000	3.0890
7.000	3.1107
8.000	3.1351
9.000	3.1509
13.00	3.2031
15.00	3.2225
18.00	3.2465
20.00	3.2570
23.00	3.2709
25.00	3.2803

Thulium	
V_b ml.(b)	pH
0.500	3.2841
0.750	3.1810
1.000	3.1214
2.000	3.0320
3.000	3.0175
4.000	3.0262
5.000	3.0520
6.000	3.0758
7.000	3.1015
8.000	3.1158
9.000	3.1370
10.00	3.1520
13.00 a	3.1969
15.00	3.2140
18.00 a	3.2415
20.00	3.2499
23.00 a	3.2696
25.00	3.2730

Ytterbium	
V_b ml.(b)	pH
0.500	3.2642
0.750	3.1600
1.000	3.1005
2.000	3.0035
3.000	2.9900
4.000	3.0025
5.000	3.0290
6.000	3.0560
7.000	3.0778
8.050	3.1045
9.000	3.1218
10.00	3.1398
13.00 a	3.1918
15.00	3.2095
18.00 a	3.2396
20.00	3.2480
23.00 a	3.2701
25.00	3.2741

Lutetium	
V_b ml.(b)	pH
0.500	3.2515
0.750	3.1485
1.000	3.0840
2.000	2.9815
3.000	2.9590
4.000	2.9815
5.000	3.0130
6.000	3.0415
7.000	3.0659
8.000	3.0945
9.000	3.1173
10.00	3.1365
13.00 a	3.1808
15.00	3.2025
18.00 a	3.2291
20.00 a	3.2449
23.00 a	3.2601
25.00	3.2645

Yttrium	
V_b ml.(b)	pH
0.500	5.3330
0.750	3.2500
1.000	3.1982
2.000	3.0950
3.000	3.0866
4.000	3.0939
5.000	3.1138
6.000	3.1283
7.000	3.1440
8.000	3.1550
9.000	3.1700
10.00	3.1861
13.00 a	3.2172
15.00	3.2305
18.00 a	3.2529
20.00	3.2618
23.00 a	3.2807
25.00	3.2855

<u>Ionization constant</u>	
<u>V_b ml.(a)</u>	<u>pH</u>
0.500	3.6120
0.750	3.5477
1.000 b	3.5019
2.000	3.4379
4.000	3.4021
5.000	3.3970
6.000	3.3910
7.000 b	3.3817
10.00 b	3.3797
13.00	3.3802
15.00 b	3.3777
18.00	3.3820
20.00 b	3.3817
23.00	3.3850
25.00	3.3819

APPENDIX C: EXPERIMENTAL DATA FOR THE
RARE-EARTH DILACTATES

Buffer solution: a) 0.04927 M dilactic acid
0.04936 M sodium dilactate

b) 0.04883 M dilactic acid
0.04936 M sodium dilactate

c) 0.01935 M dilactic acid
0.01939 M sodium dilactate

Rare-earth solutions: 0.100 M rare-earth perchlorate

Ce⁺³ solution: 0.1000 M Ce⁺³
0.002605 M HClO₄

Sample: V_b ml. of buffer, 2.00 ml. of 0.1 M rare-earth perchlorate plus sufficient sodium perchlorate and water to make 50.00 ml. total volume at an ionic strength of 0.1 M.

Lanthanum		Cerium		Praseodymium	
V _b ml.(b)	pH	V _b ml.(b)	pH	V _b ml.(b)	pH
0.500	3.0781	0.500	3.0191	0.500	3.0580
0.750	2.9370	0.850	2.8356	0.750	2.8905
1.000	2.8483	1.000	2.7860	1.000	2.7863
1.250	2.7918	1.250	2.7240	1.250	2.7158
1.500	2.7533	1.500	2.6860	1.500	2.6660
2.000	2.7150	2.000	2.6439	2.000	2.6158
2.500	2.7050	2.500	2.6291	2.500	2.6019
3.000	2.7147	3.000	2.6380	3.000	2.6075
4.000	2.7521	4.000	2.6730	4.000	2.6411
5.000	2.7987	5.000	2.7150	5.000	2.6875
6.000	2.8470	6.000	2.7619	6.000	2.7315
8.000	2.9280	8.000	2.8540	8.000	2.8175
10.00	2.9959	10.00	2.9280	10.00	2.8980
12.00	3.0517	12.00	2.9910	12.00	2.9716
14.00	3.0990	14.00	3.0508	14.00	3.0300
16.00	3.1396	16.00	3.0978	16.00	3.0776
18.00	3.1721	18.00	3.1366	18.00	3.1169
20.00	3.2005	20.10	3.1706	20.00	3.1522

Neodymium	
V_b ml.(a)	pH
0.500	3.0520
0.750	2.8774
1.000	2.7708
1.250	2.6960
1.500	2.6445
2.000	2.5890
2.500	2.5719
3.000	2.5746
4.000	2.6030
5.000	2.6452
6.000	2.6890
8.000	2.7795
10.00	2.8588
12.00	2.9355
14.00	2.9978
16.00	3.0480
18.00	3.0919
20.00	3.1279

Samarium	
V_b ml.(a)	pH
0.500	3.0409
0.750	2.8685
1.000	2.7550
1.250	2.6735
1.500	2.6185
2.000	2.5550
2.500	2.5358
3.000	2.5340
4.000	2.5515
5.000	2.5856
6.000	2.6275
8.000	2.7130
10.00	2.8090
12.00	2.8945
14.00	2.9667
16.00	3.0240
18.00	3.0705
20.00	3.1040

Europium	
V_b ml.(a)	pH
0.500	3.0366
0.750	2.8721
1.000	2.7570
1.250	2.6769
1.500	2.6195
2.000	2.5530
2.550	2.5200
3.000	2.5180
4.000	2.5322
5.000	2.5632
6.000	2.6030
8.000	2.6959
10.10	2.7972
12.00	2.8740
14.00	2.9465
16.00	3.0019
18.00	3.0520
20.00	3.0862

Gadolinium	
V_b ml.(a)	pH
0.500	3.0395
0.750	2.8730
1.000	2.7615
1.250	2.6820
1.500	2.6298
2.000	2.5617
2.500	2.5287
3.000	2.5210
4.000	2.5284
5.000	2.5541
6.000	2.5921
8.000	2.6849
10.00	2.7830
12.00	2.8740
14.00	2.9455
18.00	3.0519
20.00	3.0907

Terbium	
V_b ml.(a)	pH
0.500	3.0370
0.750	2.8750
1.000	2.7564
1.250	2.6775
1.500	2.6160
2.000	2.5503
2.500	2.5149
3.000	2.4981
4.000	2.5025
5.000	2.5281
6.000	2.5630
8.000	2.6595
10.00	2.7680
12.00	2.8652
14.00	2.9403
16.00	3.0021
18.00	3.0520
20.00	3.0919

Dysprosium	
V_b ml.(a)	pH
0.500	3.0400
0.750	2.8710
1.000	2.7485
1.250	2.6650
1.500	2.6050
2.000	2.5319
2.500	2.4905
3.000	2.4757
4.000	2.4781
5.000	2.5022
6.000	2.5422
8.000	2.6496
10.00	2.7699
12.00	2.8680
14.00	2.9557
16.00	3.0110
18.00	3.0638
20.00	3.1075

Holmium	
V_b ml.(a)	pH
0.500	3.0380
0.750	2.8590
1.000	2.7416
1.250	2.6580
1.500	2.5990
2.000	2.5181
2.500	2.4780
3.000	2.4600
4.000	2.4580
5.000	2.4820
6.000	2.5223
8.000	2.6381
10.00	2.7691
12.00	2.8790
14.00	2.9620
16.00	3.0250
18.00	3.0780
20.00	3.1175

Erbium	
V_b ml.(a)	pH
0.500	3.0380
0.750	2.8595
1.000	2.7490
1.250	2.6542
1.500	2.5886
2.050	2.4990
2.500	2.4600
3.000	2.4390
4.000	2.4344
5.000	2.4578
6.000	2.5025
8.000	2.6250
10.00	2.7705
12.00	2.8975
14.00	2.9880
16.00	3.0560
18.00	3.1075
20.00	3.1481

Thulium	
V_b ml.(a)	pH
0.500	3.0411
0.750	2.8558
1.000	2.7360
1.250	2.6480
1.500	2.5785
2.000	2.4938
2.500	2.4423
3.000	2.4185
4.000	2.4121
5.000	2.4309
6.000	2.4780
8.000	2.6132
10.00	2.7678
12.00	2.9024
14.00	2.9960
16.00	3.0660
18.00	3.1195
20.00	3.1599

Ytterbium	
V_b ml.(b)	pH
0.500	3.0400
0.750	2.8581
1.000	2.7395
1.250	2.6490
1.500	2.5765
2.000	2.4842
2.550	2.4270
3.000	2.4045
4.000	2.3944
5.000	2.4037
6.000	2.4620
8.000	2.6480
10.00	2.7795
12.00	2.9195
14.00	3.0135
16.00	3.0825
18.00	3.1357
20.20	3.1800

Lutetium	
V_b ml.(b)	pH
0.500	3.0423
0.750	2.8582
1.000	2.7421
1.250	2.6500
1.500	2.5779
2.000	2.4778
2.500	2.4218
3.000	2.3890
4.000	2.3759
5.000	2.3968
6.000	2.4370
8.000	2.5978
10.00	2.7701
12.00	2.9130
14.00	3.0100
16.00	3.0806
18.00	3.1353
20.00	3.1810

Yttrium	
V_b ml.(b)	pH
0.500	3.0432
0.750	2.8745
1.000	2.7579
1.250	2.6753
1.500	2.6160
2.000	2.5449
2.500	2.5058
3.000	2.4861
4.000	2.4870
5.000	2.5119
6.000	2.5500
8.000	2.6580
10.00	2.7891
12.00	2.9050
14.00	2.9870
16.00	3.0635
20.00	3.1491

Ionization constant

<u>V_b ml.(c)</u>	<u>pH</u>
2.00	3.6711
3.00	3.6165
4.00	3.5820
5.00	3.5600
6.00	3.5465
7.00	3.5330
8.00	3.5260
9.00	3.5199
10.00	3.5121
12.00	3.5060
14.00	3.5030
16.00	3.4986
18.00	3.4950
20.00	3.4925
10.00 a	3.4819
12.00 a	3.4767
14.00 a	3.4760
16.00 a	3.4756
18.00 a	3.4745
20.00 a	3.4738

Ionization constant

<u>Concentration¹</u> <u>of H₂A</u>	<u>Concentration¹</u> <u>of Na₂A</u>	<u>pH</u>
.007667	.03378	4.3979
.01611	.02534	3.7641
.009775	.03168	4.1978
.01400	.02745	3.9079
.02667	.01478	3.1625
.03300	.00845	2.8490
.01935	.01939	3.5060

¹12.00 ml. of the concentration given was added in every case.