1963

Formation constants of some rare-earth complexes

William Ray Stagg
Iowa State University

Recommended Citation

Stagg, William Ray, "Formation constants of some rare-earth complexes " (1963). *Retrospective Theses and Dissertations*. 2975.
https://lib.dr.iastate.edu/rtd/2975

STAGG, William Ray, 1937–
FORMATION CONSTANTS OF SOME RARE-EARTH COMPLEXES.

Iowa State University of Science and Technology
Ph.D., 1963
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan

FORMATION CONSTANTS OF SOME RARE-EARTH COMPLEXES

by

William Ray Stagg

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1963

TABLE OF CONTENTS

I. INTRODUCTION

The group of elements with atomic numbers ranging from 57 (lanthanum) through 71 (lutetium) plus number 39 (yttrium) and known collectively as the rare earths have been a chemical curiosity for many years. Attempts to study their chemical and physical properties often met with failure or only partial success because of the difficulty of isolating any one of them by conventional separation techniques. With the advent of nuclear reactors, interest in the rare-earth elements increased. Some of the rare earths occur as fission by-products, and because of their high neutron capture cross-sections they may function as reactor poisons. For this reason it became desirable to obtain pure samples of the rare earths and characterize their individual chemical and physical properties.

All of the rare earths are readily available in such ores as monazite, gadolinite, xenotime, and bastnaesite. When these ores are dissolved in mineral acids, it is found that the metal ions all exhibit the trivalent oxidation state. Two of them have been found to exist in other valence states in aqueous solution: cerium in the tetravalent state and europium in the divalent state. Repeated crystallization of the double ammonium nitrate salts yields relatively pure samples of lanthanum, praseodymium and neodymium, and pure cerium may be obtained by precipitation as the tetravalent hydroxide at a pH of 3 to 4 (1). Fractional crystallization does not give satisfactory results for the remainder of the rare earths. Two modern separation techniques appear to offer the best means of separating the heavier members of the series. These are solvent extraction (2) and ion-exchange chromatography (3, 4). The ion-exchange technique has been developed into a commercial process.

The ion-exchange technique is simple in principle. It consists of adsorbing a mixture of rare earths on a bed of cation-exchange resin and then eluting the mixture from the resin with a solution of a complexing agent. The mixture is fractionated since the individual rare earths pass through the bed at different rates depending upon their relative affinities for the complexing agent. The complexing agents used have generally been the anions of carboxylic acids and amino-carboxylic acids. Examples are citrate, ethylenediamine-N,N,N',N'-tetraacetate (EDTA), and N-hydroxyethylethylene-diamine-N,N',N'-triacetate (HEDTA). At first glance one might suspect that the relative affinity of a rare-earth ion for one of these ligands (and hence its relative elution order from an ion-exchange bed) might depend upon the density of the electrical charge-cloud surrounding the ion. Since all the metals are present in the trivalent state in aqueous solution, this would depend upon the inverse of the ionic radius of the cation. This is often found to be true and is illustrated in Table 1 which gives the trivalent ionic radius (5) and the elution sequence for the rare earths with EDTA (6). Also shown is the logarithm of the formation constant (or stability constant) for formation of the 1:1 rare-earth EDTA complex (7). This stability constant may be represented by the expression

$$\beta_1 = \frac{(RV^-)}{(R^{+3})(V^{-4})}$$

where (R^{+3}) is the concentration of rare-earth ion,

(V^{-4}) is the concentration of EDTA anion,

(RV^-) is the concentration of the complex.

Table 1. Comparison of trivalent crystal radius with elution order and stability constant for the rare-earth EDTA complexes

Metal	Crystal radius (5)	Elution order (6)	Log β_1 (7)
La	1.061 Å	13	14.72
Ce	1.034	12	15.39
Pr	1.013	11	15.75
Nd	0.995	10	16.06
Sm	0.964	9	16.55
Eu	0.950	-	16.69
Gd	0.938	8	16.70
Tb	0.923	7	17.38
Dy	0.908	6	17.75
Ho	0.894	5	18.31
Er	0.881	4	18.55
Tm	0.869	3	19.07
Yb	0.858	2	19.39
Lu	0.848	1	19.65

It has been found that not all ligands give the same elution order as EDTA. It has also been shown that the elution order for a given ligand may be predicted if the stability constants for formation of the complexes are known. The separation factor for a binary mixture of rare earths may also be approximated from the stability constants (3, 4). At the present time, the direct measurement of the stability constants for the complexes between the rare earths and a ligand appears to be the most rapid and economical method for evaluating a potential eluant. The purpose of the research reported in this dissertation was to determine the stability constants for the complexes between the rare earths and the three ligands isobutyrate, α-hydroxyisobutyrate, and α,β,β'-trihydroxyisobutyrate. The relative merits of these ligands might then be ascertained.

II. REVIEW OF LITERATURE ON RARE-EARTH COMPLEXES

The weakest complexes which have been reported for the rare earths appear to be those with chloride (8, 9, 10, 11), bromide (8, 9, 10), iodide (9, 10), nitrate (11), carbonate (12) and sulfate (13). Sets of stability constants for the entire rare-earth series with any one of these ligands have not been reported. Evidence of perchlorate complexes with some of the rare earths has been cited (10), and the relative strengths of the complexes appear to be $Cl^- > Br^- > I^- > ClO_4^-$. Hydrolysis of the rare earths is an easily observable phenomenon. The stability constants for formation of the hydroxy complexes, i.e., 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 (14, 15).

Acetate complexes of the rare earths were reported by Sonesson (16, 17, 18, 19) and by Kolat and Powell (20). It was found that the stabilities of these complexes increased from lanthanum through europium but then dropped off so that the heavy rare-earth complexes were generally less stable than those of the lighter elements. This same behavior was observed for the rare-earth propionate complexes (21). Isobutyrate complexes have been reported for neodymium (22) as well as for copper (23), calcium (24) and iron(III) (25).

Rare-earth glycolate complexes have been reported by numerous authors (18, 19, 26, 27, 28, 29, 30). The glycolate ligand is bidentate and apparently forms 1:1, 2:1, 3:1 and 4:1 complexes with the rare earths. The glycinate anion has been found to form stronger complexes with lanthanum, cerium, praseodymium and neodymium than does glycolate (26). Thioglycolate and methoxyacetate complexes have been reported which are weaker than corresponding acetate complexes (26, 31). Apparently the sulfhydryl and methoxy groups contribute little or nothing to complex formation. The mercaptoacetate complexes have been found to be weaker than the corresponding acetate complexes (32).

The rare-earth lactate complexes have also received considerable study (27, 28, 29). The lactate complexes are stronger than the corresponding glycolates. The lanthanum, cerium, praseodymium and neodymium complexes of β-alaninate, β-hydroxypropionate, and β-mercaptopropionate decrease in stability in the order of the ligands listed (26). The α-hydroxyisobutyrate complexes have been studied also and were found to be stronger than the corresponding lactate and glycolate species (27, 29). Anionic 4:1 complexes have also been reported for the α-hydroxyisobutyrates (28). Salicylate, anthranilate, thiomalate, malate, and aspartate have been reported to form complexes with some of the rare earths with stabilities increasing in the order listed (26, 33).

Grenthe and Fernelius have reported stability constants for the rare-earth acetylacetonate complexes (34, 35).

Thompson has measured the 1:1 and 2:1 complexity constants of the rare-earth iminodiacetates (36) and ethylenediamine-N,N'-diacetates (EDDA) (37) and found EDDA to be the stronger ligand of the two. The formation of an additional chelate ring in the case of EDDA seems to be responsible for this. Grenthe has studied the rare-earth dipicolinate system and found it to exhibit some steric inhibition with respect to adding a third ligand (38). Anderegg (39), Moeller and Ferrus (40), and Levy and Powell (41) have studied the nitrilotriacetate (NTA) system and reported both 1:1 and 2:1 complexes. The latter two papers also reported enthalpy and entropy data which indicate that the strength of the complexes is due in great part to a large configurational entropy contribution. The NTA complexes are stronger than the corresponding EDDA complexes.

Mackey and Powell have studied the rare-earth complexes of N-hydroxyethylethylenediamine-N,N',N'-triacetate (HEDTA) and found them to be more stable than the corresponding complexes with NTA (42, 43). James and Powell found that the elution sequence of the rare earths with HEDTA eluant was not accurately predicted by the stability constants (6). However, the elutions were made at a pH of 7.5, and the complexes probably hydrolyzed appreciably. If the stability constants are suitably modified to account for this hydrolysis using the data of Gupta and Powell (44), the predicted sequence more nearly matches that which was observed. Wheelwright, Spedding, and Schwarzenbach studied the rare-earth complexes of ethylenediamine-N,N,N',N'-tetraacetate (EDTA) and postulated that the peculiar break in the regularly increasing trend of the equilibrium constants which occurred at gadolinium was due to a change in coordination of the ligand with decreasing cationic radius (7). Betts and Dahlinger measured the enthalpy and entropy of chelation for the rare-earth EDTA series and suggested that the change in coordination was from pentadentate to to tetradentate (45). It should be noted here that the "gadolinium break" seems to be characteristic of most rare-earth complexes, even the presumably unidentate acetate and propionate complexes.

The "gadolinium break" is prominent in the rare-earth complexes of 1,2-bis-[2-di(carboxymethyl)-aminoethoxy] ethane (EGTA) and 2,2'-bis-[di(carboxymethyl)-amino] diethyl ether (EEDTA) (46) and also in those of trans-1,2-diaminocyclohexane-N,N'-tetraacetate (DCTA) (47, 48). In the case of the diethylenetriamine-N,N,N',N',N"-pentaacetate (DTPA) complexes, Harder and Chaberek (49) and Moeller and Thompson (50) found that the equilibrium constants increased to a maximum at dysprosium and then gradually decreased.

In addition to these complexes, Thompson and Loraas (51) have reported mixed complexes of the rare-earth HEDTA series with glycinate, EDDA, iminodiacetate, and N-hydroxyethyliminodiacetate. These data indicate that the maximum coordination number of the rare earths is greater than six, but its exact value cannot be assigned unequivocally.

The logarithms of the first formation constants of ten of the ligands discussed above are plotted as a function of atomic number in Figures 1 and 2.

Some conclusions and generalities may now be stated based upon the data available in the literature.

1) Coordinate bonds to the rare-earth ions may be formed by $-COO^-$, $-OH$, $-NH_2$, $-\underset{|}{N}H$, $-\overset{|}{\underset{|}{N}}$, and $-COS^-$ which are stronger than those of H_2O, but bonds from $-SH$ and $-OCH_3$ are weaker than those of the solvate. The strength of the bonds is in the order $-COO^- > -COS^-$, $-NH_2 > -OH > -OCH_3 > -SH$. Thus chelation (ring formation) can occur in carboxylic acids which have an amine or hydroxyl substituent but not in those with sulfhydryl or methoxy substituents.

2) Stability of a complex is enhanced if the number of coordinating sites on the ligand is increased, <u>i.e.</u>, the number of chelate rings which can form is increased.

3) Stability generally increases as the ionic radius of the cation decreases, and this indicates that the bonding is primarily due to coulombic forces. However, there are many exceptions to this rule. The acetates and propionates exhibit a minimum in the Ho-Er region. The HEDTA complexes show a

Figure 1. Logarithms of the 1:1 stability constants of some rare-earth complexes
a: acetate (20)
b: glycolate (27)
c: acetylacetonate (34)
d: iminodiacetate (36)
e: ethylenediamine-N,N'-diacetate (37)

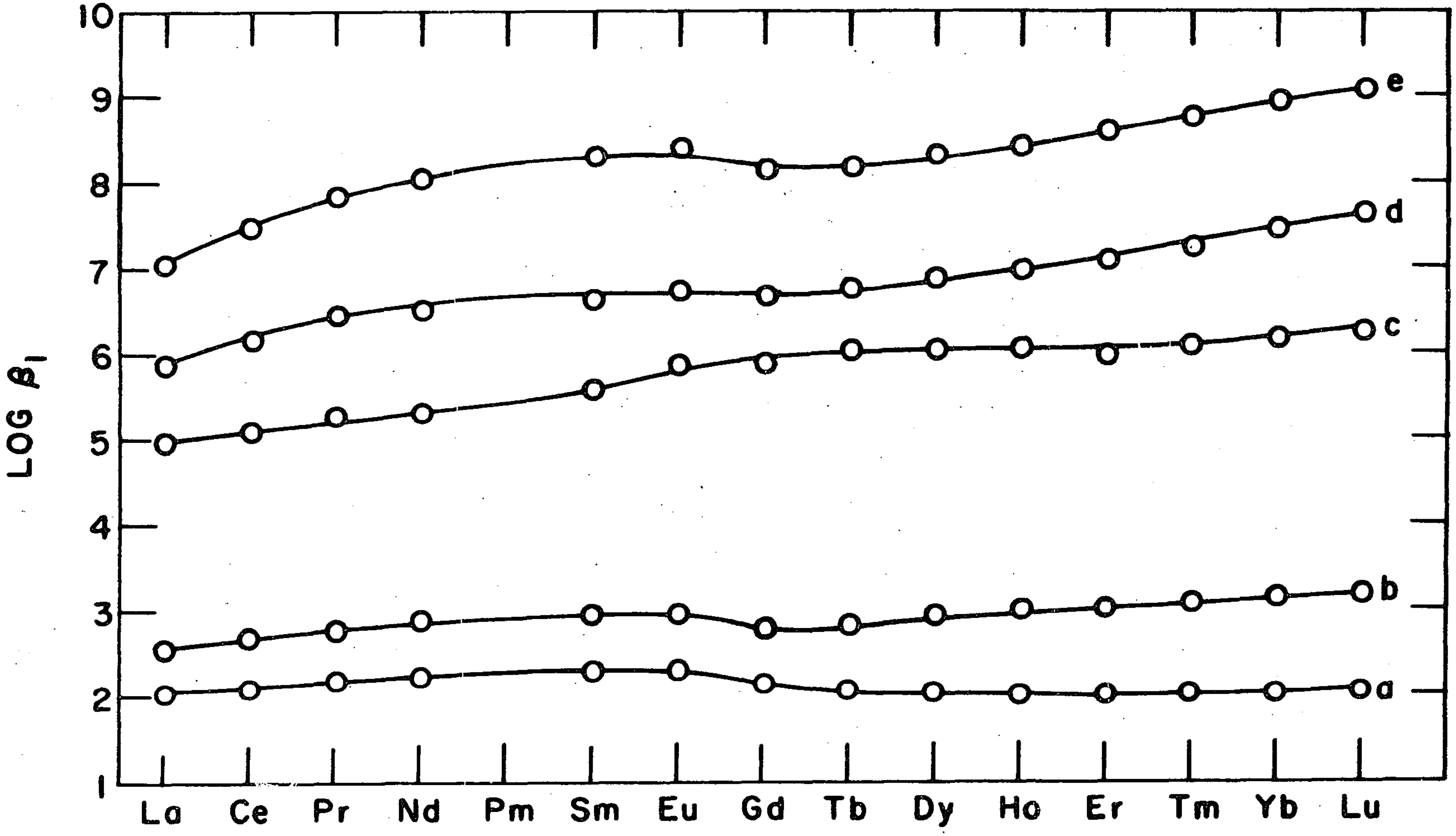
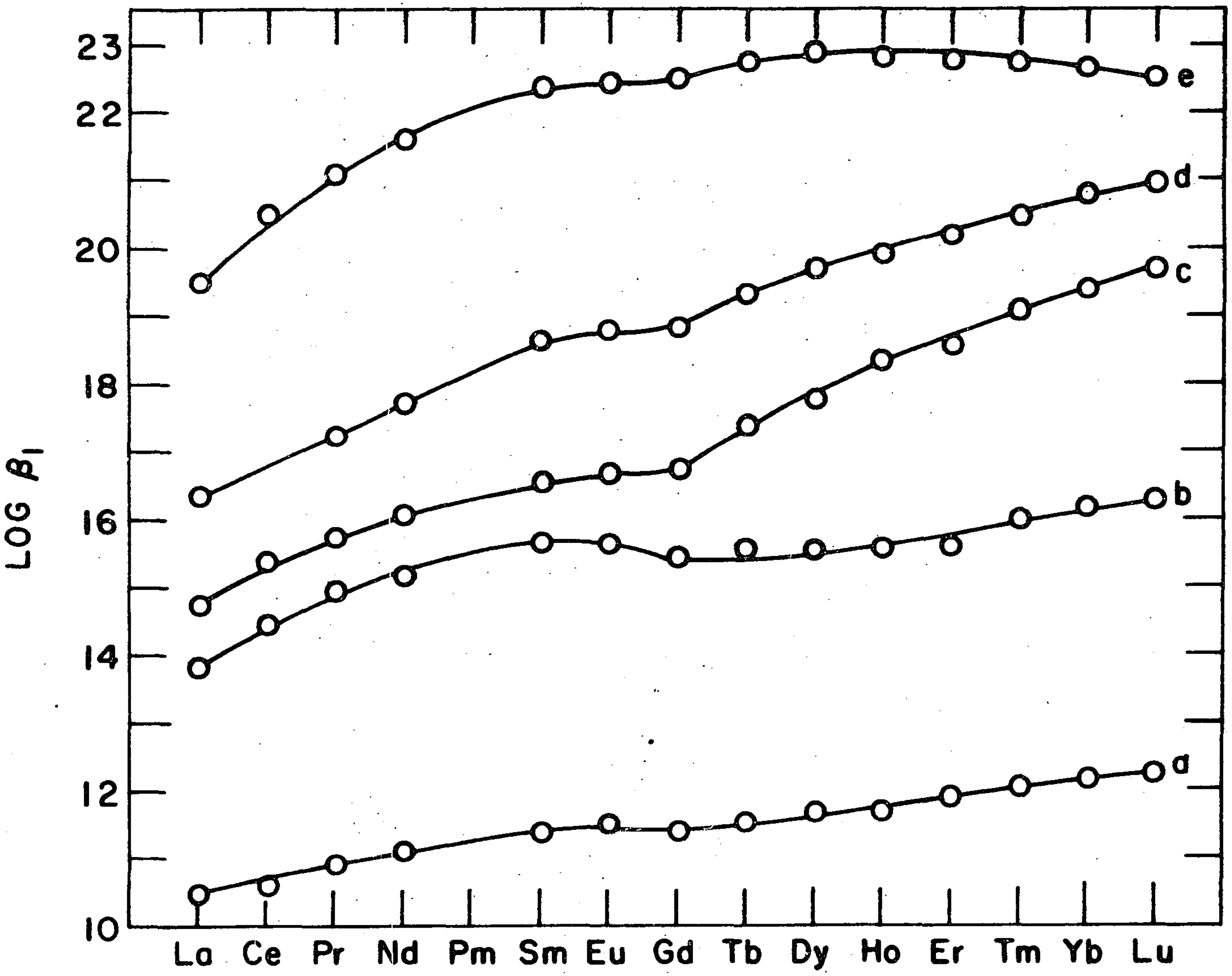

LOG β_1
10
9
8
7
6
5
4
3
2
1
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
e
d
c
b
a

Figure 2. Logarithms of the 1:1 stability constants of some rare-earth complexes
a: nitrilotriacetate (41)
b: N-hydroxyethylethylenediamine-N,N',N'-triacetate (42)
c: ethylenediamine-N,N,N'N'-tetraacetate (7)
d: trans-1,2-diaminocyclohexane-N,N'-tetraacetate (47)
e: diethylenetriamine-N,N,N',N',N"-pentaacetate (50)


LOG β_1
23
22
20
18
16
14
12
10
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
e
d
c
b
a

flat region from Gd to Er, and the DTPA complexes decrease in stability from Dy through Lu.

4) Spatial crowding of ligands is an important factor in the stability of successive complexes, especially for large ligands.

5) Stability of complexes of polydentate ligands is due to a great extent to a large configurational entropy contribution from these ligands. This may be one reason for the "gadolinium break."

6) Although several investigators have suggested that ligand field stabilization may contribute to the observed stability constant data, no quantitative confirmation of this has been made. Ballhausen (52) has pointed out that the properties of the rare-earth complexes are more or less a continuous reflection of the lanthanide contraction with the anticipated singularities at or near the xenon structure, the half-completed 4f shell and the completed 4f shell.

III. MATHEMATICAL COMPUTATION OF STABILITY CONSTANTS

A. The General Approach

The computation of stability constants (formation constants, equilibrium constants) is essentially a process of obtaining empirical parameters which best describe a chemical system within the limits of a physical model. Consider an aqueous solution containing a cation B^{+h} and an anionic ligand A^{-j}. One way in which these two species might interact to form a chemical complex would be,

$$B(H_2O)_x^{+h} + A(aq)^{-j} = B(H_2O)_{x-y}A^{+h-j} + yH_2O \; .$$

Here one sees that the ligand has replaced y molecules of water in the coordination sphere of the cation. Since experimental techniques do not generally permit the investigator to determine the number of solvent molecules in the coordination sphere, the water may be omitted from the equation. Oxidation-reduction reactions are not being considered so the charges on the cations may also be omitted. Thus the reaction may simply be represented as,

$$B + A = BA \; . \qquad (1)$$

Equation 1 is not the only conceivable reaction which might occur. A whole series of mononuclear complexes may be present in the solution simultaneously. Thus there would be the additional reactions:

$$\begin{aligned} &BA + A = BA_2, \\ &BA_2 + A = BA_3, \\ &\ldots\ldots\ldots\ldots\ldots, \\ &BA_{N-1} + A = BA_N \;. \end{aligned} \qquad (2)$$

There could also be a series of polynuclear complexes present. These would be represented by

$$pB + qA = B_pA_q \qquad (3)$$

where p ranges from 1 to P and q ranges from 1 to Q. Since polynuclear species were not found to exist in physically significant concentrations in the systems reported in this dissertation, they will not be considered further. A good discussion of polynuclear complexes has been given by Rossotti and Rossotti (53, p. 344).

The reactions shown in Equations 1 and 2 may be represented by equilibrium constants which, from a rigorous point of view, should be written in terms of the activities of the species present. This means that in a system in which the highest complex formed is BA_N, exactly (N+2) activities must be measured accurately. This alone would be a formidable task and the errors associated with the results would hardly make the job worth the effort. Fortunately there are alternatives to this. The Debye-Hückel theory is valid for dilute electrolyte solutions. One might write the equilibrium constants in terms of concentrations instead of activities, measure these stoichiometric equilibrium constants at different concentrations of a non-participating electrolyte, and then extrapolate these values to zero concentration of the electrolyte. The extrapolated values would be the thermodynamic equilibrium constants in the hypothetical standard state. Generally the work required for such an extrapolation is not necessary. For practical purposes, as much information may be extracted from the stoichiometric constants as can be gotten from the thermodynamic constants. Experimenters make use of the fact, derived from the Debye-Hückel theory, that the activities of ionic species in a solution are primarily a function of the ionic strength of the solution and perform their experiments at a constant high concentration of a non-participating background electrolyte. Such an approach has been used in the research reported in this dissertation, and in the remainder of this work concentrations will be used instead of activities.

The equilibrium constants representing Equations 1 and 2 may now be written as

$$k_1 = \frac{(BA)}{(B)(A)} ,$$

$$k_2 = \frac{(BA_2)}{(BA)(A)} ,$$

$$k_3 = \frac{(BA_3)}{(BA_2)(A)} \, ,$$

$$\dots\dots\dots\dots \, ,$$

$$k_N = \frac{(BA_N)}{(BA_{N-1})(A)} \, ; \tag{4}$$

where the parentheses represent the concentrations of the species contained therein. The constants k_n are referred to as step formation constants. Overall formation constants may also be written for the reactions,

$$B + A = BA \, ,$$

$$B + 2A = BA_2 \, ,$$

$$\dots\dots\dots\dots \, ,$$

$$B + NA = BA_N \, . \tag{5}$$

These constants are,

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

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

$$\dots\dots\dots\dots \, ,$$

$$\beta_N = \frac{(BA_N)}{(B)(A)^N} \, . \tag{6}$$

Obviously

$$\beta_n = \prod_{i=1}^{n} k_i \, . \tag{7}$$

For convenience, β_0 is defined as unity.

The following definitions must now be made:

A = total ligand concentration in the solution,
a = free (uncomplexed) ligand concentration,
B = total metal concentration
b = free (uncomplexed) metal concentration.

The quantities A and B are generally known for a system or can be determined without much difficulty. If one of the quantities a or b can be measured, then the constants represented by Equations 4 or 6 may be computed. In the research reported here, the free ligand concentration may be more readily measured than the free metal concentration. The mean ligand number $\bar{n}$ (54) is defined by

$$\bar{n} = \frac{A - a}{B} . \qquad (8)$$

It is readily seen that

$$A = a + b \sum_{n=0}^{N} n\beta_n a^n , \qquad (9)$$

$$B = b \sum_{n=0}^{N} \beta_n a^n . \qquad (10)$$

Equation 8 then becomes

$$\bar{n} = \frac{\sum_{n=0}^{N} n\beta_n a^n}{\sum_{n=0}^{N} \beta_n a^n} = \frac{A - a}{B} . \qquad (11)$$

Equation 11 is the fundamental equation which must be solved for the parameters β_n. A few of the techniques for accomplishing this will now be discussed. Many more may be found in Rossotti and Rossotti (53, p. 83).

In principle Equation 11 may be solved for N constants if exactly N sets of data (A_i, B_i, a_i) are available. In practice the random error usually associated with the experimental data would give rise to dubious values for such parameters. Thus the investigator usually accumulates more than N sets of data and tries to find the set of N β_n which best describe the data.

B. The Bjerrum (n-1/2) Approximation

Bjerrum (54) has described two methods for solving Equation 11. The first of these is an approximate technique. If only two complex species BA_{n-1} and BA_n exist in significant concentration in the solution, then Equations 2, 4, 9, 10 and 11 become

$$BA_{n-1} + A = BA_n \ ,$$

$$k_n = \frac{(BA_n)}{(BA_{n-1})a} \ ,$$

$$A = (n-1)(BA_{n-1}) + n(BA_n) + a \ ,$$

$$B = (BA_{n-1}) + (BA_n) \ ,$$

$$\bar{n} = \frac{n - 1 + nak_n}{1 + ak_n} \ .$$

If $\bar{n} = n - 1/2$, this last expression becomes

$$k_n = (1/a)_{\bar{n} = n-1/2} \ . \tag{12}$$

Obviously this method can give accurate results only if the species BA_{n-2} and BA_{n+1} are present to an insignificant extent.

C. Bjerrum's Successive Approximations Method

The second Bjerrum technique involves solving Equation 11 for each of the step stability constants k_n. Thus

$$k_n = \frac{1}{a} \cdot \frac{\displaystyle\sum_{t=0}^{n-1} \frac{\bar{n}-n+1+t}{a^t k_1 k_2 \cdots k_t}}{\displaystyle\sum_{t=0}^{N-n} (n-\bar{n}+t) a^t k_{n+1} k_{n+2} \cdots k_{n+t}} \ .$$

Experimental data $\bar{n}$ and a and approximate constants k_j ($j \neq n$) are put into this equation and each k_n computed. This gives a second set of constants k_j', and the computation is repeated until convergence is obtained. Randall, Martin and Moeller (55) have adapted this equation to use with a digital computer for $N = 3$. They computed k_1 from the data $0.3 < \bar{n} < 0.7$, k_2 from $1.3 < \bar{n} < 1.7$, and k_3 from $2.3 < \bar{n} < 2.7$. It was necessary to exclude the data near $\bar{n} = n$ because of the large indeterminancy in these regions. A simplification of this last equation is to set $\bar{n} = n-1/2$ and use only those data $(\bar{n}, a)$ for which $\bar{n} = 0.5, 1.5, 2.5, \cdots, N-1/2$. The equation then becomes

$$k_n = (\frac{1}{a}) \cdot \frac{1 + \sum_{t=1}^{n-1} \frac{1+2t}{a^t k_1 k_2 \cdots k_t}}{1 + \sum_{t=1}^{N-n} (1+2t) a^t k_{n+1} \cdots k_{n+t}} \quad . \qquad (13)$$

This last method points out a characteristic of most computational techniques. The value of N, the maximum ligand number, must usually be determined or arbitrarily chosen before calculations can be made. This is not difficult since a graph of $\bar{n}$ *versus* a will usually indicate the maximum value that $\bar{n}$ (and therefore N) is likely to attain.

D. Poë's Successive Approximations Method

Poë (56) has recently published a technique similar to Bjerrum's. He has solved Equation 11 explicitly for β_n and used the data $(\bar{n}, a)$ and approximate values of the β_j's $(j \neq n)$ to compute β_n by successive approximations. Thus

$$\beta_n = \frac{\bar{n}}{(n-\bar{n})a^n} \left\{ 1 + \sum_{p=1}^{n-1} \frac{(n-p)a^p \beta_p}{\bar{n}} + \sum_{q=n+1}^{N} \frac{(\bar{n}-q)a^q \beta_q}{n} \right\} \quad . \qquad (14)$$

E. The Fronaeus Method

A useful graphical technique was devised by Fronaeus (57). If the denominator of Equation 11 is denoted by X, then it is apparent that

$$X = \sum_{n=0}^{N} \beta_n a^n \;, \qquad (15)$$

$$X' = dX/da = \sum_{n=0}^{N} n\beta_n a^{n-1} \, . \tag{16}$$

Inserting these into Equation 11 gives the differential equation,

$$\bar{n} = aX'/X \, , \tag{17}$$

which may be solved to give

$$\ln X_i = \int_0^{a_i} (\bar{n}/a)da \, . \tag{18}$$

The integral in Equation 18 may be evaluated graphically or numerically to give sets of data (X_i,a_i). From Equation 15 the function F_1 may be defined as

$$F_1 = (X-1)/a = \beta_1 + \beta_2 a + \ldots + \beta_N a^N \, . \tag{19}$$

A graph of F_1 <u>versus</u> a plotted from the data (X_i,a_i) may then be extrapolated to a=0 to give β_1. Similarly the function F_2 defined by

$$F_2 = (F_1 - \beta_1)/a = \beta_2 + \beta_3 a + \ldots + \beta_N a^{N-1} \tag{20}$$

may be extrapolated to give β_2 and so forth. Finally the graph of F_{N-1} *versus* a is a straight line with intercept β_{N-1} and slope β_N. This technique provides a useful means of determining N.

F. The Method of Rossotti and Rossotti

A second graphical technique, which is quite useful for data restricted to low values of $\bar{n}$, has been reported by Rossotti and Rossotti (58). The method does not require an integration. Equation 11 may be rearranged to give

$$\frac{\bar{n}}{(1-\bar{n})a} = \beta_1 + \beta_2 \frac{(2-\bar{n})a}{(1-\bar{n})} + \sum_{n=3}^{N} \frac{n-\bar{n}}{1-\bar{n}} \beta_n a^{n-1} \qquad (21)$$

or in general

$$\sum_{n=0}^{t-1} \frac{\bar{n}-n}{t-\bar{n}} \beta_n a^{n-t} = \beta_t + \beta_{t+1} \frac{(t+1-\bar{n})a}{t-\bar{n}} + \sum_{n=t-2}^{N} \frac{n-\bar{n}}{t-\bar{n}} \beta_n a^{n-t}. \qquad (22)$$

A graph of $\bar{n}/(1-\bar{n})a$ versus $(2-\bar{n})a/(1-\bar{n})$ gives β_1 as an intercept and β_2 as a limiting slope. The method places no *a priori* restriction upon N.

G. The Least Squares Method
Used in this Research

This author wrote Equation 11 in the form

$$\sum_{n=0}^{N} (A_i - a_i - nB_i)\beta_n a_i^n = 0 \qquad (23)$$

and attempted to compute the parameters by the method of least squares. It was found that the data were so poorly conditioned that no physically meaningful results could be obtained. Recourse was then made to a weighting procedure which had been described by Sullivan, Rydberg and Miller (59) and Rydberg (60). The residual of a given set of data (A_i, B_i, a_i) is given by

$$U_i = \sum_{n=0}^{N} (A_i - a_i - nB_i)\beta_n a_i^n \, . \tag{24}$$

The weighted sum of the squares of these residuals is then

$$S = \sum_{i=1}^{I} W_i U_i^2 \tag{25}$$

where the summation is carried out over I sets of data. This sum is then minimized with respect to each of the parameters, that is,

$$\partial S / \partial \beta_n = 0 \, . \tag{26}$$

This gives N equations in the β_n which may then be solved using Cramer's rule or matrix algebra. If the matrix technique is used, the standard deviation of each of the parameters may be computed from the diagonal elements of the inverse of the matrix of the coefficients of the β_n's (59). This deviation is given by

$$\sigma_{\beta_n} = \pm \sqrt{r_{nn} S / (I - N)} \tag{27}$$

where r_{nn} is the diagonal element of the inverse coefficient matrix. The choice of weight factor is arbitrary. The one used in this research is given by

$$W_i = 1/\delta U_i^2 \,, \tag{28}$$

$$\delta U_i = (\partial U_i/\partial a_i)a_i m \,. \tag{29}$$

The quantity m is the estimated relative error in the free ligand concentration. Thus each point is weighted with respect to the relative precision of the measured free ligand concentration and with respect to the variance of the residual with free ligand concentration. In practice the β_n's are approximated using Equations 12 and 7, the weight factors computed from Equations 28 and 29, and the second order approximations of the β_n's computed by solving Equations 25 and 26. The process is repeated until convergence is obtained to within acceptable limits. Since several iterations may be required to get palatable results, the computation is best done on a digital computer.

H. Other Methods

Chopoorian et al. (61) have reported a least squares solution of Equation 11 in which that equation is rearranged in the form

$$R_j = \frac{\bar{n}_j}{a_j} - \frac{\sum_{n=1}^{N} n\beta_n a_j^{n-1}}{1 + \sum_{n=1}^{N} \beta_n a_j^n} \,. \tag{30}$$

The residual R_j is then minimized with respect to the parameters. A successive approximations approach is used in which each datum is weighted by the factor b_j/B.

An approximate method which has not been mentioned yet is useful for obtaining β_1. If Equation 11 is divided by a and the limit of this quotient taken as a goes to zero then

$$\lim_{a \to 0} (\bar{n}/a) = \beta_1. \qquad (31)$$

I. Comparison of Methods

A comparison of some of these techniques may be made by using the data for the dysprosium α,β,β'-trihydroxyisobutyrate system. The data $(\bar{n}_i, a_i)$ are given in Table 2 and plotted in Figure 3. The data $\bar{n}_i/a_i$ are plotted against a_i in Figure 4. This graph was integrated with a planimeter to give sets of data (X_j, a_j), as in the Fronaeus method, and the resulting graphs of F_1 and F_2 are shown in Figures 5 and 6. The results of this calculation are given in Table 3. Figures 7 and 8 show the plots obtained using the methods of Rossotti and Rossotti, the results of which are also given in Table 3. The results obtained using the (n-1/2) approximation (Equations 7 and 12), the Bjerrum successive approximation for two iterations (Equation 13), the limiting slope method (Equation 31), and the least squares method of Sullivan *et al.* are also tabulated. The curve of $\bar{n}$ as a function of a was computed from Equation 11 using the parameters from the least

Table 2. Dysprosium α,β,β'-trihydroxyisobutyrate data at 25°C, 0.004 M Dy, μ=0.5 ($NaClO_4$)

a x 10^3 M	$\bar{n}$
0.557	0.234
1.030	0.408
1.504	0.563
1.992	0.703
2.500	0.832
3.062	0.941
3.622	1.050
4.214	1.147
4.819	1.241
5.442	1.329
6.788	1.474
8.149	1.614
9.804	1.696
11.22	1.792
12.78	1.872
14.42	1.925
15.95	2.010
17.54	2.073
19.21	2.111
20.74	2.187
23.16	2.257
25.77	2.271
29.07	2.323

squares calculation and is shown in Figure 3. Table 3 shows that the (n-1/2) approximation gives very poor results for β_1 and β_2 but acceptable results for β_3 in comparison to the other data while the Bjerrum successive approximations method using only the data $\bar{n}$ = 0.5, 1.5, and 2.5 gives poor agreement for β_2 and β_3. Both of these emphasize the fallacy of using

Figure 3. $\bar{n}$ *versus* a for the dysprosium α,β,β'-trihydroxyisobutyrate system

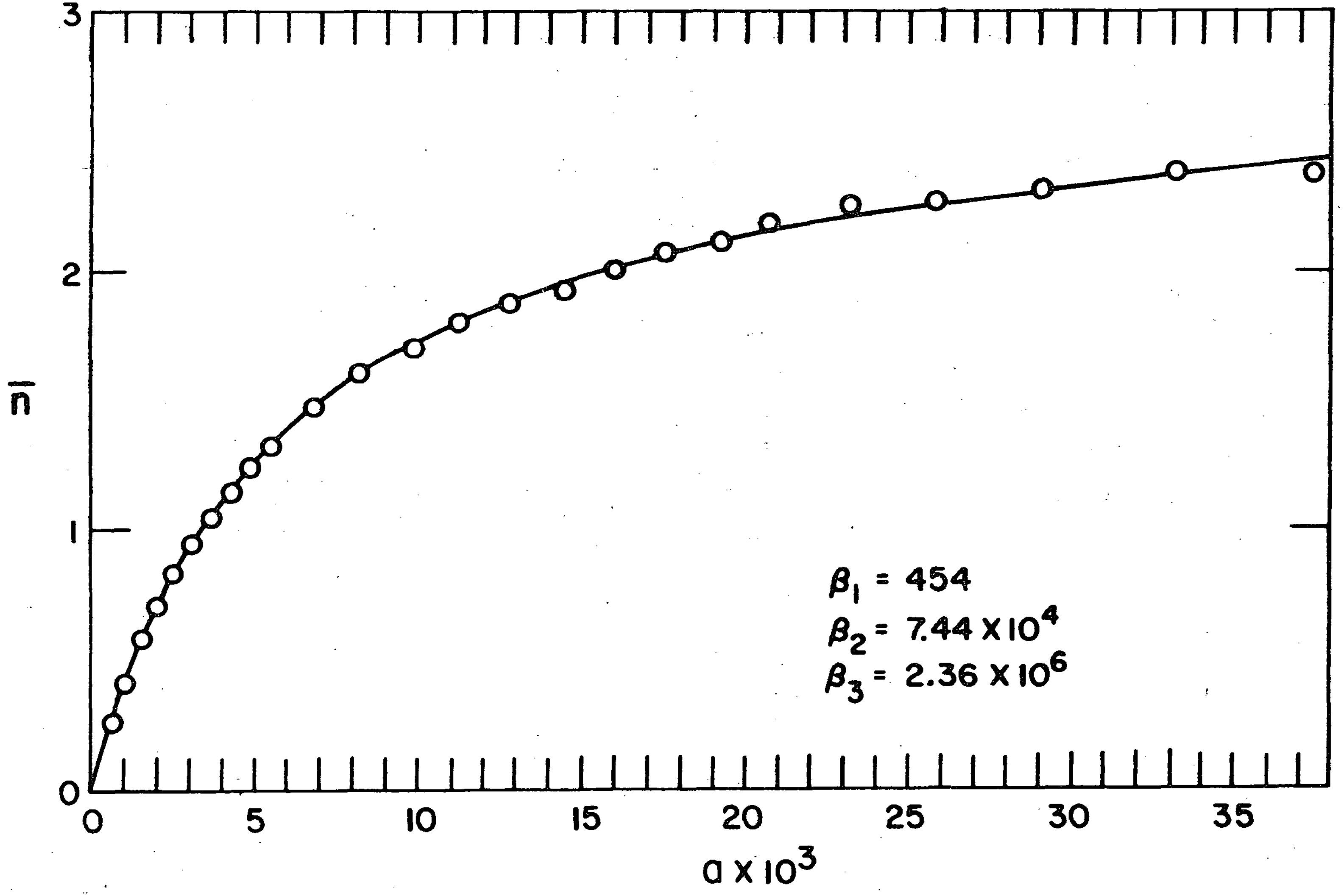

3
2
1
0
$\bar{n}$
0
5
10
15
20
25
30
35
$a \times 10^3$
$\beta_1 = 454$
$\beta_2 = 7.44 \times 10^4$
$\beta_3 = 2.36 \times 10^6$

Figure 4. $\bar{n}/a$ *versus* a for the dysprosium α,β,β'-trihydroxyisobutyrate system

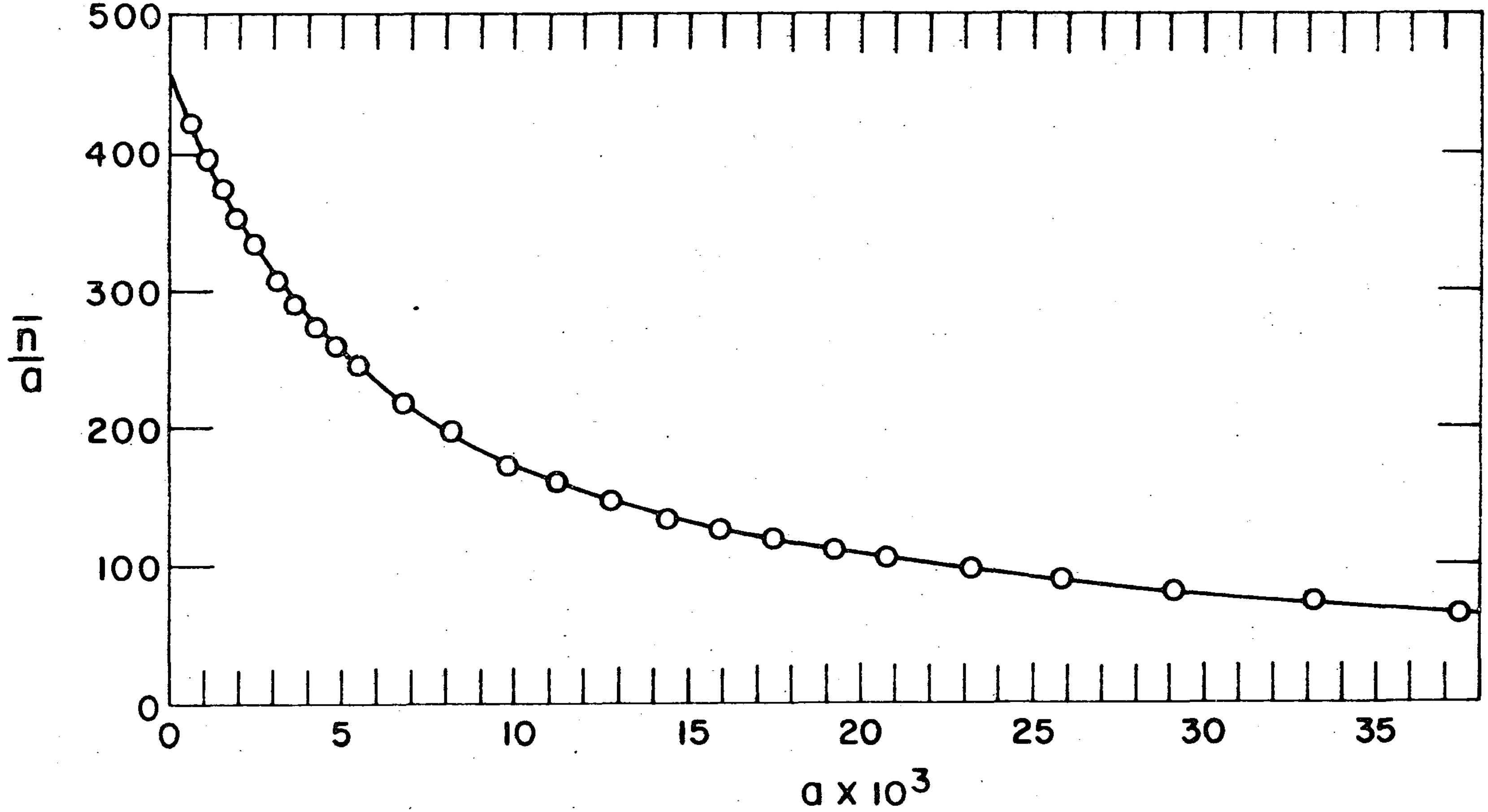

500
400
300
200
100
0
$\frac{\bar{n}}{a}$
0
5
10
15
20
25
30
35
$a \times 10^3$

Figure 5. F_1 *versus* a for the dysprosium α,β,β'-trihydroxyisobutyrate system

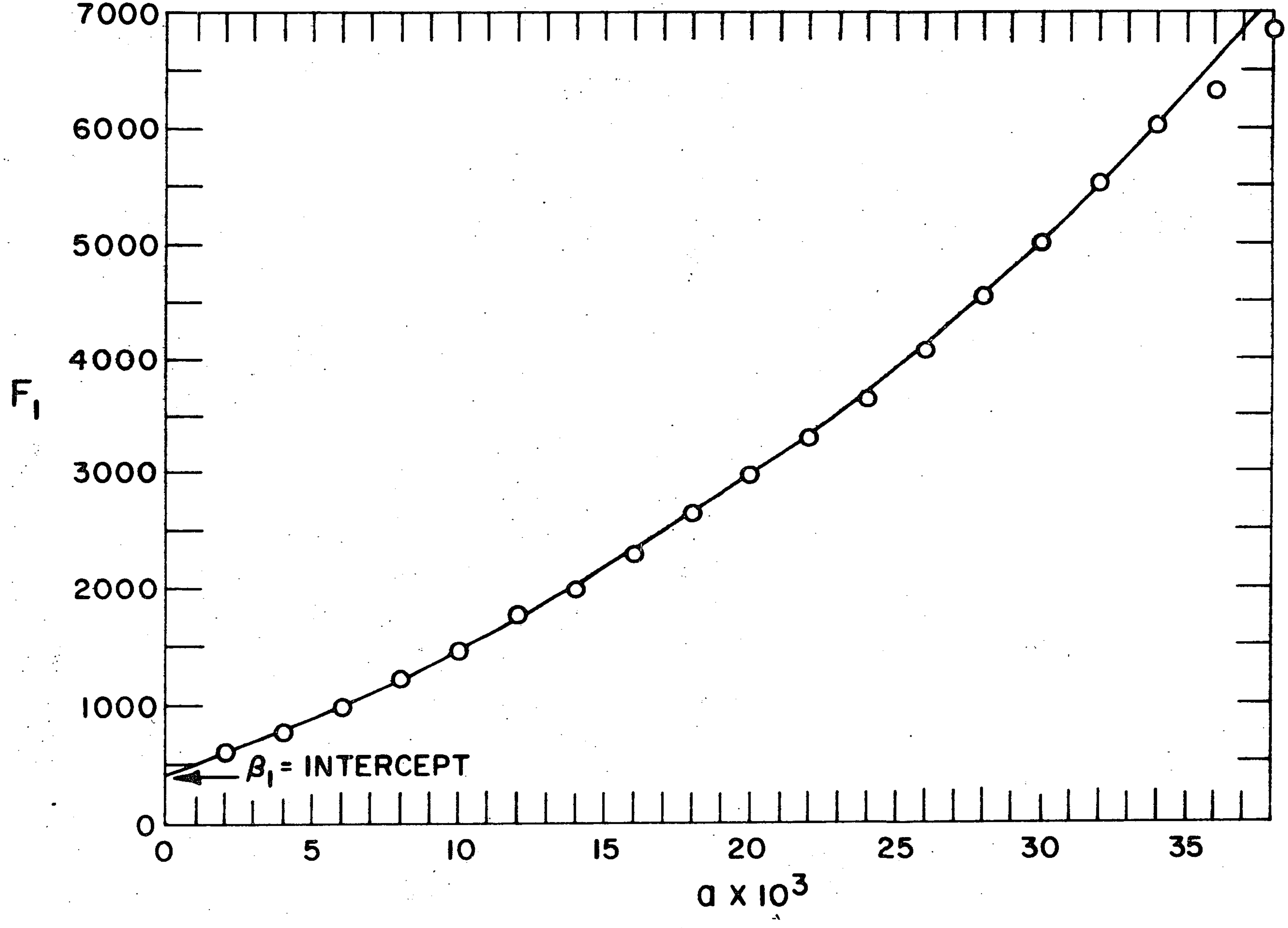

7000
6000
5000
4000
3000
2000
1000
0
F_1
β_1 = INTERCEPT
0
5
10
15
20
25
30
35
$a \times 10^3$

Figure 6. F_2 versus a for the dysprosium α,β,β'-trihydroxyisobutyrate system

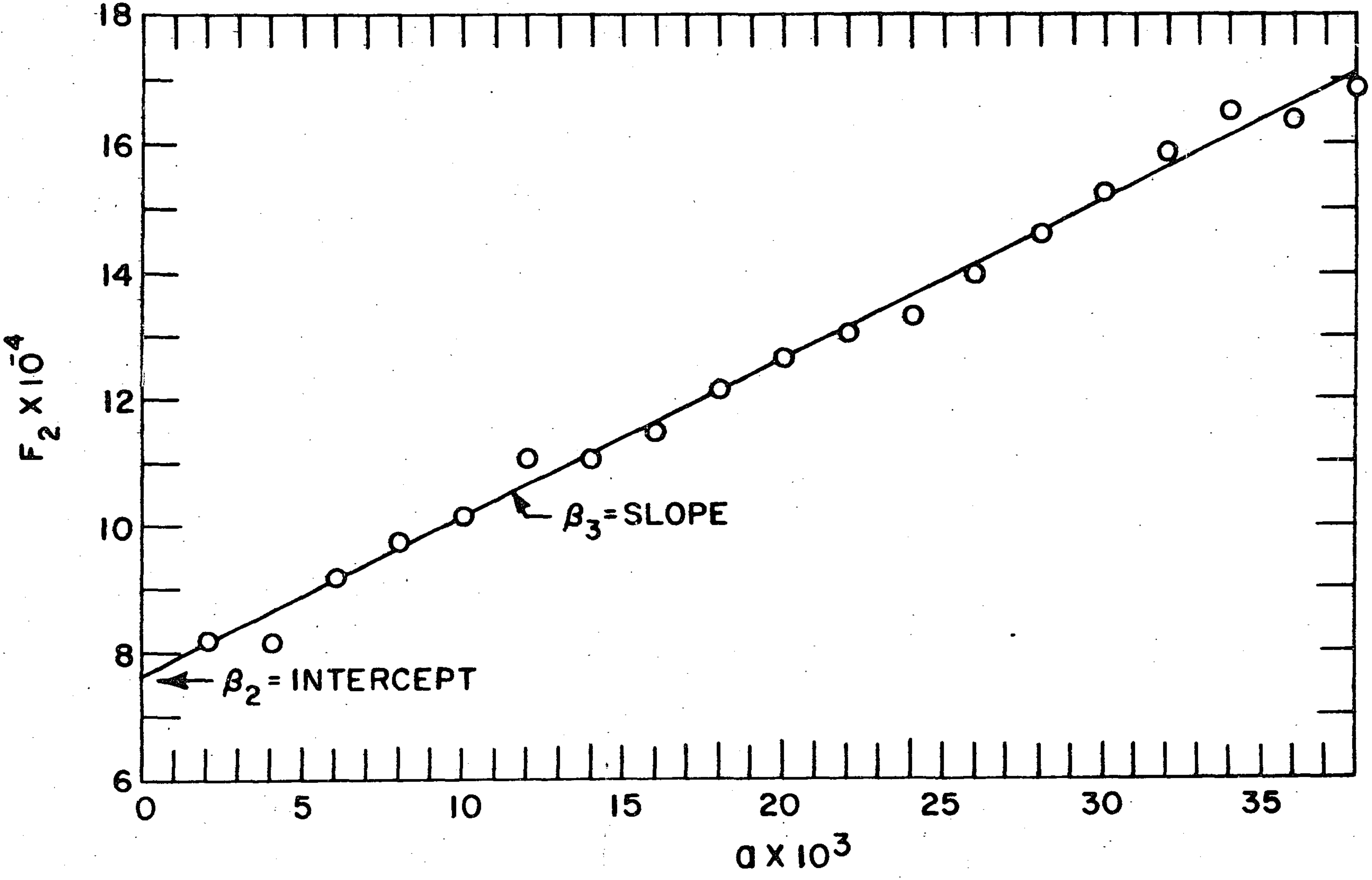

18
16
14
12
10
8
6
0
5
10
15
20
25
30
35
$F_2 \times 10^{-4}$
$a \times 10^3$
β_3 = SLOPE
β_2 = INTERCEPT

Figure 7. $\frac{\bar{n}}{(1-\bar{n})}$ versus $\frac{(2-\bar{n})a}{(1-\bar{n})}$ for the dysprosium α,β,β'-trihydroxyisobutyrate system

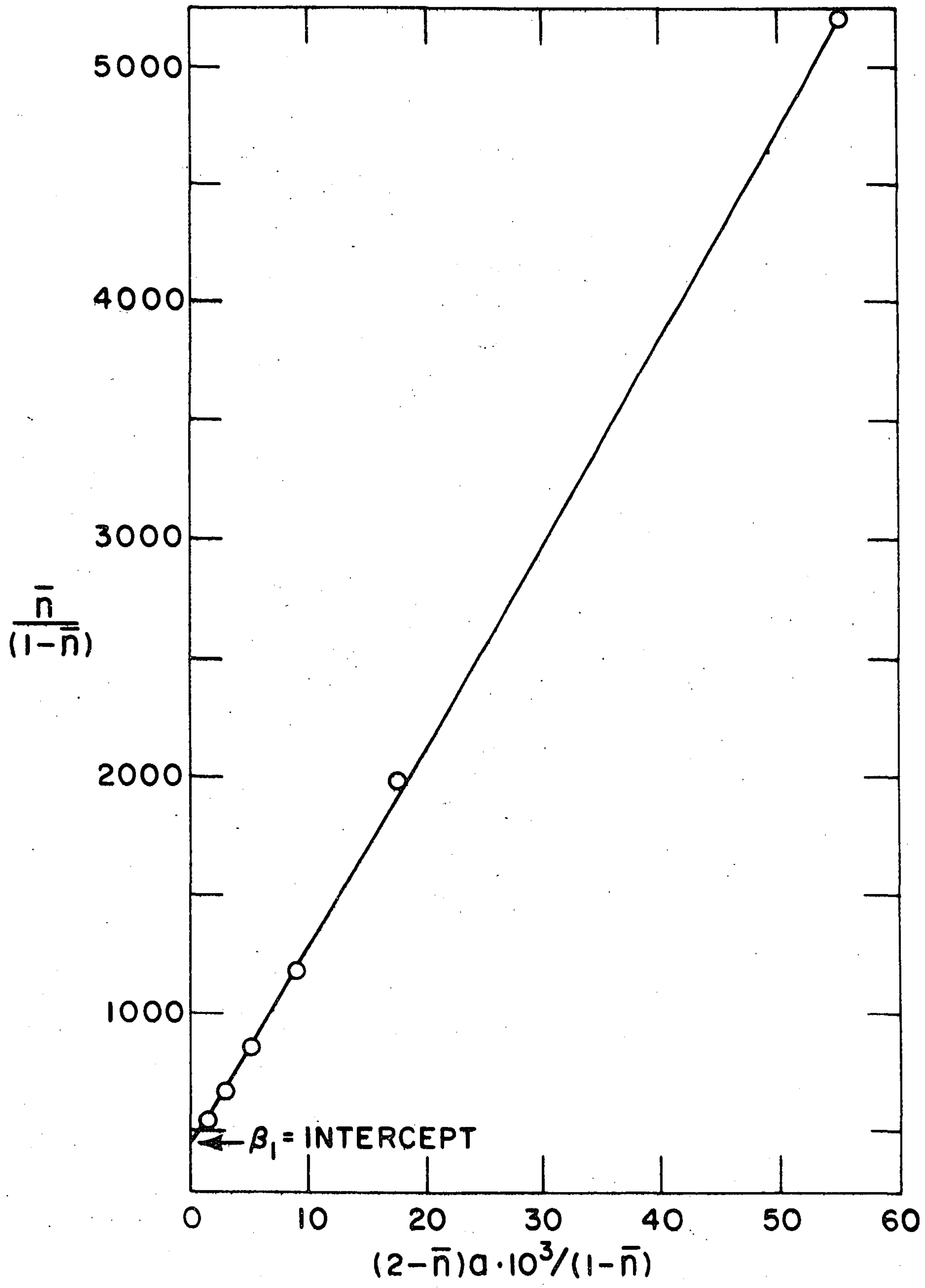

5000
4000
3000
2000
1000
$\frac{\bar{n}}{(1-\bar{n})}$
β_1 = INTERCEPT
0
10
20
30
40
50
60
$(2-\bar{n})a\cdot10^3/(1-\bar{n})$

Figure 8. $\frac{\bar{n}-(1-\bar{n})a\beta_1}{(2-\bar{n})a^2}$ <u>versus</u> $\frac{(3-\bar{n})a}{(2-\bar{n})}$ for the dysprosium α,β,β'-trihydroxyisobutyrate system

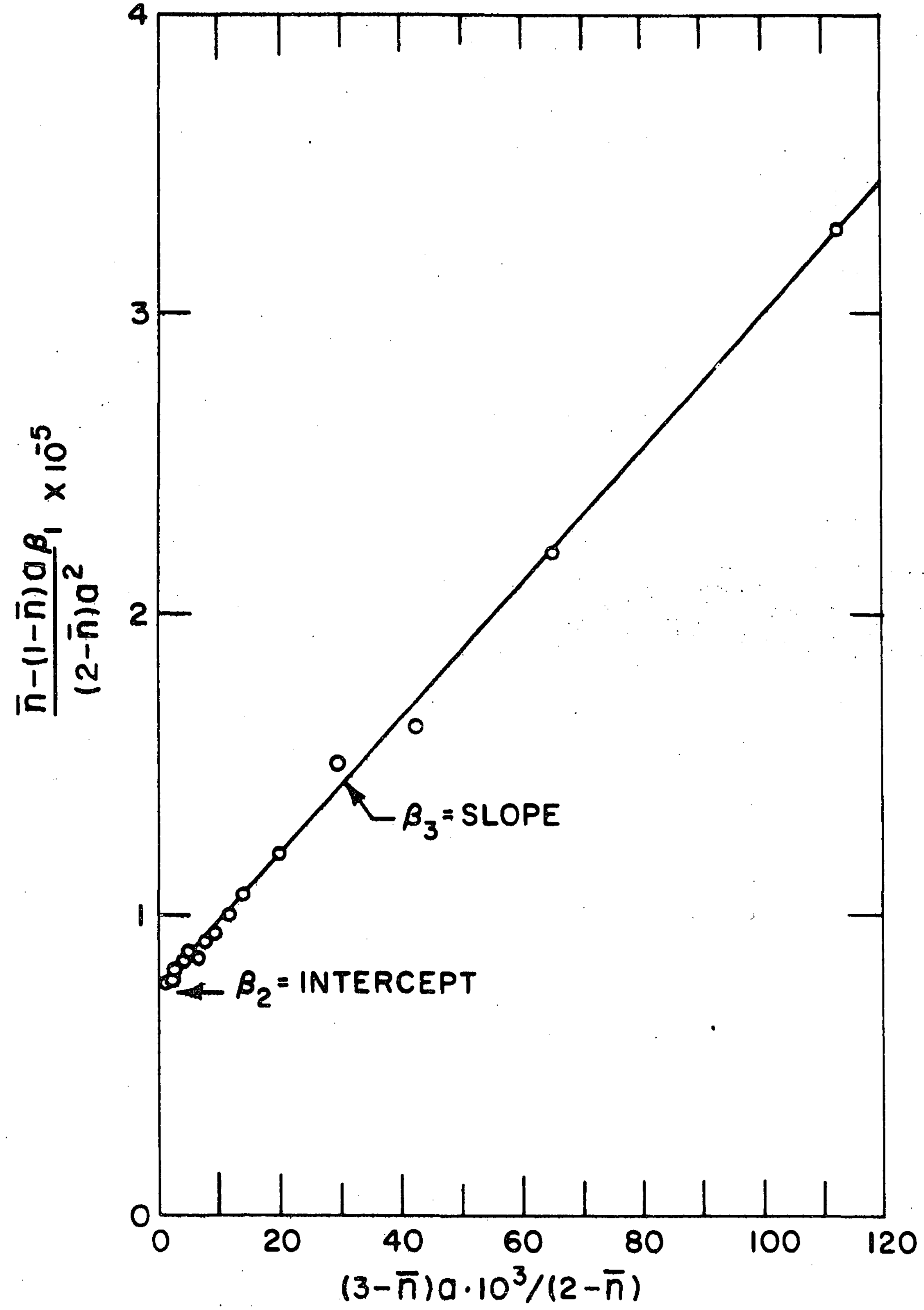

$\frac{\bar{n}-(1-\bar{n})a\beta_1}{(2-\bar{n})a^2} \times 10^{-5}$
0
1
2
3
4
0
20
40
60
80
100
120
$(3-\bar{n})a\cdot10^3/(2-\bar{n})$
β_3 = SLOPE
β_2 = INTERCEPT

Table 3. Comparison of stability constants obtained by different computational methods for the dysprosium α,β,β'-trihydroxyisobutyrate system

Method	β_1	$\beta_2 \times 10^{-4}$	$\beta_3 \times 10^{-6}$
Fronaeus	440	7.67	2.48
Rossotti	450	7.60	2.24
$\bar{n} = n-1/2$	800	11.3	2.65
Bjerrum	425	1.93	6.27
limit of slope	427	---	---
least squares	454	7.44	2.36

only N sets of data to compute N constants.

Actually, none of the methods is completely faultless. Because of their graphical nature, both the Fronaeus and the Rossotti and Rossotti methods lack precision, and errors tend to accumulate in the successive constants. There is also a tendency to smooth or prejudice the data. The direct computational techniques of Bjerrum and Poë are tedious but could be adapted to a computer. Both of these methods lack somewhat in objectivity since a choice of N must be made before computation can be begun.

IV. EXPERIMENTAL DETAILS

A. Technique

Since the ligands studied in this research were anions of monobasic carboxylic acids, the experimental method of Fronaeus was chosen (16, 17, 57). This method consists of titrating a solution of the cation being studied with a buffer solution of the carboxylic acid while maintaining a constant ionic strength in the system. The method has the advantage of supplying a relatively high concentration of the ligand (the anions) while keeping the pH low enough to suppress hydrolysis of the cation. With the ligands studied, the pH remained below five in all cases. The hydrolysis constants of the rare earths indicate that hydrolysis is insignificant under these conditions (14, 15). Several investigators have shown that the undissociated carboxylic acids do not form detectable complexes with the rare earths (16, 17, 27, 29). Thus any changes in pH observed during a titration may be attributed to complex formation between the metal ion and the carboxylate ligand. The equations used to convert hydrogen-ion concentrations and the known stoichiometry into mean ligand numbers and free ligand concentrations are,

$$C_A = \frac{V_b C_A^b}{V_o + V_b} , \qquad (32)$$

$$C_{HA} = \frac{V_b C_{HA}^{b}}{V_o+V_b} , \tag{33}$$

$$C_H = \frac{V_B C_H^{B}}{V_o+V_b} , \tag{34}$$

$$B = \frac{V_B B_o}{V_o+V_b} , \tag{35}$$

$$a = \frac{K_a(C_{HA}-h+C_H)}{h} , \tag{36}$$

$$\bar{n} = \frac{(C_A+h-C_H)-a}{B} . \tag{37}$$

The symbols used in Equations 32 through 37 are:

C_A = total ligand concentration in the solution,

C_A^{b} = ligand concentration in the buffer,

V_b = volume of buffer used,

V_o = initial volume of sample before addition of buffer,

C_{HA} = total concentration of the undissociated carboxylic acid in the solution,

C_{HA}^{b} = concentration of undissociated acid in the buffer,

C_H = concentration of hydrogen ion due to excess acid in the metal salt solution,

V_B = volume of metal salt solution used to prepare sample,

C_H^{B} = concentration of hydrogen ion in the metal salt solution,

B = total metal ion concentration in sample,

B_o = metal ion concentration in metal salt stock solution,

a = free ligand concentration,

K_a = ionization constant of the carboxylic acid,

h = hydrogen ion concentration in the sample,

$\bar{n}$ = mean ligand number.

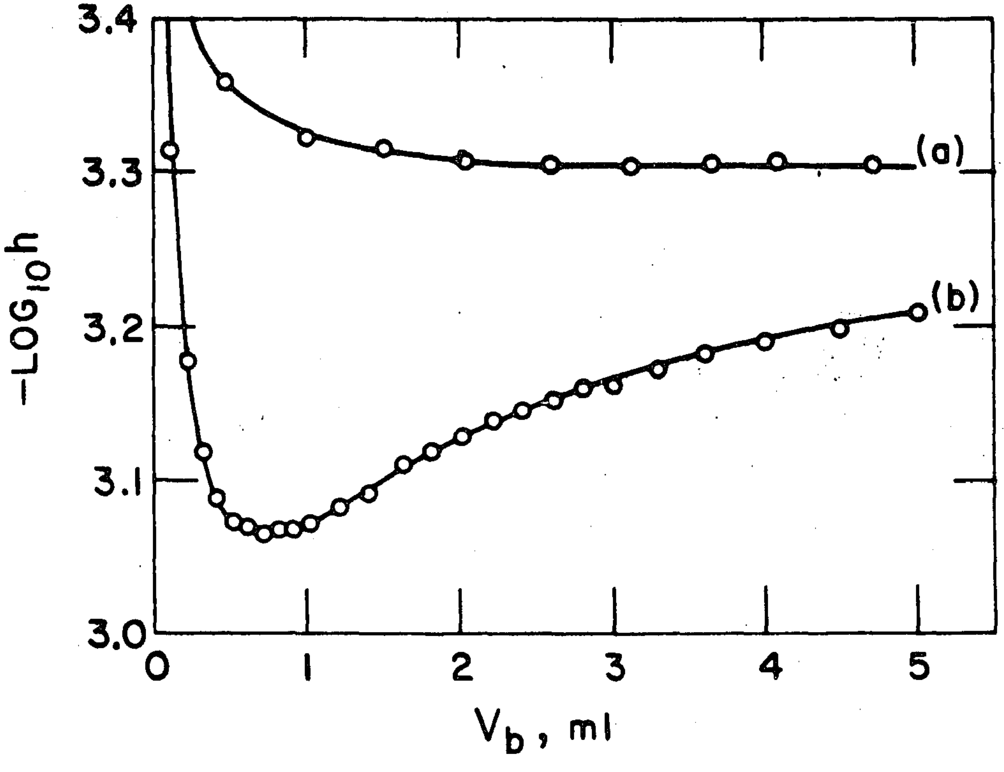
The ionization constants of the acids were determined by titrations in which the metal ions were omitted. Under these circumstances,

$$K_a = \frac{h(C_A+h)}{C_{HA}-h} . \tag{38}$$

Typical titration curves are shown in Figure 9 for the dysprosium α,β,β'-trihydroxyisobutyrate system. The upper curve is a titration without the metal ion from which the value of K_a was calculated. The lower curve is a titration in the presence of 0.004 M Dy^{+3} from which β_1, β_2, and β_3 were calculated.

The experimental technique used in this research consisted of mixing appropriate amounts of metal perchlorate solution, sodium perchlorate solution and water to give a fifty milliliter sample containing approximately 0.004 M rare-earth ion at an ionic strength of 0.4 M. The ionic strength was estimated from the equation

Figure 9. Titration curve for the dysprosium α,β,β'-trihydroxyisobutyrate system


3.4
3.3
3.2
3.1
3.0
$-\log_{10}h$
0
1
2
3
4
5
V_b, ml
(a)
(b)

$$\mu = 1/2 \sum_{i=1}^{r} c_i z_i^2$$

where c_i = molar concentration of species i,

z_i = ionic charge on species i,

r = number of kinds of ionic species in solution,

μ = ionic strength.

The sample was then titrated at constant temperature with a 1:1 buffer of the appropriate carboxylic acid in which the sodium salt of the ligand was 0.5 <u>M</u>. Sodium perchlorate was used as a supporting electrolyte since it has been shown that if perchlorate complexes of the rare earths exist they are probably not significant at the concentrations employed in this research (10, 62). The total volume of buffer used in each experiment was five milliliters. Under these conditions it is conceivable that the ionic strength could vary by 4% if 100% complexing occurred. An experiment in which the ionic strength was deliberately varied by 5% indicated that the variation was not significant within the limits of error of the measurements.

B. Preparation of Reagents

Rare-earth perchlorate solutions

All rare-earth oxides except cerium, europium and promethium were supplied by the rare-earth separation group at the Ames Laboratory of the United States Atomic Energy

Commission. Europium oxide was purchased from the Michigan Chemical Corporation, Saint Louis, Michigan and cerium(III) perchlorate was purchased from the Lindsay Chemical Division of American Potash and Chemical Corporation, West Chicago, Illinois. No work was done with promethium. All samples were 99.9% pure.

Approximately 0.5 M rare-earth perchlorate solutions were prepared by dissolving the necessary amounts of the oxides in a slight excess of perchloric acid and boiling to dryness. Some of the salt underwent pyrohydrolysis, and the resultant solutions were basic with respect to their neutral equivalence points upon redissolution. An aliquot of each solution was titrated with dilute perchloric acid using a Beckman Zeromatic pH Meter with glass and calomel electrodes as an indicator, and the end point was found by using a Gran plot (63). Each solution was then adjusted to its equivalence point using the same acid solution. This technique was used to obtain neutral solutions of all the rare earths except cerium. In the case of cerium, excess acid was left in the solution to stabilize the trivalent oxidation state, and this excess was determined by titration with standard KOH using Gran's method to find the end point.

These stock solutions were analysed in two ways: 1) aliquots were treated with oxalic acid and the resulting oxalates ignited to the oxides; 2) aliquots were titrated with standard EDTA solution using naphthylazoxine S indicator according to the method of Fritz, Abbink, and Payne (64). Average concentrations from five to seven determinations were used. Exactly 0.01 M solutions were prepared from these stock solutions by dilution.

Sodium hydroxide solution

An approximately 1 M carbonate-free sodium hydroxide solution was prepared by the method of Powell and Hiller (65) and standardized against potassium acid phthalate.

Sodium perchlorate solution

An approximately 1 M sodium perchlorate solution was prepared from G. Frederick Smith anhydrous sodium perchlorate. After filtering, the solution was passed through a bed of sodium-form Dowex-50 cation-exchange resin to remove possible cationic contaminants. The solution was analysed 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 0.5 M. This solution was used to standardize the pH meter prior to each experiment so that ($-\log_{10} h$) could be read directly. This method of calibration has been shown to be generally valid (66).

Isobutyrate buffer

Matheson, Coleman and Bell isobutyric acid was fractionally distilled, and a fraction from the middle of the distillate was obtained with a boiling point range of 152.5° to 153.5°C. This sample was analyzed by vapor phase chromatography and was found to contain a small amount of a lower boiling fraction. If this impurity were assumed to be propionic acid, the chromatogram indicated that the sample was better than 97% pure. In view of the weakness of the complexes formed by this ligand, the impurity was considered insignificant. Approximately 0.25 mole of this was mixed with exactly 0.125 mole of the NaOH and diluted to 250 milliliters. The concentration of unneutralized acid was determined by titration of aliquots with standard KOH.

α-Hydroxyisobutyrate buffer

α-Hydroxyisobutyric acid (Eastman Organic Chemicals # 3025) was recrystallized from a mixture of ten parts benzene and three parts diethyl ether and then boiled in distilled water with activated carbon. After filtering, the solution was evaporated down and standardized by titration of aliquots with standard KOH. Exactly 0.250 moles of this solution was then mixed with 0.125 moles of NaOH and diluted to 250 milliliters.

<u>α,β,β'-Trihydroxyisobutyrate buffer</u>

α,β,β'-Trihydroxyisobutyric acid was prepared by Dr. J. E. Powell and Mr. H. R. Burkholder using the method of Coleman and Glattfeld (67). The material was recrystallized from boiling acetone and analyzed by titration with standard KOH. The equivalent weight was found to be 135.5 ± 0.1 (theoretical, 136.1) and the melting point was 115.8° to 116.8°C. Exactly 0.250 mole of the material was weighed out, mixed with 0.125 mole of NaOH and diluted to 250 milliliters.

C. Experimental Apparatus

The apparatus consisted of a titration cell, a five milliliter microburet, a thermostat and a pH meter. The titration cell was fashioned from a 250 milliliter beaker sealed inside a 400 milliliter beaker and equipped with ground glass ball joint inlet and outlet ports so that water could be circulated through the jacket during a titration. There was also an inlet port for flushing the cell with an inert gas. The thermostat was maintained at 25.00° ± 0.05°C by a Precision Microset Thermoregulator and Electronic Relay using a 500-watt lamp as a heat source. Water from the bath was circulated through the titration cell by a small centrifugal pump. The sample was stirred by a magnetic stirrer.

The pH meter used was a Beckman Model 76 Expanded Scale pH Meter with a saturated calomel reference electrode and a glass indicator electrode. The potassium chloride in the calomel electrode was replaced with a saturated sodium chloride solution to eliminate erratic behavior due to the formation of slightly soluble potassium perchlorate in the fiber junction. The instrument was used on the expanded scale and could be read to 0.001 unit of (-log h) with a reproducibility of ± 0.003 unit. The instrument was calibrated against the 0.001 M $HClO_4$ prior to each titration and was observed to maintain its calibration for periods of up to twenty-eight hours. Only one calibration point was necessary since it has been shown that the Nernst law is valid for concentrated sodium perchlorate solutions (68).

V. EXPERIMENTAL RESULTS

A. Computation of Parameters and Errors

The stability constants of the isobutyrate (IBU) complexes, α-hydroxyisobutyrate (AHIB) complexes and α,β,β'-trihydroxyisobutyrate (THIB) complexes were computed from the observed hydrogen ion concentrations and the known stoichiometry of the samples using an IBM 7074 computer and programs patterned after that of Sullivan _et al._ (59). The values of $\bar{n}$ and a were computed initially and examined for irregularities such as decreasing values of $\bar{n}$ with increasing a and discontinuities in the graph of $\bar{n}$ _versus_ a. The maximum value of N was then selected as the smallest integer greater than the highest value of $\bar{n}$, and the values of the β_n's were approximated using Equations 7 and 12. Computer programs were written for N = 2 and N = 3. The IBU data and La, Ce, Pr, Nd, and Sm data for AHIB were computed with the two parameter program, and the remainder of the AHIB data and all the THIB data were computed with the three parameter program. There was no evidence of a fourth complex in any of these experiments. The computer programs were written so that they would reiterate until successive values of the β_n's differed from each other by less than one part per thousand and until the value of each parameter minus one standard deviation in that parameter was positive. A limit of 500 was placed upon the number of iterations. It was observed that if these conditions were not met within five or six iterations, they would not be met at all.

The relative error in the free ligand concentration was estimated using the usual formulas for probable errors (69). For the IBU data this was found to be about 1.7% and for the AHIB and THIB data about 2.3%. However, it was found that identical results were obtained for a given set of data when the value of m was varied between the limits of 0.5% and 10% so the selection of this quantity was not critical.

The standard deviation in each parameter was computed using Equation 28. The deviations reported are the errors of internal consistency, that is, they relate to the relative errors of the data in a given experiment. They reveal nothing about systematic errors which may have been made in the ionization constants of the acids, concentration of metal perchlorate solutions, variations in ionic strength, and so forth. Consequently, computations were made in which the input data were varied within their estimated maximum limits of error using the Dy THIB data which has been used as an example throughout this dissertation. The results were that the relative errors in β_1, β_2, and β_3 might be as great as ± 10%, ± 25%, and ± 50%, respectively. The relative errors for a two parameter system such as dysprosium isobutyrate would be ± 25% for β_1 and ± 50% for β_2.

The Dy THIB system was studied at an ionic strength of

0.475 to see what effect a 5% variation in ionic strength would have upon the β_n's. The results are shown in Table 4. As was mentioned before, it was concluded that the variation in ionic strength was not significant.

Table 4. Effect of variation in ionic strength upon the stability constants of the dysprosium α,β,β'-trihydroxyisobutyrate system

μ	β_1	$\beta_2 \times 10^{-4}$	$\beta_3 \times 10^{-6}$
0.500	454 ± 4	7.44 ± 0.08	2.36 ± 0.06
0.475	435 ± 7	7.00 ± 0.17	2.93 ± 0.12

B. The Isobutyrate Complexes

The results obtained for the rare-earth isobutyrate complexes are shown in Table 5. Sonesson (17, 19) has reported dinuclear complexes for some of the rare-earth acetates. To check on this possibility, a titration was run on dysprosium in which the initial metal concentration was increased to approximately 0.02 M. The results were,

$$\beta_1 = 50.5 \pm 0.1 \,,$$
$$\beta_2 = 1028 \pm 9 \,.$$

These values are within the limits of random error given above for β_1 and β_2. Sonesson pointed out that the presence

Table 5. Stability constants of the rare-earth isobutyrate complexes, T=25°, μ=0.5 with $NaClO_4$

Metal	β_1	β_2	k_2
La	43.8 ± 1.5	143 ± 54	3.26
Ce	61.1 ± 0.9	210 ± 36	3.44
Pr	82.9 ± 0.8	1499 ± 43	18.08
Nd	95.4 ± 1.3	1250 ± 75	13.10
Sm	112 ± 2	2068 ± 126	18.46
Eu	94.6 ± 1.5	726 ± 73	7.67
Gd	73.7 ± 1.3	1900 ± 77	25.78
Tb	65.5 ± 1.0	689 ± 77	10.52
Dy	55.1 ± 1.1	371 ± 48	6.73
Ho	49.7 ± 0.8	838 ± 29	16.86
Er	49.3 ± 0.8	385 ± 33	7.81
Tm	49.5 ± 0.8	191 ± 36	3.86
Yb	60.7 ± 1.8	1264 ± 94	20.82
Lu	65.1 ± 1.3	208 ± 53	3.20
Y	39.8 ± 0.6	516 ± 25	12.96

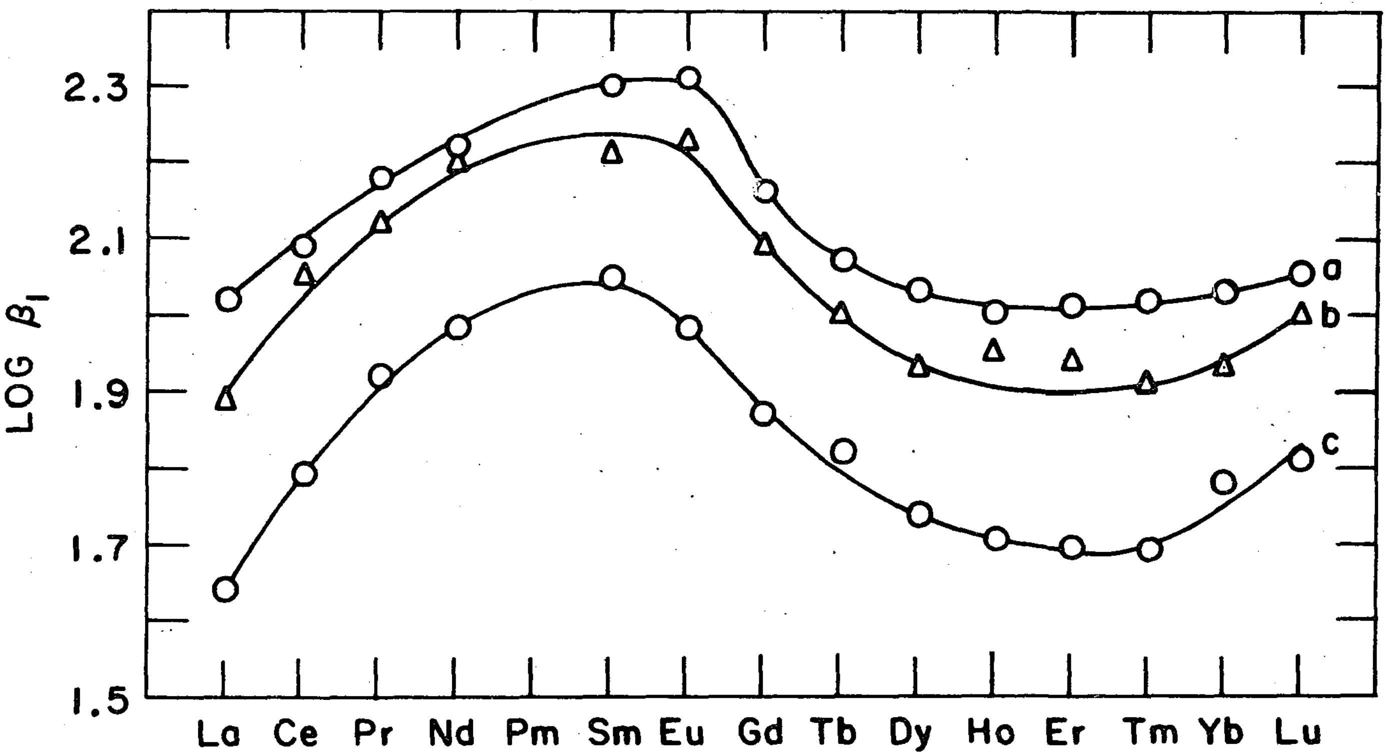
of polynuclear species would cause an apparent increase in β_1 if the metal ion concentration were increased.

The ionization constant for isobutyric acid at 25°C and an ionic strength of 0.5 was found to be: $K_a = (2.295 \pm 0.030) \times 10^{-5}$, $pK_a = 4.639 \pm 0.005$.

The values of β_1 for the isobutyrates may be compared qualitatively with those for the acetates (20) and propionates (21). Figure 10 gives such a comparison of the logarithms of these constants. Curve (a) represents the acetate system at 20°C and an ionic strength of 0.1, curve (b) represents the propionate system at 20°C and an ionic strength of 0.1, and

Figure 10. Logarithms of the first stability constants of the rare earth complexes with

a: acetate at 20°C, $\mu = 0.1$ (20)
b: propionate at 20°C, $\mu = 0.1$ (21)
c: isobutyrate at 25°C, $\mu = 0.5$


LOG β_1
2.3
2.1
1.9
1.7
1.5
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
a
b
c

curve (c) represents the isobutyrate system reported here. The isobutyrate curve is displaced downward somewhat more than would be expected from the difference in the acetate and propionate curves because of the five-fold difference in ionic strength; the five degree difference in temperature would have little effect on this scale.

It can be seen that the constants lie in the order acetate > propionate > isobutyrate. The isobutyrate constants increase from lanthanum to samarium as would be expected from the lanthanide contraction, i.e., the decrease in ionic radius as shown in Table 1. They then decrease in what appears to be a characteristic fashion to a minimum in the Ho-Er-Tm region before increasing again with Yb and Lu. The effect is not so readily observed in the β_2's because of the large errors in these constants. The experimental data for the isobutyrate system are given in Appendix A.

C. The α-Hydroxyisobutyrate Complexes

The results for the rare-earth AHIB complexes are shown in Table 6. A check for polynuclear complexes on the dysprosium AHIB system using a sample containing 0.02 M Dy^{+3} gave the results

$$\beta_1 = 777 \pm 13$$

$$\beta_2 = (24.2 \pm 0.8) \times 10^4$$

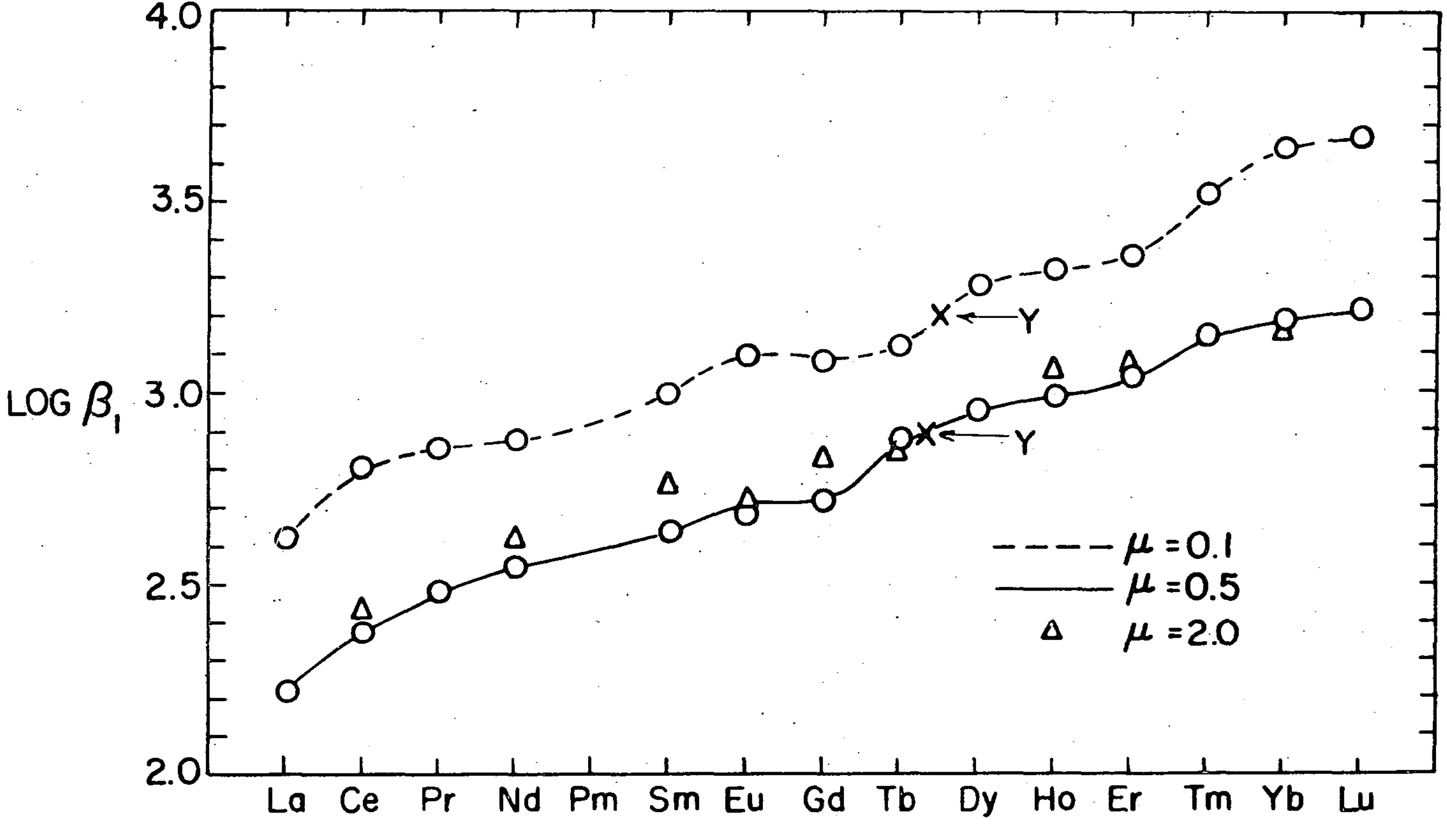
$$\beta_3 = (1.40 \pm 0.08) \times 10^7.$$

Table 6. Stability constants of the rare-earth α-hydroxyisobutyrate complexes, t=25°, μ=0.5 ($NaClO_4$)

Metal	β_1	$\beta_2 \times 10^{-4}$	$\beta_3 \times 10^{-7}$	k_2	k_3
La	166 ± 4	0.472± 0.036	---	28.8	---
Ce	237 ± 5	1.02 ± 0.05	---	43.0	---
Pr	301 ± 4	1.32 ± 0.04	---	43.9	
Nd	343 ± 4	2.09 ± 0.05	---	60.9	---
Sm	426 ± 64	3.97 ± 0.90	---	93.2	---
Eu	512 ± 7	8.41 ± 0.18	0.0805± 0.0103	164	9.6
Gd	514 ± 5	9.37 ± 0.13	0.103 ± 0.008	182	11
Tb	744 ± 11	16.3 ± 0.4	0.814 ± 0.036	219	50
Dy	895 ± 9	20.8 ± 0.4	1.76 ± 0.04	232	85
Ho	949 ± 14	26.2 ± 0.6	2.60 ± 0.08	276	99
Er	1073 ± 15	34.9 ± 0.6	3.59 ± 0.10	325	103
Tm	1365 ± 26	41.8 ± 1.3	6.97 ± 0.24	306	167
Yb	1527 ± 30	57.1 ± 1.7	10.4 ± 0.3	374	182
Lu	1617 ± 77	70.8 ± 4.7	16.2 ± 1.1	438	229
Y	767 ± 14	21.1 ± 0.5	0.562 ± 0.043	275	27

These are just within the limits of error cited earlier. The logarithms of β_1 for the rare-earth AHIB complexes are shown in Figure 11 (full curve) and are compared with the data of Choppin and Chopoorian (29) at 25°C and an ionic strength of 2.0 (triangles) and with the data of Powell *et al.* (27) at 20°C and an ionic strength of 0.1 (dashed curve). The data show that β_1 increases steadily with decreasing cationic radius. The fact that some of the data at μ = 2 lie between that 0.1 and 0.5 may be accounted for by the fact that the function

Figure 11. Logarithms of the first stability constants of the rare-earth α-hydroxyisobutyrate complexes


4.0
3.5
3.0
2.5
2.0
LOG β_1
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
X ← Y
X ← Y
μ = 0.1
μ = 0.5
Δ μ = 2.0

$$\text{Log } K = f(\mu)$$

may pass through a minimum as predicted by the Debye-Hückel theory (53, p. 32).

The third constant could not be computed for lanthanum, cerium, praseodymium, neodymium and samarium because the values of $\bar{n}$ did not rise to sufficiently high values, i.e., there was not a high enough concentration of the 3:1 complex to permit computation of a parameter to represent it.

The ionization constant for the α-hydroxyisobutyric acid at 25°C and an ionic strength of 0.5 was found to be: $K_a = (1.757 \pm 0.010) \times 10^{-4}$, $pK_a = 3.755 \pm 0.003$.

The experimental data for the rare-earth α-hydroxyisobutyrate complexes are given in Appendix B.

D. The α,β,β'-Trihydroxyisobutyrate Complexes

The results for the rare-earth THIB complexes are shown in Table 7. The check for polynuclear complexes was made on the dysprosium THIB system using 0.02 M Dy^{+3}. The results were

$$\beta_1 = 495 \pm 5 \; ,$$
$$\beta_2 = (7.51 \pm 0.15) \times 10^4 \; ,$$
$$\beta_3 = (2.14 \pm 0.10) \times 10^6 \; .$$

Again these are within the limits of experimental error of the values obtained at 0.004 M Dy^{+3}.

The logarithms of β_1 are shown in Figure 12 (dashed

Table 7. Stability constants of the rare earth α,β,β'-trihydroxyisobutyrate complexes, T=25°C, μ=0.5 ($NaClO_4$)

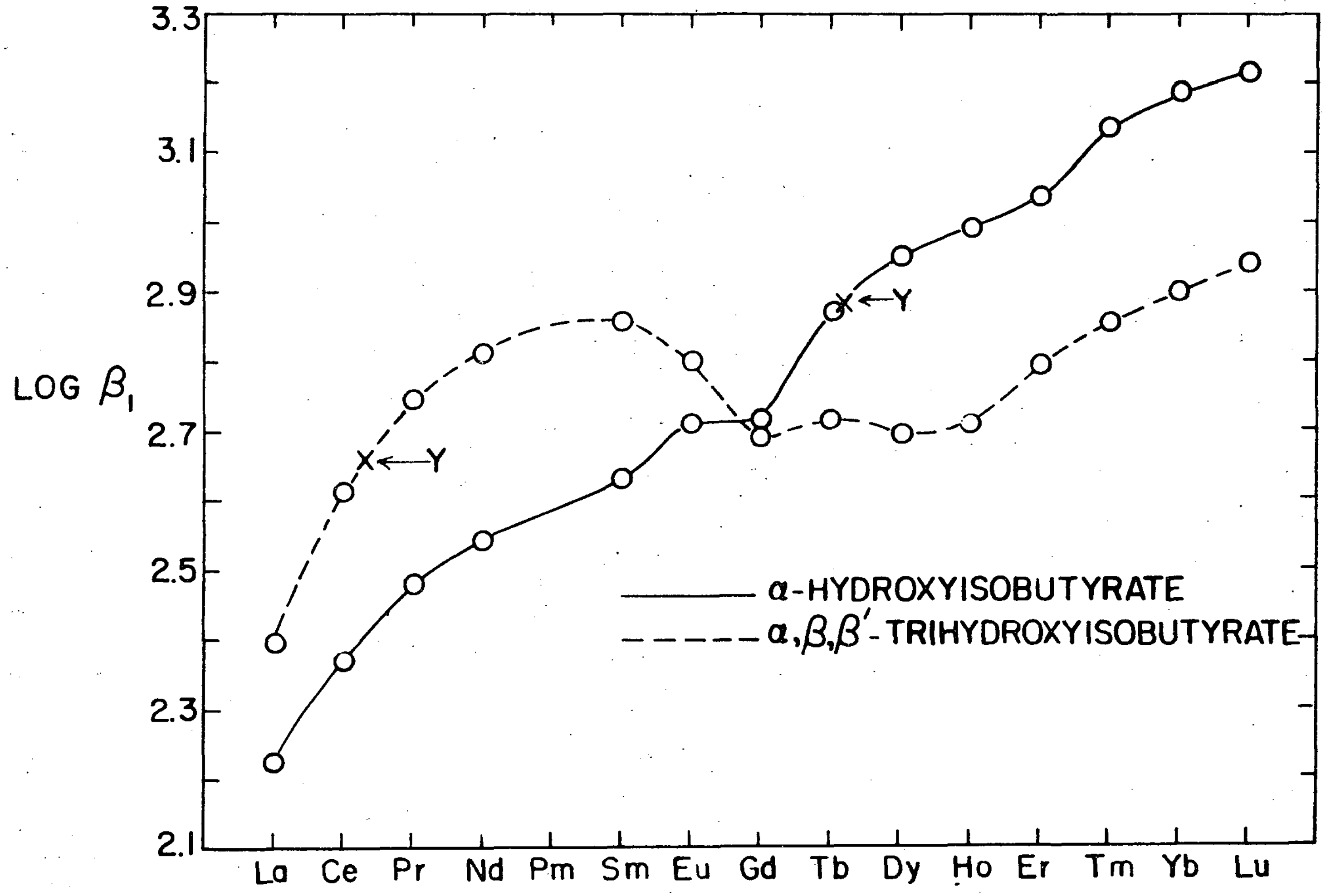
Metal	β_1	$\beta_2 \times 10^{-4}$	$\beta_3 \times 10^{-6}$	k_2	k_3
La	249 ± 4	0.751 ± 0.053	0.0800 ± 0.0128	30.2	11
Ce	409 ± 6	2.80 ± 0.12	0.964 ± 0.052	68.5	34
Pr	559 ± 6	4.90 ± 0.13	1.41 ± 0.06	87.7	29
Nd	646 ± 74	4.20 ± 1.64	2.30 ± 0.91	65.0	55
Sm	720 ± 10	11.8 ± 0.3	3.22 ± 0.17	164	27
Eu	631 ± 7	9.99 ± 0.19	2.81 ± 0.11	158	28
Gd	486 ± 9	9.70 ± 0.25	2.56 ± 0.15	200	26
Tb	519 ± 10	7.52 ± 0.27	3.78 ± 0.18	145	50
Dy	454 ± 4	7.44 ± 0.08	2.36 ± 0.06	164	32
Ho	511 ± 8	7.81 ± 0.21	1.67 ± 0.11	153	21
Er	619 ± 7	6.82 ± 0.19	3.74 ± 0.12	110	55
Tm	711 ± 8	9.23 ± 0.20	3.23 ± 0.12	130	35
Yb	789 ± 12	11.7 ± 0.3	3.19 ± 0.20	148	27
Lu	874 ± 26	15.4 ± 0.8	8.00 ± 0.70	176	52
Y	451 ± 7	4.70 ± 0.17	0.180 ± 0.009	104	3.8

curve) and are compared with those for the AHIB system (full curve) under identical experimental conditions. It can be seen that the β_1's increase from lanthanum through samarium and then decrease to a minimum in the Tb-Dy-Ho region before they begin to increase again.

The ionization constant for the acid at 25°C and an ionic strength of 0.5 was found to be: $K_a = (5.147 \pm 0.070) \times 10^{-4}$, $pK_a = 3.288 \pm 0.006$.

The experimental data for the rare-earth α,β,β'-trihydroxyisobutyrate complexes are given in Appendix C.

Figure 12. Logarithms of the first stability constants of the rare-earth α-hydroxyisobutyrate complexes (full curve) and the rare-earth α,β,β'-trihydroxyisobutyrate complexes (dashed curve) at 25°C and 0.5 ionic strength


LOG β_1
3.3
3.1
2.9
2.7
2.5
2.3
2.1
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
X←Y
X←Y
α-HYDROXYISOBUTYRATE
α,β,β′-TRIHYDROXYISOBUTYRATE

VI. DISCUSSION

The behavior of these three series of rare-earth complexes may be discussed in terms of electronic effects and entropy effects. The electronic effects may be divided into three groups: simple coulombic interactions, "resonance" effects, and ligand field interactions.

Calvin and Wilson (70) reported that a linear relationship existed between log β_1 and log K_a for complexes of a series of similar ligands and Cu(II). Schwarzenbach, Ackermann, and Ruckstuhl (71) found that a similar relationship existed for many alkaline-earth complexes. Duncan (72) pointed out that such relationships are basically relationships between free energy and enthalpy and therefore between enthalpy and the reciprocal of the ionic radius since entropy effects are essentially constant in these studies. Jones (73) has pointed out that a plot of log β_1 versus z^2/r for the rare-earth EDTA complexes is essentially linear and, therefore, implies that ionic bonding predominates. That such observations are fortuitous is illustrated by the data reported in this dissertation. If only the AHIB data in Figure 11 and Table 6 are considered, then the conclusion that coulombic interactions predominated would have been an obvious and satisfactory expnanation. However, the IBU data in Table 5 and Figure 10 and the THIB data in Table 7 and Figure 12 would seem to contradict this. In both of these systems the same general trend of increasing stability with decreasing radius should also have been observed if the bonding had followed a simple coulombic model. That these complexes differed significantly from this trend is evidence that more than simple electrostatic interactions need be considered.

The "resonance" effect mentioned above has been dubbed the "chelate effect" by Schwarzenbach (74). Like resonance, it is a fiction devised to account for the enhanced stability of the heterocyclic structures characterizing chelate compounds. In the research reported in this dissertation, the inductive effect of hydroxyl substitution on the isobutyrate skeleton is obvious. The ionization constants of the acids are 2.295×10^{-5} for isobutyric acid, 1.757×10^{-4} for α-hydroxyisobutyric acid, and 5.147×10^{-4} for α,β,β'-trihydroxyisobutyric acid. This variation reflects the weakening of the carboxyl O-H bond with the addition of hydroxyl substituents to the isobutyric acid skeleton. If coordination took place only by means of coordination through the carboxyl oxygens, the expected order of stability of the complexes would be IBU > AHIB > THIB. The fact that the AHIB complexes are more stable than the corresponding IBU complexes and that some of the THIB complexes are more stable than corresponding AHIB complexes is evidence of the "chelate effect" in operation. It is also evidence that bonding to the cation occurs through more than one coordinating position on the ligand.

Vickery (22) has measured the absorption spectra of complexes between neodymium and a large number of carboxylic acid anions. He found some degree of correlation between the stability constants of the complexes and the shift of the 576 mμ band of $NdCl_3$ upon complexing. He suggested that dsp hybridization plus some contribution from the 4f orbitals was involved but did not put this on a quantitative basis. Moeller and Brantley (75) found that the visible absorption bands of neodymium split into two or more branches in the presence of EDTA suggesting significant involvement of the 4f electrons in complex formation. Further evidence of involvement of the 4f electrons has been given by Holleck and Liebold (76, 77) who found a more or less linear relationship between log β_1 and the molar magnetic susceptibility of a number of 1:1 complexes of neodymium. Similar evidence has been reported by Fritz *et al.* (78) who have pointed out that the Curie constants differ from the values predicted by the Van Vleck theory to a greater extent for the rare-earth EDTA complexes than for the corresponding acetylacetonate complexes.

That ligand field effects can contribute significantly to the observed stability constants is open to question. Orgel (79) has pointed out that ligands which coordinate through oxygen produce crystal fields similar to those of water; therefore, the stability of their complexes (with respect to the solvated cation) will not be much affected by ligand field effects while complexes which are formed by coordination through nitrogen may be strongly stabilized because of the large fields produced by the nitrogen. Griffith (80) pointed out that the stability constant of a complex is related to the entropy of formation by the expression

$$\Delta F^\circ = -RT\ln K = \Delta H^\circ - T\Delta S^\circ$$

in which only the ΔH° term directly reflects ligand field effects. The entropy contribution is not necessarily either small or exactly the same for all metal ions with the same ligand. The entropy of formation includes contributions from possible ground state degeneracy and a variable contribution which is a function of the metal-ligand bond. The variations in enthalpy with a variation in cation are frequently small compared to $T\Delta S^\circ$. So when deviations occur from even the simplest version of ligand field theory, it is difficult to assign the origin of the deviation with any degree of certainty.

Bowers and Owen (81) have estimated that ligand field splitting for the rare earths is about 100 cm^{-1}. This is equivalent to 286 calories per mole or about 0.39 units of

$\log \beta_n$. Contributions of this order of magnitude should certainly be discernible in stability constant data as George, McClure, Griffith and Orgel have observed (82).

Free energy, enthalpy and entropy data have been reported for many rare-earth complexes (40, 41, 45, 47, 50, 83, 84). Most of these data were obtained by measuring the stability constants at different temperatures and then applying the relationships

$$\Delta F° = -RT \ln K \ ,$$

$$\Delta H° = -R\frac{d\ln K}{d(1/T)} \ ,$$

$$\Delta S° = \frac{\Delta H° - \Delta F°}{T} \ .$$

The fact that stoichiometric stability constants were used instead of standard state data may be generally reconciled by the argument that the trends apparent in the standard state would also be observed at finite ionic strengths. There have been some calorimetric measurements which generally substantiate the other data (83, 84). From such data as are available, it may be concluded that variations in configurational entropy are rather large and variations are observed which could account for the "gadolinium break" and other such anomalies (40, 41, 45, 47). However in the cases of EDTA (83, 84) and DTPA (50), the entropy is found to increase regularly with 1/r so the issue is not completely settled.

Cobble (85, 86) has derived some useful empirical rules for estimating the entropies of complex ions in solution. Using these rules, one may estimate that the entropy change would be -2.7 entropy units if a metal-hydrogen bond in the rare-earth THIB complexes were broken and the site were then occupied by a water molecule. This would correspond to 0.59 units of log β_n. If this quantity were added to log β_1 for the THIB complexes of gadolinium through lutetium, the anomalous decrease in stability of these complexes with respect to the corresponding AHIB complexes is more or less resolved. Such a correction is shown in Table 8. The correction is crude but does suggest a plausible explanation for these data.

As was mentioned in the introduction, the separation factors for ion-exchange separations may be approximated from the stability constants. The separation factor α is given by

$$\alpha = \frac{(B/\bar{B})}{(B'/\bar{B}')} , \qquad (39)$$

where $\bar{B}$ = concentration of metal B in the resin,

$\bar{B}'$ = concentration of metal B' in the resin,

B = total concentration of metal B in solution,

B' = total concentration of metal B' in solution.

Using Equation 10 for the metal ion concentrations in solution gives

Table 8. Comparison of corrected[a] THIB stability constants with the AHIB stability constants

Metal	AHIB log β_1	THIB[a] log β_1
La	2.22	2.40
Ce	2.37	2.61
Pr	2.48	2.75
Nd	2.54	2.81
Sm	2.63	2.86
Eu	2.71	2.80
Gd	2.71	3.28
Tb	2.87	3.31
Dy	2.95	3.25
Ho	2.98	3.30
Er	3.03	3.38
Tm	3.14	3.44
Yb	3.18	3.49
Lu	3.21	3.53
Y	2.89	3.24

[a] Log β_1 = Log β_1 + 0.59 for Gd through Lu plus Y.

$$\alpha = \frac{\bar{B}'}{B} \cdot \frac{b \sum_{n=0}^{N} \beta_n a^n}{b' \sum_{n=0}^{N} \beta'_n a^n} \;. \qquad (40)$$

Although it is not exactly true that the relative affinity of the resin for the trivalent rare earths is the same for all the metals (87), it is true to a first approximation. Thus it is approximately true that

$$\frac{\overline{B}'}{\overline{B}} = \frac{b'}{b} \; .$$

Therefore, the expression for α becomes

$$\alpha = \frac{\sum_{n=0}^{N} \beta_n a^n}{\sum_{n=0}^{N} \beta'_n a^n} \; . \tag{41}$$

Table 9. Separation factors with respect to gadolinium for the rare-earth complexes of IBU, AHIB, and THIB, T=25°C, μ=0.5 <u>M</u> with $NaClO_4$

Metal	IBU	AHIB	THIB
La	4.55	31.6	19.9
Ce	3.22	16.1	2.79
Pr	1.98	12.5	1.10
Nd	1.20	4.98	1.29
Sm	0.827	4.59	0.800
Eu	1.49	1.19	0.924
Gd	1.00	1.00	1.00
Tb	1.96	0.205	0.781
Dy	2.86	0.102	1.14
Ho	1.98	0.0703	1.43
Er	3.00	0.0511	1.80
Tm	3.85	0.0273	0.847
Yb	1.41	0.0184	0.806
Lu	3.07	0.0119	0.372
Y	2.88	0.259	5.15

Using the stability constants from Tables 5, 6 and 7, Equation 41, and an assumed free ligand concentration of 0.1 M, the separation factors α_{M}^{Gd} were computed and are listed in Table 9. In all of these, B represents gadolinium and B' represents the other metal. From the range of the factors, it is apparent that the AHIB is the superior eluant of the three for separations involving mixtures of all of the rare earths.

VII. SUMMARY

The stoichiometric stability constants of the complexes formed between lanthanum, yttrium and all of the rare earths, except promethium, and the anions of isobutyric acid, α-hydroxyisobutyric acid and α,β,β'-trihydroxyisobutyric acid were measured at 25°C and an ionic strength of 0.5 M using sodium perchlorate as a supporting electrolyte. The buffer titration technique of S. Fronaeus was employed. Optimum values of the successive equilibrium constants were computed via a least squares technique using an IBM 7074 computer. It was found that for the rare earths lanthanum through europium the order of increasing stability was isobutyrate, α-hydroxyisobutyrate, α,β,β'-trihydroxyisobutyrate; for the rare earths gadolinium through lutetium, the order of increasing stability was isobutyrate, α,β,β'-trihydroxyisobutyrate, α-hydroxyisobutyrate. It was postulated that the inversion of the relative stabilities of the latter two ligands with increasing atomic number was due to a change in coordination of the α,β,β'-trihydroxyisobutyrate ligand.

VIII. BIBLIOGRAPHY

1. Healy, R. M. and Kremers, H. E. Separation of rare earths by fractional crystallization. In Spedding, F. H. and Daane, A. H., eds. The rare earths. pp. 29-37. New York, New York, John Wiley and Sons, Inc. 1961.

2. Peppard, D. F. Separation of rare earths by liquid-liquid extraction. In Spedding, F. H. and Daane, A. H., eds. The rare earths. pp. 38-54. New York, New York, John Wiley and Sons, Inc. 1961.

3. Powell, J. E. and Spedding, F. H. Chem. Eng. Progr. Symposium Ser., 55, No. 24, 101 (1959).

4. Powell, J. E. Separation of rare earths by ion exchange. In Spedding, F. H. and Daane, A. H., eds. The rare earths. pp. 55-73. New York, New York, John Wiley and Sons, Inc. 1961.

5. Templeton, D. H. and Dauben, C. H., J. Am. Chem. Soc., 76, 5237 (1954).

6. James, D. B. and Powell, J. E., U. S. Atomic Energy Commission Report IS-329 [Iowa State Univ. of Science and Technology, Ames. Inst. for Atomic Research.] (1960).

7. Wheelwright, E. H., Spedding, F. H., and Schwarzenbach, G., J. Am. Chem. Soc., 75, 4196 (1953).

8. Paul, A. D., J. Phys. Chem., 66, 1248 (1962).

9. Choppin, G. R. and Unrein, P. J., J. Inorg. Nucl. Chem., 25, 387 (1963).

10. Choppin, G. R. and Dinius, R. H., Inorg. Chem., 1, 140 (1962).

11. Peppard, D. F., Mason, G. W. and Hucher, I., J. Inorg. Nucl. Chem., 24, 881 (1962).

12. Poluektov, N. S. and Kononenko, L. I., Zhur. Neorg. Khim., 6, 1837 (1961). Original available but not translated; abstracted in Nuclear Science Abstracts 16: 5338. 1962.

13. Fronaeus, S., Svensk Kem. Tidskr., 64, 317 (1952).

14. Moeller, T., *J. Phys. Chem.*, *50*, 242 (1946).

15. Biedermann, G. and Ciavatta, L., *Acta Chem. Scand.*, *15*, 1347 (1961).

16. Sonesson, A., *Acta Chem. Scand.*, *12*, 165 (1958).

17. ________, *Acta Chem. Scand.*, *12*, 1937 (1958).

18. ________, *Acta Chem. Scand.*, *13*, 1437 (1959).

19. ________, *Acta Chem. Scand.*, *14*, 1495 (1960).

20. Kolat, R. S. and Powell, J. E., *Inorg. Chem.*, *1*, 293 (1962).

21. Paul, G. S. A study of the rare earth metal propionate complexes. Unpublished M. S. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1963.

22. Vickery, R. C., *J. Mol. Spectroscopy*, *2*, 308 (1958).

23. Lloyd, M., Wycherley, V., and Monk, C. B., *J. Chem. Soc.*, 1786 (1951).

24. Coleman-Porter, C. A. and Monk, C. B., *J. Chem. Soc.*, 4363 (1952).

25. Perrin, D. D., *J. Chem. Soc.*, 1710 (1959).

26. Cefola, M., Thompa, A. S., Celiano, A. V., and Gentile, P. S., *Inorg. Chem.*, *1*, 290 (1962).

27. Powell, J. E., Karraker, R. H., Kolat, R. S., and Farrell, J. L. Complex systems of the rare earth metals with glycolate, lactate, and α-hydroxyisobutyrate ligands. Unpublished paper presented at Third Rare Earth Research Conference, Clearwater, Florida, April 21-24, 1963. Mimeographed. Ames, Iowa, Department of Chemistry and Institute for Atomic Research, Iowa State University of Science and Technology. *ca.* 1963.

28. Holm, L. W., Choppin, G. R., and Moy, D., *J. Inorg. Nucl. Chem.*, *19*, 251 (1961).

29. Choppin, G. R. and Chopoorian, J. A., *J. Inorg. Nucl. Chem.*, *22*, 97 (1961).

30. Sonesson, A., *Acta Chem. Scand.*, *13*, 998 (1959).

31. Kolat, R. S. A study of the rare earth metal complexes. Unpublished Ph. D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1961.

32. Bear, J. L., Choppin, G. R., and Quagliano, J. V., *J. Inorg. Nucl. Chem.*, *24*, 1601 (1962).

33. Batyaev, I. M., Larionov, S. V., and Shul'man, V. M., *Zhur. Neorg. Khim.*, *6*, 153 (1961). Original available but not translated; abstracted in Nuclear Science Abstracts 15: 14283. 1961.

34. Grenthe, I. and Fernelius, W. C., *J. Am. Chem. Soc.*, *82*, 6258 (1960).

35. ________ and ________ Formation constants and magnetic behavior of some rare earth chelates. In Kleber, E. V., ed. Rare earth research. pp. 12-25. New York, New York, The Macmillan Company. 1961.

36. Thompson, L. C., *Inorg. Chem.*, *1*, 490 (1962).

37. ________, *J. Inorg. Nucl. Chem.*, *24*, 1083 (1962).

38. Grenthe, I., *J. Am. Chem. Soc.*, *83*, 360 (1961).

39. Anderegg, G., *Helv. Chim. Acta*, *43*, 825 (1960).

40. Moeller, T. and Ferrus, R., *Inorg. Chem.*, *1*, 49 (1962).

41. Levy, S. C. and Powell, J. E., *U. S. Atomic Energy Commission Report IS-421* [Iowa State Univ. of Science and Technology, Ames. Inst. for Atomic Research.] (1961)

42. Mackey, J. L. and Powell, J. E., *Inorg. Chem.*, *1*, 418 (1962).

43. ________ and ________ Determination of the rare-earth-HEDTA stability constants with the mercury electrode. In Nachman, J. F. and Lundin, C. E., eds. Rare earth research. pp. 47-58. New York, New York, Gordon and Breach. 1962.

44. Gupta, A. K. and Powell, J. E., *Inorg. Chem.*, *1*, 955 (1962).

45. Betts, R. H. and Dahlinger, O. F., *Can. J. Chem.*, *37*, 91 (1959).

46. Mackey, J. L., Hiller, M. A., and Powell, J. E., J. Phys. Chem., 66, 311 (1962).

47. Moeller, T., and Hseu, T. M., J. Inorg. Nucl. Chem., 24, 1635 (1962).

48. Karraker, R. H. Stability constants of some rare-earth-metal chelates. Unpublished Ph. D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1961.

49. Harder, R. and Chaberek, S., J. Inorg. Nucl. Chem., 11, 197 (1959).

50. Moeller, T. and Thompson, L. C., J. Inorg. Nucl. Chem., 24, 499 (1962).

51. Thompson, L. C. and Loraas, J. A., Inorg. Chem., 2, 89 (1963).

52. Ballhausen, C. J. Introduction to ligand field theory. New York, New York, McGraw-Hill Book Co., Inc. 1962.

53. Rossotti, F. J. C. and Rossotti, H. The determination of stability constants. New York, New York, McGraw-Hill Book Co., Inc. 1961.

54. Bjerrum, J. Metal ammine formation in aqueous solution. Copenhagen, Denmark, P. Haase and Son. 1941.

55. Randall, W. J., Martin, D. F., and Moeller, T., Proc. Chem. Soc., 340 (1961).

56. Poë, J. A., J. Phys. Chem., 67, 1070 (1963).

57. Fronaeus, S. Komplexsystem hos kopper. Unpublished Ph. D. thesis. Gleerupska Universitets-Bok-handeln, Lund. 1948. Original not available; cited in Rossotti, F. J. C. and Rossotti, H. The determination of stability constants. p. 108. New York, New York, McGraw-Hill Book Co., Inc. 1961.

58. Rossotti, F. J. C. and Rossotti, H., Acta Chem. Scand., 9, 1166 (1955).

59. Sullivan, J. C., Rydberg, J., and Miller, W. F., Acta Chem. Scand., 13, 2023 (1959).

60. Rydberg, J., Acta Chem. Scand., 14, 157 (1960).

61. Chopoorian, J. A., Choppin, G. R., Griffith, H. C., and Chandler, R., *J. Inorg. Nucl. Chem.*, *21*, 21 (1961).

62. Larkins, T. H. and Jones, M. M., *Inorg. Chem.*, *2*, 139 (1963).

63. Gran, G., *Analyst*, *77*, 661 (1952).

64. Fritz, J. S., Abbink, J. E., and Payne, M. A., *Anal. Chem.*, *33*, 1381 (1961).

65. Powell, J. E. and Hiller, M. A., *J. Chem. Ed.*, *34*, 330 (1957).

66. Atkinson, G. and Bauman, J. E., *Inorg. Chem.*, *1*, 900 (1962).

67. Coleman, H. M. and Glattfeld, J. W. E., *J. Am. Chem. Soc.*, *66*, 1183 (1944).

68. Tate, J. F. and Jones, M. M., *J. Inorg. Nucl. Chem.*, *24*, 1010 (1962).

69. Margenau, H. and Murphy, G. M. The mathematics of physics and chemistry. Princeton, New Jersey, D. Van Nostrand Co., Inc. 1957.

70. Calvin, M. and Wilson, K. W., *J. Am. Chem. Soc.*, *67*, 2003 (1945).

71. Schwarzenbach, G., Ackermann, H., and Ruckstuhl, P., *Helv. Chim. Acta*, *32*, 1175 (1949).

72. Duncan, J. F., *Australian J. Chem.*, *12*, 356 (1959).

73. Jones, M. M., *Science*, *121*, 371 (1955).

74. Schwarzenbach, G., *Helv. Chim. Acta*, *35*, 2344 (1952).

75. Moeller, T. and Brantley, J. C., *J. Am. Chem. Soc.*, *72*, 5447 (1950).

76. Holleck, L. and Liebold, G., *Naturwissenschaften*, *44*, 583 (1957).

77. ________ and ________, *Naturwissenschaften*, *44*, 582 (1957).

78. Fritz, J. J., Grenthe, I., Field, P. E., and Fernelius, W. C., *J. Am. Chem. Soc.*, *82*, 6199 (1960).

79. Orgel, L. E. An introduction to transition metal chemistry. New York, New York, John Wiley and Sons, Inc. 1960.

80. Griffith, J. S. The theory of transition-metal ions. Cambridge, England, Cambridge University Press. 1961.

81. Bowers, K. D. and Owen, J., Reports Prog. Physics, **18**, 304 (1955).

82. George, P., McClure, D. S., Griffith, J. S., and Orgel, L. E., J. Chem. Phys., **24**, 1269 (1956).

83. Mackey, J. L., Powell, J. E., and Spedding, F. H., J. Am. Chem. Soc., **84**, 2047 (1962).

84. Staveley, L. A. K. and Randall, T., Disc. Faraday Soc., **26**, 157 (1958).

85. Cobble, J. W., J. Chem. Phys., **21**, 1446 (1953).

86. ________, J. Chem. Phys., **21**, 1451 (1953).

87. Surls, J. P. and Choppin, G. R., J. Am. Chem. Soc., **79**, 855 (1957).

IX. ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. J. E. Powell for his advice and encouragement during the author's graduate career. The relaxed atmosphere which he has developed among his graduate students has done much to make the author's research a pleasant and rewarding experience.

The author would also like to thank his wife, Anne, for her encouragement and moral support during the past year and for her help in preparing this manuscript.

Thanks are also due to Mr. H. R. Burkholder who, with Dr. Powell, prepared one of the reagents used in this research.

X. APPENDIX A: EXPERIMENTAL DATA FOR THE RARE-EARTH ISOBUTYRATES

Buffer solution:	0.500 M sodium isobutyrate 0.5192 M isobutyric acid
Rare-earth solutions:	0.0100 M rare-earth perchlorate 0.0000 M $HClO_4$ except Ce^{+3}
Ce^{+3} solution:	0.0100 M Ce^{+3} 0.0002604 M $HClO_4$
Sample:	20.00 ml. of 0.01 M rare-earth perchlorate plus sufficient sodium perchlorate and water to make 50.00 ml. total volume at an ionic strength of 0.5 M except where otherwise indicated.

Lanthanum	
V_b, ml.	-Log h
0.101	4.579
0.200	4.573
0.300	4.569
0.400	4.567
0.500	4.567
0.600	4.568
0.700	4.570
0.800	4.570
0.900	4.569
1.000	4.570
1.200	4.571
1.400	4.571
1.600	4.572
1.800	4.573
2.000	4.572
2.299	4.579
2.600	4.588
2.998	4.590
3.400	4.593
3.800	4.594
4.200	4.598
4.597	4.600
5.000	4.601

Cerium	
V_b, ml.	-Log h
0.100	4.475
0.200	4.573
0.300	4.529
0.400	4.537
0.500	4.540
0.600	4.545
0.700	4.550
0.800	4.552
0.900	4.554
1.000	4.559
1.199	4.563
1.400	4.568
1.600	4.570
1.800	4.573
2.000	4.578
2.300	4.580
2.600	4.584
2.998	4.589
3.398	4.595
3.799	4.598
4.200	4.600
4.600	4.604
5.010	4.607

Praseodymium	
V_b, ml.	-Log h
0.101	4.526
0.200	4.521
0.300	4.520
0.400	4.520
0.500	4.521
0.700	4.526
0.800	4.529
0.900	4.530
1.000	4.530
1.200	4.535
1.400	4.540
1.600	4.545
1.800	4.547
2.000	4.549
2.200	4.551
2.400	4.554
2.600	4.560
2.800	4.560
3.000	4.563
3.299	4.568
3.600	4.570
4.000	4.573
4.500	4.579
5.001	4.581

Neodymium

V_b, ml.	-Log h
0.101	4.520
0.200	4.510
0.300	4.510
0.400	4.510
0.500	4.510
0.600	4.513
0.700	4.518
0.800	4.521
0.900	4.525
1.000	4.529
1.199	4.534
1.600	4.544
1.800	4.548
2.000	4.551
2.200	4.553
2.400	4.559
2.600	4.560
2.800	4.562
3.000	4.568
3.300	4.570
3.598	4.573
4.000	4.579
4.500	4.578
5.000	4.587

Samarium

V_b, ml.	-Log h
0.100	4.498
0.200	4.497
0.300	4.493
0.400	4.494
0.500	4.497
0.600	4.500
0.700	4.505
0.800	4.505
0.900	4.509
1.000	4.509
1.207	4.515
1.400	4.529
1.600	4.534
1.800	4.537
2.000	4.542
2.200	4.549
2.400	4.551
2.600	4.556
2.800	4.558
3.000	4.560
3.300	4.565
3.600	4.569
4.000	4.574
4.508	4.577
5.000	4.581

Europium

V_b, ml.	-Log h
0.100	4.523
0.202	4.510
0.300	4.511
0.402	4.513
0.500	4.519
0.605	4.521
0.700	4.523
0.800	4.528
0.900	4.531
1.000	4.532
1.200	4.538
1.400	4.541
1.600	4.548
1.800	4.551
2.000	4.557
2.200	4.560
2.400	4.561
2.600	4.567
2.800	4.570
3.000	4.570
3.297	4.577
3.600	4.579
4.000	4.583
4.502	4.589
5.000	4.592

Gadolinium

V_b, ml.	-Log h
0.101	4.543
0.200	4.529
0.300	4.527
0.400	4.521
0.500	4.523
0.599	4.524
0.700	4.526
0.800	4.529
0.900	4.531
1.000	4.532
1.198	4.533
1.400	4.537
1.600	4.540
1.800	4.542
2.200	4.550
2.400	4.552
2.600	4.555
2.800	4.559
3.000	4.560
3.300	4.562
3.600	4.567
4.000	4.571
4.500	4.578
5.000	4.582

Terbium

V_b, ml.	-Log h
0.101	4.545
0.200	4.541
0.300	4.543
0.400	4.545
0.500	4.542
0.600	4.542
0.700	4.544
0.801	4.544
0.905	4.543
1.000	4.549
1.200	4.554
1.400	4.556
1.601	4.559
1.802	4.561
2.000	4.563
2.205	4.565
2.400	4.569
2.600	4.571
2.800	4.572
3.000	4.574
3.300	4.577
3.600	4.581
4.007	4.587
4.500	4.591
5.008	4.595

Dysprosium

V_b, ml.	-Log h
0.100	4.562
0.200	4.557
0.300	4.555
0.402	4.552
0.500	4.552
0.600	4.554
0.701	4.555
0.801	4.553
0.903	4.559
1.000	4.561
1.200	4.561
1.400	4.565
1.598	4.563
1.796	4.567
2.000	4.570
2.200	4.573
2.412	4.576
2.618	4.577
2.800	4.580
3.000	4.582
3.300	4.585
3.598	4.588
3.991	4.590
4.508	4.597
4.996	4.600

Holmium

V_b, ml.	-Log h
0.100	4.569
0.200	4.561
0.300	4.560
0.400	4.562
0.500	4.562
0.600	4.563
0.700	4.565
0.800	4.568
0.900	4.569
1.000	4.570
1.200	4.571
1.400	4.570
1.600	4.574
1.800	4.574
2.003	4.576
2.200	4.579
2.400	4.580
2.600	4.583
2.800	4.587
3.000	4.589
3.300	4.590
3.608	4.592
4.000	4.594
4.500	4.599
4.999	4.600

Erbium

V_b, ml.	-Log h
0.100	4.569
0.200	4.559
0.300	4.561
0.400	4.562
0.500	4.561
0.600	4.561
0.700	4.561
0.800	4.561
0.900	4.562
1.000	4.562
1.200	4.565
1.405	4.568
1.600	4.569
1.803	4.569
2.000	4.572
2.209	4.574
2.400	4.575
2.799	4.579
3.000	4.580
3.300	4.582
3.609	4.585
4,000	4.590
4.500	4.591
5.000	4.595

Thulium

V_b, ml.	-Log h
0.103	4.575
0.200	4.562
0.300	4.559
0.399	4.560
0.501	4.560
0.600	4.560
0.700	4.560
0.800	4.563
0.900	4.565
1.000	4.566
1.100	4.569
1.200	4.570
1.403	4.570
1.597	4.571
1.808	4.573
2.000	4.576
2.210	4.569
2.410	4.580
2.800	4.583
3.000	4.587
3.300	4.589
3.609	4.591
4.000	4.595
4.502	4.599
5.006	4.602

Ytterbium

V_b, ml.	-Log h
0.100	4.553
0.200	4.548
0.301	4.545
0.402	4.547
0.500	4.541
0.600	4.537
0.704	4.540
0.800	4.541
0.900	4.542
1.002	4.542
1.200	4.543
1.405	4.547
1.600	4.550
1.799	4.551
2.001	4.552
2.199	4.554
2.402	4.559
2.608	4.561
2.800	4.568
3.000	4.569
3.300	4.576
3.600	4.571
4.000	4.580
4.506	4.583
4.998	4.588

Lutetium

V_b, ml.	-Log h
0.100	4.557
0.200	4.544
0.300	4.540
0.400	4.542
0.500	4.546
0.600	4.548
0.701	4.550
0.800	4.552
0.900	4.554
1.000	4.555
1.198	4.559
1.401	4.559
1.598	4.562
1.800	4.562
2.004	4.569
2.204	4.570
2.400	4.574
2.600	4.579
2.800	4.580
3.000	4.581
3.300	4.584
3.601	4.589
4.000	4.591
4.498	4.597
5.000	4.600

Yttrium

V_b, ml.	-Log h
0.103	4.583
0.205	4.571
0.308	4.569
0.400	4.570
0.500	4.568
0.608	4.568
0.705	4.568
0.800	4.568
0.900	4.568
1.008	4.568
1.198	4.569
1.400	4.569
1.603	4.570
1.802	4.571
2.000	4.573
2.200	4.576
2.398	4.575
2.600	4.577
2.801	4.579
3.000	4.580
3.309	4.581
3.601	4.584
4.000	4.588
4.500	4.590
5.000	4.591

Dysprosium[a]

V_b, ml.	-Log h
0.101	4.366
0.204	4.352
0.305	4.350
0.405	4.347
0.500	4.347
0.606	4.350
0.706	4.350
0.803	4.351
0.900	4.351
1.008	4.351
1.201	4.355
1.400	4.360
1.601	4.362
1.800	4.368
2.000	4.370
2.200	4.373
2.400	4.380
2.600	4.382
2.800	4.384
3.000	4.390
3.300	4.396
3.600	4.401
4.000	4.408
4.500	4.419
5.000	4.427

Ionization constant[b]

V_b, ml.	-Log h
0.200	4.627
0.400	4.627
0.600	4.622
0.800	4.615
1.000	4.616
1.199	4.624
1.400	4.620
1.599	4.620
1.800	4.622
2.000	4.624
2.200	4.624
2.400	4.627
2.600	4.620
2.800	4.628
3.000	4.630
3.500	4.630
3.998	4.630
4.500	4.631
5.000	4.632

---

[a] This sample contained 1.989 ml. of 0.4768 M $Dy(ClO_4)_3$ plus sufficient sodium perchlorate and water to give 50.00 ml. initial volume at an ionic strength of 0.5.

[b] This titration was performed on 50.00 ml. of 0.5 M sodium perchlorate. No other metal was present.

XI. APPENDIX B: EXPERIMENTAL DATA FOR THE RARE-EARTH α-HYDROXYISOBUTYRATES

Buffer solution: 0.5000 M sodium α-hydroxyisobutyrate
0.5000 M α-hydroxyisobutyric acid

Rare-earth solutions: 0.0100 M rare-earth perchlorate
0.0000 M $HClO_4$ except Ce^{+3}

Ce^{+3} solution: 0.0100 M Ce^{+3}
0.0002604 M $HClO_4$

Sample: 20.00 ml. of 0.01 M rare-earth perchlorate plus sufficient sodium perchlorate and water to make 50.00 ml. total volume at an ionic strength of 0.5 M except where otherwise indicated.

Lanthanum		Cerium		Praseodymium	
V_b, ml.	-Log h	V_b, ml.	-Log h	V_b, ml.	-Log h
0.101	3.709	0.102	3.615	0.100	3.644
0.200	3.652	0.200	3.572	0.203	3.577
0.300	3.641	0.300	3.561	0.300	3.560
0.401	3.638	0.400	3.557	0.400	3.557
0.500	3.635	0.500	3.560	0.500	3.560
0.600	3.622	0.600	3.569	0.600	3.569
0.700	3.638	0.700	3.578	0.700	3.570
0.809	3.628	0.800	3.586	0.800	3.578
0.895	3.626	0.900	3.593	0.900	3.584
1.000	3.630	1.000	3.598	1.000	3.591
1.200	3.641	1.200	3.609	1.200	3.610
1.400	3.649	1.400	3.620	1.400	3.619
1.600	3.655	1.600	3.630	1.600	3.629
1.800	3.660	1.800	3.637	1.800	3.640
2.000	3.665	2.000	3.646	2.000	3.647
2.300	3.672	2.300	3.657	2.300	3.659
2.600	3.678	2.600	3.666	2.600	3.669
3.000	3.689	3.000	3.679	2.999	3.678
3.500	3.693	3.500	3.690	3.500	3.691
4.000	3.699	3.999	3.700	4.000	3.699
4.500	3.706	4.500	3.705	4.500	3.708
5.000	3.710	4.999	3.714	5.000	3.711

Neodymium

V_b, ml.	-Log h
0.100	3.624
0.202	3.552
0.300	3.536
0.400	3.533
0.500	3.537
0.600	3.548
0.700	3.548
0.800	3.559
0.900	3.565
1.000	3.574
1.200	3.589
1.400	3.601
1.600	3.614
1.800	3.627
2.000	3.638
2.300	3.649
2.600	3.660
3.000	3.671
3.500	3.684
4.000	3.697
4.500	3.705
5.000	3.714

Samarium

V_b, ml.	-Log h
0.101	3.559
0.200	3.479
0.300	3.467
0.400	3.466
0.500	3.472
0.500	3.480
0.700	3.490
0.800	3.498
0.900	3.509
1.000	3.518
1.200	3.536
1.400	3.558
1.600	3.574
1.800	3.578
2.000	3.597
2.300	3.608
2.600	3.630
3.000	3.640
3.500	3.655
4.000	3.670
4.499	3.680
5.000	3.693

Europium

V_b, ml.	-Log h
0.105	3.540
0.200	3.466
0.300	3.440
0.400	3.440
0.500	3.444
0.600	3.454
0.700	3.460
0.800	3.471
0.900	3.481
1.000	3.499
1.209	3.521
1.400	3.539
1.600	3.558
1.800	3.572
2.000	3.585
2.200	3.599
2.600	3.621
3.000	3.638
3.500	3.653
4.001	3.664
4.500	3.675
5.000	3.687

Gadolinium

V_b, ml.	-Log h
0.100	3.546
0.201	3.460
0.300	3.433
0.400	3.430
0.500	3.435
0.600	3.443
0.700	3.452
0.801	3.464
0.900	3.474
1.000	3.488
1.200	3.511
1.400	3.531
1.600	3.550
1.800	3.568
2.000	3.583
2.300	3.599
2.600	3.617
3.000	3.634
3.500	3.651
4.000	3.665
4.500	3.671
5.000	3.683

Terbium

V_b, ml.	-Log h
0.100	3.484
0.200	3.394
0.300	3.370
0.400	3.368
0.500	3.368
0.600	3.379
0.700	3.390
0.800	3.404
0.900	3.419
1.000	3.432
1.199	3.460
1.400	3.481
1.600	3.504
1.800	3.523
2.000	3.542
2.300	3.563
2.600	3.582
3.000	3.605
3.500	3.628
4.000	3.644
4.500	3.659
5.000	3.669

Dysprosium

V_b, ml.	-Log h
0.101	3.453
0.200	3.364
0.301	3.337
0.400	3.333
0.500	3.336
0.600	3.344
0.701	3.359
0.800	3.371
0.900	3.390
1.007	3.403
1.203	3.432
1.400	3.459
1.600	3.484
1.800	3.495
2.000	3.524
2.300	3.549
2.600	3.567
3.000	3.590
3.500	3.612
4.000	3.630
4.500	3.645
5.000	3.658

Holmium

V_b, ml.	-Log h
0.102	3.440
0.200	3.342
0.301	3.316
0.400	3.308
0.500	3.311
0.600	3.319
0.700	3.335
0.800	3.352
0.900	3.365
1.000	3.380
1.200	3.405
1.400	3.434
1.600	3.469
1.800	3.489
2.000	3.506
2.300	3.540
2.600	3.561
3.000	3.588
3.500	3.611
4.000	3.630
4.500	3.648
5.000	3.659

Erbium

V_b, ml.	-Log h
0.101	3.418
0.200	3.317
0.300	3.287
0.400	3.278
0.501	3.281
0.600	3.291
0.700	3.308
0.800	3.324
0.902	3.344
1.000	3.360
1.200	3.393
1.400	3.428
1.600	3.456
1.800	3.480
2.000	3.501
2.298	3.530
2.600	3.557
3.000	3.583
3.500	3.610
3.999	3.632
4.500	3.649
5.000	3.660

Thulium

V_b, ml.	-Log h
0.100	3.384
0.200	3.288
0.301	3.252
0.400	3.240
0.500	3.249
0.600	3.264
0.700	3.279
0.800	3.295
0.900	3.311
1.000	3.330
1.200	3.370
1.300	3.400
1.600	3.430
1.800	3.457
2.000	3.480
2.300	3.515
2.600	3.545
3.000	3.576
3.500	3.600
3.998	3.621
4.500	3.644
4.995	3.659

Ytterbium

V_b, ml.	-Log h
0.100	3.365
0.203	3.255
0.300	3.219
0.400	3.210
0.500	3.219
0.600	3.228
0.700	3.249
0.800	3.267
0.900	3.281
1.000	3.307
1.200	3.346
1.400	3.386
1.600	3.418
1.800	3.450
2.000	3.476
2.300	3.500
2.600	3.536
3.000	3.569
3.500	3.598
4.000	3.622
4.500	3.641
5.000	3.656

Lutetium

V_b, ml.	-Log h
0.100	3.358
0.200	3.231
0.300	3.191
0.400	3.180
0.500	3.181
0.600	3.195
0.700	3.217
0.800	3.238
0.900	3.260
1.000	3.280
1.200	3.323
1.400	3.361
1.600	3.397
1.800	3.428
2.000	3.450
2.300	3.490
2.600	3.521
3.000	3.551
3.500	3.589
4.000	3.613
4.500	3.632
5.000	3.649

Yttrium

V_b, ml.	-Log h
0.100	3.475
0.200	3.379
0.300	3.351
0.400	3.346
0.500	3.355
0.600	3.367
0.700	3.380
0.800	3.396
0.900	3.411
1.000	3.430
1.200	3.454
1.400	3.486
1.600	3.510
1.800	3.534
2.000	3.553
2.300	3.579
2.600	3.600
3.000	3.621
3.500	3.641
4.000	3.659
4.500	3.678
5.000	3.690

Dysprosium[a]		Ionization constant[b]	
V_b, ml.	-Log h	V_b, ml.	-Log h
0.100	3.214	0.100	3.878
0.200	3.028	0.203	3.830
0.300	2.935	0.300	3.800
0.400	2.880	0.400	3.787
0.500	2.846	0.500	3.783
0.600	2.820	0.600	3.778
0.700	2.801	0.700	3.775
0.800	2.790	0.800	3.771
0.900	2.782	0.900	3.770
1.000	2.778	1.000	3.771
1.200	2.768	1.200	3.770
1.400	2.771	1.400	3.763
1.600	2.780	1.605	3.767
1.800	2.790	1.800	3.766
2.000	2.802	2.000	3.763
2.300	2.827	2.300	3.763
2.600	2.852	2.600	3.763
3.000	2.890	3.000	3.763
3.500	2.943	3.500	3.763
4.000	2.994	3.996	3.763
4.500	3.046	4.500	3.765
4.997	3.096	5.000	3.767

[a] This sample contained 1.989 ml. of 0.4768 M $Dy(ClO_4)_3$ plus sufficient sodium perchlorate and water to give 50.00 ml. initial volume at an ionic strength of 0.5.

[b] This titration was performed on 50.00 ml. of 0.5 M sodium perchlorate. No other metal was present.

XII. APPENDIX C: EXPERIMENTAL DATA FOR THE RARE-EARTH α,β,β'-TRIHYDROXYISOBUTYRATES

Buffer solution:	0.5000 M sodium α,β,β'-trihydroxyisobutyrate 0.5000 M α,β,β'-trihydroxyisobutyric acid
Rare-earth solutions:	0.0100 M rare-earth perchlorate 0.0000 M $HClO_4$ except Ce^{+3}
Ce^{+3} solution:	0.0100 M Ce^{+3} 0.0002604 M $HClO_4$
Sample:	20.00 ml. of 0.01 M rare-earth perchlorate plus sufficient sodium perchlorate and water to make 50.00 ml. total volume at an ionic strength of 0.5 M except where otherwise indicated.

Lanthanum		Cerium		Praseodymium	
V_b, ml.	-Log h	V_b, ml.	-Log h	V_b, ml.	-Log h
0.100	3.390	0.100	3.289	0.100	3.305
0.200	3.273	0.200	3.180	0.200	3.172
0.300	3.225	0.300	3.140	0.300	3.124
0.400	3.210	0.400	3.119	0.400	3.103
0.500	3.197	0.500	3.110	0.500	3.091
0.798	3.186	0.800	3.109	0.800	3.092
1.100	3.185	1.100	3.119	1.100	3.109
1.400	3.190	1.399	3.131	1.400	3.120
1.700	3.192	1.700	3.142	1.700	3.138
1.999	3.200	1.998	3.152	2.000	3.150
2.300	3.208	2.300	3.161	2.300	3.161
2.600	3.211	2.600	3.170	2.599	3.170
2.900	3.215	2.900	3.178	2.900	3.175
3.304	3.221	3.300	3.184	3.300	3.186
3.599	3.224	3.600	3.190	3.600	3.190
3.909	3.229	3.900	3.193	3.900	3.194
4.201	3.230	4.200	3.197	4.198	3.199
4.500	3.232	4.499	3.200	4.500	3.203
4.750	3.234	4.750	3.202	4.750	3.207
5.000	3.236	5.000	3.205	5.000	3.210

Neodymium

V_b, ml.	-Log h
0.100	3.290
0.200	3.157
0.300	3.104
0.400	3.082
0.505	3.073
0.800	3.080
1.100	3.098
1.400	3.110
1.700	3.138
2.000	3.144
2.300	3.155
2.600	3.167
2.900	3.179
3.300	3.186
3.600	3.190
3.900	3.194
4.200	3.201
4.500	3.209
4.750	3.211
5.000	3.213

Samarium

V_b, ml.	-Log h
0.100	3.269
0.200	3.131
0.300	3.077
0.400	3.045
0.500	3.040
0.800	3.045
1.100	3.069
1.399	3.090
1.700	3.109
2.000	3.123
2.300	3.140
2.600	3.153
2.900	3.165
3.300	3.180
3.600	3.188
3.900	3.193
4.200	3.198
4.500	3.202
4.750	3.209
5.001	3.211

Europium

V_b, ml.	-Log h
0.104	3.277
0.200	3.140
0.302	3.089
0.400	3.064
0.500	3.052
0.799	3.052
1.100	3.073
1.400	3.093
1.700	3.113
2.000	3.130
2.300	3.142
2.600	3.156
2.900	3.167
3.300	3.177
3.606	3.183
3.900	3.190
4.200	3.196
4.500	3.200
4.750	3.204
5.000	3.210

Gadolinium

V_b, ml.	-Log h
0.100	3.310
0.200	3.160
0.300	3.100
0.400	3.072
0.500	3.060
0.799	3.056
1.100	3.069
1.400	3.090
1.698	3.105
2.000	3.124
2.300	3.138
2.600	3.153
2.900	3.164
3.300	3.175
3.600	3.181
3.900	3.190
4.200	3.196
4.500	3.202
4.749	3.208
5.000	3.211

Terbium

V_b, ml.	-Log h
0.104	3.300
0.200	3.162
0.300	3.108
0.400	3.080
0.500	3.068
0.800	3.060
1.100	3.071
1.399	3.089
1.700	3.105
2.000	3.120
2.300	3.131
2.600	3.142
2.900	3.155
3.300	3.168
3.600	3.174
3.900	3.180
4.200	3.187
4.500	3.191
4.750	3.196
5.000	3.200

Dysprosium

V_b, ml.	-Log h
0.101	3.315
0.200	3.178
0.300	3.119
0.400	3.089
0.500	3.073
0.600	3.069
0.700	3.066
0.800	3.067
0.900	3.069
1.000	3.072
1.200	3.083
1.400	3.092
1.610	3.109
1.800	3.118
2.000	3.128
2.200	3.139
2.400	3.145
2.600	3.152
2.800	3.160
3.000	3.164
3.300	3.172
3.600	3.182
3.999	3.191
4.500	3.200
5.000	3.210

Holmium

V_b, ml.	-Log h
0.102	3.300
0.200	3.172
0.301	3.110
0.400	3.084
0.500	3.072
0.800	3.070
1.100	3.087
1.400	3.103
1.700	3.120
2.000	3.132
2.300	3.148
2.600	3.160
2.900	3.168
3.300	3.181
3.600	3.190
3.900	3.197
4.200	3.202
4.500	3.209
4.750	3.213
5.000	3.219

Erbium

V_b, ml.	-Log h
0.100	3.289
0.200	3.157
0.300	3.105
0.400	3.077
0.500	3.068
0.800	3.066
1.100	3.077
1.400	3.095
1.700	3.110
2.000	3.124
2.300	3.130
2.600	3.148
2.900	3.157
3.300	3.170
3.599	3.178
3.900	3.188
4.200	3.190
4.500	3.194
4.750	3.199
5.000	3.201

Thulium

V_b, ml.	-Log h
0.103	3.267
0.200	3.140
0.300	3.083
0.401	3.060
0.500	3.054
0.800	3.057
1.100	3.075
1.400	3.096
1.700	3.113
2.000	3.130
2.300	3.145
2.600	3.154
2.900	3.164
3.299	3.174
3.600	3.183
3.900	3.188
4.200	3.195
4.500	3.200
4.750	3.204
5.000	3.203

Ytterbium

V_b, ml.	-Log h
0.100	3.260
0.200	3.124
0.300	3.073
0.400	3.049
0.500	3.039
0.800	3.048
1.100	3.067
1.400	3.089
1.700	3.109
2.000	3.129
2.300	3.144
2.600	3.158
2.900	3.168
3.300	3.179
3.600	3.188
3.900	3.194
4.200	3.200
4.500	3.206
4.750	3.209
5.003	3.213

Lutetium

V_b, ml.	-Log h
0.100	3.249
0.200	3.108
0.300	3.044
0.400	3.028
0.500	3.015
0.800	3.009
1.100	3.050
1.400	3.072
1.699	3.094
2.000	3.111
2.300	3.128
2.601	3.140
2.900	3.152
3.300	3.160
3.600	3.169
3.900	3.176
4.200	3.181
4.500	3.187
4.750	3.190
5.000	3.193

Yttrium

V_b, ml.	-Log h
0.103	3.318
0.200	3.191
0.300	3.140
0.400	3.112
0.500	3.097
0.800	3.088
1.100	3.100
1.400	3.112
1.700	3.131
2.000	3.143
2.302	3.150
2.600	3.158
2.900	3.167
3.300	3.175
3.600	3.183
3.900	3.189
4.200	3.194
4.500	3.196
4.750	3.200
5.000	3.205

Dysprosium[a]	
V_b, ml.	-Log h
0.100	3.124
0.202	2.917
0.300	2.814
0.400	2.745
0.500	2.700
0.600	2.669
0.700	2.641
0.800	2.628
0.900	2.611
1.000	2.602
1.200	2.590
1.400	2.588
1.600	2.588
1.801	2.590
2.000	2.596
2.300	2.612
2.601	2.627
3.000	2.652
3.500	2.689
4.000	2.726
4.500	2.761
4.748	2.781
5.000	2.800

Ionization constant[b]	
V_b, ml.	-Log h
0.468	3.360
1.003	3.323
1.502	3.317
2.031	3.310
2.584	3.304
3.120	3.304
3.649	3.307
4.075	3.308
4.713	3.304

Dysprosium[c]	
V_b, ml.	-Log h
0.101	3.319
0.208	3.178
0.310	3.121
0.400	3.090
0.501	3.071
0.610	3.067
0.708	3.064
0.800	3.067
0.900	3.067
1.000	3.070
1.200	3.083
1.400	3.091
1.599	3.103
1.804	3.113
1.998	3.123
2.200	3.131
2.400	3.139
2.603	3.148
2.798	3.152
3.000	3.160
3.301	3.169
3.600	3.178
3.997	3.185
4.501	3.193
5.000	3.201

[a] This sample contained 1.989 ml. of 0.4768 M $Dy(ClO_4)_3$ plus sufficient sodium perchlorate and water to give 50.00 ml. initial volume at an ionic strength of 0.5.

[b] This titration was performed on 50.00 ml. of 0.5 M sodium perchlorate. No other metal was present.

[c] This sample contained 20.00 ml. of 0.01 M $Dy(ClO_4)_3$ plus sufficient sodium perchlorate and water to give 50.00 ml. initial volume at an ionic strength of 0.475.