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THE STABILITY CONSTANTS OF SOME CARBOXYLATE COMPLEXES OF THE TRIVALENT LANTHANONS

by

Christopher Duncan Devine

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I. INTRODUCTION

Interest in the chemistry of the rare-earth elements has grown substantially in the last decade. This development was made possible by the availability of large quantities of pure rare-earth compounds. The ion-exchange process developed by Spedding and his co-workers (1, 2) for separating the rare-earth elements from each other is primarily responsible for increasing the availability of spectroscopically pure rare earths. Although every aspect of rare-earth chemistry has received considerable recent attention, the most active field has been the coordination chemistry of the rare-earth ions.

Much of the interest in the coordination chemistry of the rare-earth ions has been stimulated by practical considerations. The ion-exchange separation method and other separation techniques, such as solvent extraction, are based on the differences in complex stability of the ions. Furthermore, the possible applicability of some rare-earth complexes as laser emitters or phosphors has led to study of the optical properties of rare-earth complexes.

Theoretical considerations have also stimulated the study of rare-earth coordination compounds. The remarkable successes achieved in understanding the properties of transition metal complexes have prompted similar approaches to the study of rare-earth complexes. However, important differences exist between the chemical behavior of the transition metal elements and that of the rare-earth elements. The coordination chemistry of the rare-earth elements is still very imperfectly understood. A sizable amount of data has been collected on rare-earth complexes (3); however, no theoretical approach to this subject has thus far been able to provide even a qualitative explanation for all the features of this data.

The coordination chemistry of the rare-earth ions is far more limited in scope than that of the transition metal ions with respect to both the number of complexes which can be prepared and the experimental techniques which can be used to study them. Because of their low charge density, the rare-earth ions form strong complexes with only a few types of ligands: nearly all of the rare-earth complexes studied thus far have been with polydentate ligands which coordinate through oxygen or nitrogen. Furthermore, for all but two of the rare earths, the trivalent state is the only oxidation state stable in aqueous solution. The optical and magnetic properties of the rare-earth ions are almost always independent of the chemical environment; thus, the spectral and magnetic techniques which are so useful in the study of transition metal complexes are of very limited help in the study of rare-earth complexes. As a result, the experimental study of rare-earth complexes has been almost entirely restricted to the acquisition and interpretation of thermodynamic data.

The research reported in this dissertation is an addition to the accurate thermodynamic data available on rare-earth coordination compounds. The complex formation equilibria of the trivalent rare-earth ions and two carboxylate ligands were studied. The ligands were the α-hydroxyisobutyrate (αHIB), and the 2,2-bis(hydroxymethyl)propionate (BHMPA); all the rare-earth elements except promethium, but including yttrium, were considered. The stability constants of all the complexes present in significant concentrations in aqueous solution were measured. The method of competitive reactions, in which complex formation is followed by measuring pH changes, was employed, and a weighted least squares technique was used to calculate the stability constants from the pH data. A constant ionic strength was used in all the measurements so that the stability constants would be independent of activity coefficient variations.

The data presented in this dissertation are of practical value inasmuch as they can be used to evaluate the two ligands as potential complexing agents for use in the ion-exchange separation process. The data are also of theoretical value: consideration of the relationship between the stability constants and such factors as ionic radius or ligand structure reveals important information about the process of complex formation. In this dissertation a model of complex formation is proposed which provides a satisfactory thermodynamic explanation for all the trends observed in the data. This model also provides a means of explaining the general features of the data found by several other workers for similar rare-earth complex systems.

II. THERMODYNAMIC CONSIDERATIONS

A. Conditional Stability Constants

The formation of a carboxylate complex by a trivalent rare-earth ion may be described by the following equation:

$$M^{3+} + nA^{-} = MA_n^{3-n}.$$

Throughout the remainder of this discussion the charges of the ionic species will be ignored, since it its understood that only trivalent rare-earth cations and monovalent carboxylate anions are under consideration.

The thermodynamic stability constant for the above process can be written,

$$*\beta_n = \frac{[MA_n]f_{MA_n}}{[M][A]^n f_M f_A^n},$$

where the brackets denote molar concentrations, and f_i represents the activity coefficient of the ith species. The ratio of concentrations is referred to as the stoichiometric stability constant, β_n. Consequently,

$$*\beta_n = \beta_n \frac{f_{MA_n}}{f_M f_A^n}.$$

For a given system, the thermodynamic stability constant is a function only of temperature; it is directly related to the free energy of complex formation by means of the equation

$$\Delta G = -RT\ln{}^{*}\beta_n. \qquad (1$$

If the activity coefficients are defined with respect to the solute standard state, they will approach one as the concentrations of all the species approach zero. Thus, in the limiting case of the infinitely dilute solution, $^{*}\beta_n$ will equal β_n. At all finite concentrations, the stoichiometric stability constant will be related to the thermodynamic stability constant as follows:

$$\beta_n = {}^{*}\beta_n \frac{f_M f_A^n}{f_{MA_n}} = {}^{*}\beta_n F(f). \qquad (2$$

In most multicomponent systems, such as the ones studied in this research, it is impossible to measure the activities or activity coefficients of all the species present. On the other hand, one can usually determine the molar concentrations of all the species present. Consequently, the stoichiometric stability constant can be obtained experimentally, but one cannot, as a rule, directly obtain the thermodynamic stability constant. This difficulty can be partially overcome if the stoichiometric stability constant is determined from data which have been determined at a constant ionic strength.

The ionic strength, I, is defined by the equation

$$I = \tfrac{1}{2}\Sigma Z_i^2 C_i. \qquad (3$$

The terms Z_i and C_i represent the charge and molar concentration, respectively, of the ith species. The summation is carried out over all the ions present in solution. The concept of ionic strength was introduced by Lewis and Randall (4); they pointed out that the activity coefficient of a given ion is the same in all solutions of identical ionic strength. Debye and Hückel later derived a quantitative relationship between activity coefficients and ionic strength (5); this relationship is usually expressed by the equation

$$\log f_i = \frac{-AZ_i^2 I^{\frac{1}{2}}}{1 + B\mathring{a}I^{\frac{1}{2}}}. \qquad (4$$

The constants A and B depend on the temperature and the properties of the solvent, while å is a property of the individual ion called the ion-size parameter. In principle, the ion-size parameter is the closest distance, in angstroms, that oppositely charged ions approach the ion in question. In practice, the ion-size parameter is usually treated as a semi-empirical constant, since its exact value is difficult to determine in most systems. The above form of the Debye-Hückel equation is valid only for relatively dilute solutions.

Stoichiometric stability constants are normally determined from a wide range of equilibrium constant data. If these data have all been obtained from dilute solutions of identical ionic strength in which equation 4 is presumed valid, all the relevant activity coefficients should have remained constant. A constant ionic strength can be maintained for a series of solutions in which the concentrations of the reactants vary if the appropriate amount of a background electrolyte is added to each solution. The concentration of the background electrolyte can be varied along with the concentration of the reactants so that each solution has the same total ionic strength. With data obtained under these conditions, the term F(f) in equation 2 should be constant; consequently, the value of the stoichiometric stability constant should be a constant for all solutions of the same ionic strength. This type of conditional stability constant obviously has a much wider range of applicability than an ordinary stoichiometric stability constant. Of course, the conditional stability constants are not as valuable as the thermodynamic stability constant; nevertheless, much useful information can be derived from them.

Once conditional stability constants have been measured, one can estimate the values of the corresponding thermodynamic stability constants in a number of ways. First, one can use equation 4, or an extended form thereof, to calculate F(f). In so doing one must estimate the value of the ion-size parameter; this is often difficult to do for complexed ions. Secondly, one can obtain conditional stability constants at several ionic strengths and extrapolate the results to zero ionic strength. At zero ionic strength, F(f) will equal one. Additional methods combine graphical extrapolation with semiempirical estimates of F(f) (6, p. 32).

In the research reported in this dissertation, an ionic strength of 0.100 molar was used throughout. This value is widely used in rare-earth stability constant studies. Both theoretical and practical considerations led to the choice of this value. The Debye-Hückel theory puts an upper limit on the ionic strength that can be used when measuring stability constants. Equation 4 is valid only for dilute solutions and low ionic strengths; it rarely holds for ionic strengths above 0.5 molar. At higher ionic strengths the activity coefficients are no longer independent of concentration. The purpose of using a constant ionic strength is to hold F(f) as nearly constant as possible while the concentrations of the reacting species are varied; this objective cannot be achieved if too high an ionic strength is used.

Other considerations, however, put lower limits on the ionic strength that can be used successfully in stability constant studies. Activity coefficients, even in dilute solution and at constant ionic strength, are not completely independent of the nature of the ionic medium. If in a series of solutions of identical ionic strength the concentrations of some of the components vary substantially, the ionic medium will not be constant and the activity coefficients will not remain strictly constant even if the usual conditions of equation 4 are satisfied. In terms of the

Debye-Hückel theory, this effect may be attributed to changes in the value of the ion-size parameter. The same effect can also be accounted for by means of Harned's theory of ionic interactions (7, 8). It will be shown later that for the systems studied in this research, the only major concentration differences in a given series of solutions are in the values of [A], the free ligand concentration, and in $[ClO_4^-]$, the concentration of background electrolyte anion. Harned's equation can provide a quantitative relationship between these concentration changes and the activity coefficient changes which result therefrom. This equation will be discussed in detail in connection with acid dissociation constants in the next section. For the present it is sufficient to state Harned's equation in the following form:

$$\Delta \log f_A = \frac{C\Delta[A]}{I}, \qquad (5$$

where $\Delta \log f_A$ is the difference in $\log f_A$ for two solutions of the same ionic strength which differ in free ligand concentration by $\Delta[A]$. The constant C depends upon the ionic strength and the specific electrolytes under study. It can be seen from this equation that $\Delta \log f_A$ may be rendered almost negligible if the ionic strength is several orders of magnitude greater than the values of free ligand concentration. This fact suggests using as large a value of ionic strength as is consistent with the validity of equation 4.

On the other hand, the values of [A] cannot be too small, since sufficient ligand and metal ion must be present to produce an easily measurable change in some solution property when complex formation takes place.

An ionic strength of 0.100 molar is the best compromise between the factors mentioned above. One can reasonably assume that equation 4 holds at this ionic strength, and at the same time one can vary the ligand concentration over a fairly wide range without substantially changing the concentration of the background electrolyte.

Sodium perchlorate was used as the background electrolyte. This salt has been widely used as a background electrolyte in stability constant studies. It is assumed that neither the sodium ion nor the perchlorate ion can form complexes with any of the other species present under the experimental conditions employed in this research.

B. Acid Dissociation Constants

The method used in this research to determine the stability constants of the rare-earth carboxylate complexes required a precise knowledge of the dissociation constants of the related carboxylic acids. Therefore, it was necessary to determine the dissociation constants of α-hydroxyisobutyric acid and 2,2-bis(hydroxymethyl)propionic acid to a high degree of accuracy under the same conditions used in the study of the carboxylate complexes.

The dissociation equilibrium of a carboxylic acid can be described as follows:

$$HA = H^{+} + A^{-},$$

where HA represents the undissociated acid, H^{+} the hydrogen ion, and A^{-} the carboxylate anion. Throughout the remainder of this discussion the charges on the hydrogen ion and the carboxylate ion will be presumed understood. The thermodynamic dissociation constant $^{*}K_a$ is defined by the equation,

$$^{*}K_a = \frac{[H][A]f_H f_A}{[HA]f_{HA}}.$$

The stoichiometric dissociation constant K_a is therefore given by the equations,

$$K_a = \frac{[H][A]}{[HA]},$$

or

$$K_a = {^{*}K_a}\frac{f_{HA}}{f_H f_A}. \qquad (6$$

Essentially the same thermodynamic considerations apply to acid dissociation constants as apply to complex-ion stability constants. The thermodynamic dissociation constants cannot be obtained directly, although stoichiometric dissociation constants can easily be measured. According to the Debye-Hückel theory, the value of K_a will, to a first approximation, be constant for all dilute solutions of the same ionic strength. According to Harned's theory of ionic interactions, if the composition of the ionic medium changes substantially, the value of K_a will vary slightly with concentration even when the ionic strength remains constant.

The same ionic strength (0.1000 molar) was used in determining the acid dissociation constants as was used in studying the rare-earth complexes. Moreover, the K_a values were measured over approximately the same range of carboxylate ion concentrations employed in studying the complexes. With both acids it was found that the value of K_a decreased slightly as the concentration of ligand increased. Dr. J. E. Powell and co-workers have noted the same phenomenon while studying several other carboxylic acids under the same conditions as used in this research (9, 10). The same effect was also studied by Ellilä (11) who found that the acid dissociation constant of acetic acid depended upon the nature and concentration of the background electrolyte even in solutions of identical ionic strength. Similar behavior has also been noted by Kilpatrick (12).

For both acids studied in this research, the variation in K_a with $[A]$ was found to be linear. By means of an ordinary least squares calculation, to be described later, the following equations were obtained: for α-hydroxyisobutyric acid

$$K_a = 1.630 \times 10^{-4} - 1.497 \times 10^{-4}[A], \qquad (7$$

and for 2,2-bis(hydroxymethyl)propionic acid

$$Ka = 3.689 \times 10^{-5} - 3.803 \times 10^{-5}[A]. \qquad (8$$

Over the range of ligand concentrations studied, the value of K_a for α-hydroxyisobutyric acid varied from 1.616×10^{-4} to 1.583×10^{-4}, while K_a for 2,2-bis(hydroxymethyl)propionic acid varied from 3.678×10^{-5} to 3.593×10^{-5}.

For many purposes the slight variation in K_a with changes in [A] could be ignored. However, Powell and Rowlands (9) showed that this variation should be taken into account in the calculation of rare-earth complex stability constants. The use of a variable K_a in their calculations resulted in lower standard deviations and improved consistency in their results. Consequently, a variable K_a was used in calculating the stability constants reported in this dissertation.

The form of equations 7 and 8 can be rationalized by means of Harned's theory of ionic interactions. From equation 6 it can be seen that the variation in K_a must be due to variations in one or more of the three activity coefficients f_H, f_A, and f_{HA}.

The undissociated acid is a nonionic species; therefore f_{HA} should be independent of changes in the ionic composition of the solution and should remain constant over the conditions under consideration.

According to Harned's approach, small variations in f_H and f_A can be expected when the concentrations of some of the components change significantly over the range of solutions under consideration. Harned's rule predicts that f_H will change as the background electrolyte cation is replaced by hydrogen ions. However, in all the solutions studied, the concentration of sodium ion remained constant at 0.0999 molar. Although the solutions contained different amounts of $NaClO_4$ and NaA, the total ionic strength remained constant and so did the sodium ion concentration. Furthermore, the variation in hydrogen ion concentration was very small over the series of solutions studied, e.g. 1.296×10^{-4} to 1.495×10^{-4} in the case of 2,2-bis(hydroxymethyl)propionic acid. Consequently, variations in f_H can also be ruled out as the cause of the variation in K_a.

According to Harned's rule, f_A will vary as the background electrolyte anion is replaced by the carboxylate anion. In the data collected for 2,2-bis(hydroxymethyl)propionic acid, $[A]$ varied from 1.63×10^{-3} to 2.51×10^{-2}, while $[ClO_4^-]$ varied from 9.84×10^{-2} to 7.48×10^{-2}. These concentration changes are significant, and one can attribute the variation in K_a to changes in f_A which result as the relative amounts of carboxylate ion and perchlorate ion are altered. Equation 5, Harned's rule, may be applied to this concentration data to obtain a quantitative relation between K_a and $[A]$.

For the systems under consideration, the term $*K_af_{HA}/f_H$ in equation 6 should be constant; if this constant is designated $*K_a'$, the equation may be rewritten

$$K_a = *K_a'/f_A,$$

or

$$\log K_a = \log *K_a' - \log f_A.$$

If the values of K_a at two different ligand concentrations, $[A]_1$ and $[A]_2$, are compared,

$$\log K_a(2) - \log K_a(1) = -[\log f_A(2) - \log f_A(1)].$$

Letting $[A]_1$ equal zero and letting $[A]_2$ equal any finite ligand concentration, Harned's rule can be introduced into the above equation to give

$$\log K_a(i) - \log K_a(0) = -C[A]_i/I.$$

The value of K_a at zero ligand concentration and a specific ionic strength I will be constant and can be defined as $*K_a''$. The above equation can then be rewritten

$$\log K_a(i) = \log *K_a'' - C[A]_i/I,$$

or

$$K_a(i) = *K_a''10^{-C[A]i/I}.$$

From the series expansion of $10^{-C[A]i/I}$ one can write

$$10^{-C[A]_i/I} = 1 - 2.3C[A]_i/I$$

for systems of constant ionic strength. Since $[A]_i$ is always much larger than $[A]_i^2$, the higher terms in the expansion can be ignored. Consequently,

$$K_a(i) = {}^*K_a'' - 2.3C{}^*K_a''[A]_i/I,$$

or

$$K_a(i) = a - b[A]_i, \qquad (9$$

where $b = (2.3C/I)a$.

Approximately the same range of ligand concentrations was used in the study of the rare-earth complex stability constants as was used in the study of the acid dissociation constants. Since the activity coefficient of one of the species was not held strictly constant during the measurement of the acid dissociation constant, one must conclude that during the measurement of the stability constants one or more of the activity coefficients were not held strictly constant either. As a result, the stability constant values should vary slightly over the range of ligand concentrations employed. Unfortunately, because of the computational difficulties involved, the functional dependence of β_n on $[A]$ cannot be determined. Nevertheless, the variation in β_n with increasing $[A]$ should be relatively small, and the stability constant values presented in this dissertation can be considered to be the average values over the ligand concentration range employed. The first three significant figures in β_n are probably independent of ligand concentration effects; hence, the variations in β_n caused by slight variations in activity coefficients are probably within the experimental error in this quantity.

III. EXPERIMENTAL METHOD

A. The Method of Competitive Reactions

The experimental method used in this research is an example of the method of competitive reactions. In this method a reaction competes for the ligand with the complex formation reactions. Such a procedure is ideally suited for the study of carboxylate complexes, since the dissociation equilibrium of the acid can be used as the competing reaction. If a partially neutralized solution of a carboxylic acid is added to a solution containing a trivalent rare-earth ion, the following equilibria are established:

$$\begin{aligned} H + A &= HA, \\ M + A &= MA, \\ MA + A &= MA_2, \\ &\ldots\ldots\ldots\ldots\ldots, \\ MA_{N-1} + A &= MA_N, \end{aligned}$$

where N represents the maximum number of ligands that the metal ion will accept. The first equilibrium in this set is governed by the acid dissociation constant, while the other equilibria are governed by the step formation constants. The step formation constant of the complex MA_n is defined as follows:

$$K_n = \frac{[MA_n]}{[MA_{n-1}][A]}.$$

These constants are directly related to the stoichiometric stability constants by means of the equation

$$\beta_n = \prod_{i=0}^{n} K_i. \qquad (10$$

In systems where the competing equilibria described above are present, the formation of complex species will obviously affect the hydrogen ion concentration. Since hydrogen ion concentrations can be measured very accurately with a pH meter, the extent of complex formation can be determined by observing pH changes.

B. Preparation of Sample Solutions

1. Stability constant measurements

Twenty sample solutions were prepared for each rare-earth carboxylate system studied. The samples were prepared in one hundred milliliter volumetric flasks. Four milliliters of a 0.1000 molar rare-earth perchlorate solution were added to each flask, along with from one to twenty-five milliliters of carboxylate buffer solution. The buffer solutions were approximately 0.1000 molar in the undissociated acid and 0.1000 molar in the sodium salt of the acid. The amount of $NaClO_4$ stock solution needed to bring the final solution to an ionic strength of 0.1000 molar was added, and the flask was brought to the mark with distilled water while suspended in a constant temperature bath set at 25.00° C.

The total metal ion concentration in each sample was 4×10^{-3} molar, while the total ligand concentration varied from 1×10^{-3} to 2.5×10^{-2} molar. The pH of the samples was in the range of three to four pH units, depending upon the particular rare-earth ion and ligand present and upon the amount of buffer solution that had been added to the sample.

The volume of sodium perchlorate stock solution needed to bring the ionic strength of each sample to 0.1000 molar must be estimated for each system studied. These estimates are based on the amounts which had been found necessary in the study of the complexes formed by the same ligand with another rare-earth ion. The computer program used to calculate the stability constants was also used to calculate $V_{sp}(i)$, the volume of sodium perchlorate stock solution that should have been added to each sample solution to achieve the desired ionic strength. These calculated values were used to check the original estimates and to estimate the values of $V_{sp}(i)$ needed for the next rare-earth complex system to be studied. If the calculated values of $V_{sp}(i)$ were significantly different from the original estimates, the measurements were repeated on new sample solutions which contained the correct amounts of sodium perchlorate.

As a rule, the rare-earth complexes of a given ligand are studied in sequence, beginning with lanthanum and concluding with lutetium. Once data have been collected for the first few members of the rare-earth series, one can note the average changes in V_{sp} for each sample upon going from one rare-earth ion to the next. These average increments can then be added to the calculated values of V_{sp} found for the previous rare-earth complex system to improve the estimates of V_{sp} for the next metal complex system in the series.

In order to estimate the values of V_{sp} needed in the study of the lanthanum complexes of a new ligand, one can only make rough guesses based on the values of V_{sp} found for solutions containing the lanthanum complexes of a similar ligand. Such guesses are usually quite inaccurate. However, once the first series of solutions containing the new ligand have been measured, the calculated values of V_{sp} for this set of solutions can be used in preparing a second set containing the correct amount of background electrolyte.

The equations used in the computer program to calculate the values of V_{sp} will be discussed in the next chapter.

2. Dissociation constant measurements

The sample solutions used in measuring the carboxylic acid dissociation constants were prepared in exactly the same way as the sample solutions described above, except that no rare-earth perchlorate solution was added to the flasks. The volume of sodium perchlorate needed to bring each sample to an ionic strength of 0.1000 molar was calculated directly from equation 3 using an approximate value of the acid dissociation constant under study.

C. pH Measurements

The pH of the sample solutions was measured with a Beckman model 1019 pH meter. The pH meter was equipped with a Beckman general purpose glass electrode and a Beckman frit-junction silver-silver chloride reference electrode. This instrument is capable of measuring the pH of a solution with an accuracy of ±0.001 pH unit and a repeatability of ±0.0005 pH unit. All measurements were made in a constant temperature bath kept at $25.00 \pm .05^{\circ}$ C.

A number of difficulties were encountered in the operation of the pH meter. Many sets of data had to be discarded when a poorly functioning pH meter or electrode resulted in data below the desired level of accuracy.

The main problems probably resulted from surface adsorption effects at the tip of the glass electrode, since it was found that the glass electrode was quite sensitive to changes in its ionic environment. When the electrodes were removed from the standard solution and placed in a sample solution containing rare-earth ions, a wait of fifteen minutes was necessary before a steady pH reading could be obtained. Furthermore, if the electrodes were washed with distilled water after each measurement, a similar time lapse was found necessary before a steady reading could be obtained with the next sample solution. In order to overcome these difficulties, a rather tedious procedure was developed for standardizing the pH meter and measuring the samples. By means of this procedure, sudden changes in the ionic environment of the electrodes were avoided.

The pH meter was standardized against a hydrochloric acid solution of known concentration. The pH of the standard was close to the pH range of the subsequent measurements, and the standards had the same ionic strength as the sample solutions. The electrodes were soaked in a portion of the standard for at least an hour before standardization was begun. After internal calibration of the pH meter against a Weston cell, the electrodes were placed in a fresh sample of the standard. The pH meter was standardized with respect to the first sample, and the standardization was repeated on new portions of the standard solution until three successive readings were in exact agreement. The electrodes were allowed to soak for five minutes in each new portion of the standard before standardization was attempted.

Once the pH meter had been standardized, the pH readings were made in a similar fashion. Each sample solution was divided into three portions. The first portion was used to rinse the electrodes, which were then soaked in the second portion for three minutes. The reading was taken on the third portion. By use of this method, it was no longer necessary to rinse the electrodes with distilled water between readings to remove contaminants from the preceding solution.

Since a concentration standard rather than an activity standard was employed, the pH meter read the hydrogen ion concentration directly.

D. Preparation of Reagents

1. Standard sodium hydroxide solutions

Sodium hydroxide solutions of approximately one molar and one tenth molar concentrations were used in this research.

A 0.1082 ± 0.0002 molar stock solution had been prepared by Y. Suzuki using the method of Powell and Hiller (13). This solution was restandardized periodically against potassium acid phthalate. This solution was used to titrate the buffer solutions and to standardize the hydrochloric acid solutions used as pH standards.

The one molar stock solutions were used in preparing the carboxylate buffer solutions. Two methods were used in preparing these solutions. In the earlier stages of this research, the solutions were prepared by the barium chloride method of Vogel (14, p. 239). A saturated solution of NaOH was prepared from reagent grade NaOH pellets. Any insoluble material was filtered off, and then $BaCl_2$ was added to precipitate any carbonate ion present in the solution. After filtration, the excess barium ion was removed by passing the solution through an ion-exchange column containing Dowex-50 resin in the sodium form. During this process, several precautions were taken to prevent contact of the solution with carbon dioxide from the atmosphere. The resulting carbonate-free solution was diluted with freshly boiled distilled water and then standardized against potassium acid phthalate.

In the latter stages of this research, one molar NaOH stock solutions were prepared from carbonate-free NaOH ampules obtained from the Anachemia Chemical Co., Montreal, Canada. These solutions were also standardized against potassium acid phthalate.

2. pH standards

An approximately 0.0200 molar hydrochloric acid solution was prepared and standardized several times against standard sodium hydroxide solution. Ten milliliter aliquots of this solution were used to prepare two liters of standard solution. The pH of the standards was thus approximately four. The standard solutions were brought to an ionic strength of 0.1000 molar by the addition of the appropriate amount of sodium perchlorate stock solution. The pH of the first standard was taken to be that calculated from the stoichiometric concentration of hydrochloric acid in the stock solution. Subsequently prepared standards were checked potentiometrically against the first standard and against each other to insure mutual consistency.

3. Rare-earth perchlorate solutions

Rare-earth perchlorate stock solutions of 0.1000 molar concentration were prepared by dilution from approximately 0.5000 molar stock solutions that had been prepared by W. R. Stagg. The details of the preparation and standardization of Stagg's solutions are given in his doctoral dissertation (15). The concentration of the 0.1000 molar rare-earth perchlorate solutions was checked by EDTA titration using arsenazo as an indicator. In each case, the concentration was found to be 0.1000 ± 0.0005 molar. Deviations of ± 0.0005 are within the experimental error of the EDTA titration method. Thus, it was assumed that Stagg's solutions had been accurately standardized and that no significant error was introduced by diluting them to 0.1000 molar.

4. Sodium perchlorate solutions

Sodium perchlorate stock solutions were prepared from anhydrous $NaClO_4$ obtained from the G. Frederick Smith Co.. The reagent as obtained from the manufacturer contained a substantial amount of impurities and required extensive purification. In order to remove the insoluble material, a nearly saturated solution was prepared and filtered several times through two thicknesses of Schleicher and Schuell blue ribbon grade filter paper. In order to remove any cationic contaminants, the solution was then passed through an ion-exchange column containing Dowex-50 resin in the sodium form. The $NaClO_4$ solution was diluted to approximately one molar and standardized by an ion-exchange method. In this case a column containing Dowex-50 resin in the hydrogen form was used. Aliquots of the $NaClO_4$ solution were eluted through the column, and the perchloric acid liberated was titrated with standard NaOH solution. This method gives the molarity of the solution with a reproducibility of ± 0.001.

5. α-Hydroxyisobutyric acid buffer solution

Crystalline α-hydroxyisobutyric acid was obtained from the Aldrich Chemical Co., Milwaukee, Wisconsin. After recrystallization from carbon tetrachloride, the acid was found by titration to be in excess of 99.5% pure.

Two liters of a half-neutralized buffer solution were prepared by weighing out four tenths of a mole of the acid, adding two tenths of a mole of the one molar NaOH solution, and diluting with distilled water, The resulting solution was 0.1000 ± 0.0002 molar in the sodium salt of the acid and approximately 0.1000 molar in the unneutalized acid. The exact concentration of the unneutralized acid was determined by titration with standard base.

6. 2,2-Bis(hydroxymethyl)propionic acid buffer solution

The 2,2-bis(hydroxymethyl)propionic acid was also obtained from the Aldrich Chemical Co.. In order to purify the acid it was dissolved in warm methanol and then reprecipitated by the addition of carbon tetrachloride. After one recrystallization the purity of the acid was found by titration to be in excess of 99.5%.

A half-neutralized buffer solution of this acid was prepared in the same way the α-hydroxyisobutyrate buffer was prepared.

IV. MATHEMATICAL METHOD

A. Preliminary Calculations

1. Acid dissociation constants

The previous chapter described the preparation of the sample solutions used in the determination of the acid dissociation constants. The pH readings and stoichiometric data on these solutions were used to calculate K_a, the acid dissociation constant, for each sample solution. Equations 7 and 8, which relate the changes in K_a to changes in the free ligand concentration $[A]$, were then obtained by a simple least squares computation.

The relevant experimental quantities are defined as follows:

V_t = total volume of each sample,

$V_b(i)$ = volume of buffer solution added to the ith sample,

C_{HA} = concentration of unneutralized acid in the buffer solution,

C_A = concentration of carboxylate anion in buffer solution,

$V_{sp}(i)$ = volume of $NaClO_4$ stock solution added to the ith sample,

C_{sp} = concentration of $NaClO_4$ stock solution,

pH(i) = pH of the ith sample solution.

The hydrogen ion concentration of each solution was calculated from the pH of the sample by means of the equation

$$[H]_i = 10^{-pH(i)}. \qquad (11$$

The concentration of undissociated acid in each sample, $[HA]_i$, and the concentration of free carboxylate ion in each sample, $[A]_i$, were calculated by means of the equations

$$[HA]_i = \frac{Vb(i)C_{HA}}{Vt} - [H]_i, \qquad (12$$

and

$$[A]_i = \frac{Vb(i)C_A}{Vt} + [H]_i. \qquad (13$$

The values of $K_a(i)$ were then calculated by the equation

$$K_a(i) = \frac{[H]_i[A]_i}{[HA]_i}. \qquad (14$$

The relation between $K_a(i)$ and $[A]_i$, as expressed by equation 9, was found by a simple least squares treatment of the I sets of concentration data. The y intercept (a) and slope (-b) in equation 9 were thus found from the formulas

$$a = \frac{\sum_i^I K_a(i) \sum_i^I [A]_i^2 - \sum_i^I (K_a(i)[A]_i) \sum_i^I [A]_i}{I\sum_i^I [A]_i^2 - (\sum_i^I [A]_i)^2},$$

and

$$-b = \frac{I\sum_{i}^{I}(K_a(i)[A]_i) - \sum_{i}^{I}K_a(i)\sum_{i}^{I}[A]_i}{I\sum_{i}^{I}[A]_i^2 - (\sum_{i}^{I}[A]_i)^2}.$$

In order to determine whether the correct amount of $NaClO_4$ stock solution had been added to each sample, the exact amount of $NaClO_4$ needed to achieve the desired ionic strength was calculated from the equation

$$V_{sp}(i) = \frac{I - [A]_i}{C_{sp}V_t}.$$

The calculated values of $V_{sp}(i)$ were then compared with the original estimates.

The mutual consistency of the experimental data can be checked by recalculating each value of $K_a(i)$ from equation 9 and comparing this value with the value obtained from equation 14. If the percentage difference between these two values exceeds one percent for a given set of concentration data, that set can be dropped from consideration, and a new, more precise, least squares calculation made with the remaining data.

2. Free ligand concentration and ligand number

Prior to the calculation of the stability constants, the pH readings and stoichiometric data on the sample solutions containing rare-earth complexes were used in several necessary preliminary calculations. In particular, the concentrations of the various species, other than complexes, present in the solutions, especially the free ligand concentration, were calculated. The mean ligand number for each sample solution was also calculated.

In addition to the quantities introduced in the previous section, the following terms must be defined.

$V_M(i)$ = volume of rare-earth perchlorate stock solution added to the ith sample.

C_M = concentration of rare-earth perchlorate stock solution.

$Z(i)$ = total concentration of rare-earth ion, either free or complexed, in the ith sample solution.

C_{MH} = concentration of perchloric acid in cerous perchlorate stock solution.

$[HClO_4]_i$ = concentration of perchloric acid in the ith sample solution due to the presence of cerous perchlorate.

$Y(i)$ = total concentration of ligand, either free or complexed, in the ith sample solution.

As in the case of the acid dissociation constants, the values of $[H]_i$ and $[HA]_i$ were calculated from equations 11 and 12. These two concentrations can then be used to calculate $[A]_i$ from the value of $K_a(i)$. However, since $K_a(i)$ in turn depends on $[A]_i$, an iterative process must be used. The value of $[A]_i$ was initially approximated by $Y(i)$. The value of $Y(i)$ was readily calculated by means of the equation

$$Y(i) = [H]_i + \frac{Vb(i)C_A}{Vt}.$$

Equation 9 was then used to calculate an approximate set of $K_a(i)$ values using $Y(i)$ as an approximation for $[A]_i$. A better approximation of $[A]_i$ was found from the first approximations of $K_a(i)$ by means of the equation

$$[A]_i = \frac{K_a(i)[HA]_i}{[H]_i}.$$

This second approximation of $[A]_i$ was then substituted into equation 9 to obtain a second approximation of $K_a(i)$. The cycle of calculations was repeated until convergence was obtained. In practice, convergence was obtained after only three iterations. The iterative process was easily incorporated into the computer program used for calculating the stability constants.

Some complications arose in the study of the cerous complexes: the cerous perchlorate stock solution contained a small amount of perchloric acid in order to retard the oxidation of the cerous ion. The presence of this acid had to be taken into account in the calculation of $[HA]_i$ and $Y(i)$ for these solutions. The concentration of perchloric acid present in each sample containing cerous complexes was calculated from the equation

$$[HClO_4]_i = \frac{V_M(i)C_{MH}}{V_t}.$$

Instead of equation 12, the following equation was used to calculate the concentration of unneutralized acid:

$$[HA]_i = \frac{V_b(i)C_{HA}}{V_t} + [HClO_4]_i - [H]_i.$$

Also, the value of Y(i) was calculated from the equation

$$Y(i) = \frac{V_b(i)C_A}{V_t} - [HClO_4]_i + [H]_i.$$

The concept of mean ligand number was introduced by Bjerrum (16); it is defined as the average number of ligands bound to each metal ion in a mixture of complexes. The quantity $Y(i) - [A]_i$ equals the concentration of ligands bound to metal ions; thus the ligand number, $\bar{n}$, will be given by the equation

$$\bar{n} = \frac{Y(i) - [A]_i}{Z(i)}. \qquad (15$$

A plot of $\bar{n}$ _versus_ [A] is often used to determine N, the maximum number of ligands that the metal ion will accept. The value of $\bar{n}$ approaches N asymptotically as [A] increases.

The ligand number is directly related to the complex-ion stability constants. In general,

$$Y - [A] = [MA] + 2[MA_2] + \dots + N[MA_N],$$

and

$$Z = [M] + [MA] + [MA_2] + \ldots + [MA_N],$$

hence

$$\bar{n} = \frac{\sum_{n=0}^{N} n\beta_n[A]^n}{\sum_{n=0}^{N} \beta_n[A]^n}. \qquad (16$$

In the above equation, the quantity β_0, although physically meaningless, has been set equal to one for the sake of notational convenience. Equations 15 and 16 are the starting points of most methods of calculating complex ion stability constants.

B. Calculation of Stability Constants

The methods that have been used to calculate the stability constants of rare-earth carboxylate complexes can be divided into three categories: successive approximation methods, graphical integration techniques, and least squares computations. Although a least squares method was used in this research, for purposes of comparison the basic concepts of the other two methods will be briefly discussed.

An example of a successive approximation method is Bjerrum's method (16). In this case the values of the step formation constants, K_n for n from one to N, are calculated from $\bar{n}$ and [A] data. In order to begin the calculations, one must make crude estimates of the values of K_n. Equation 16 is then solved for each value of K_n using the $\bar{n}$ and $[A]$ data and the estimates of the other step formation constants. Thus for n = t, the appropriate equation has the form

$$K_t = \frac{\sum_{n=0}^{n=t-1} (\bar{n} - n)\beta_n[A]^n}{[A]\sum_{n=t}^{n=N} (n - \bar{n})\beta_n[A]^{n-1}K_t^{-1}}. \qquad (17$$

The values of K_n resulting from these calculations are a better approximation of the true values than the first estimates; they can be used as the estimates in a second set of calculations of the same type. The process is repeated until no significant difference is obtained in the results of successive calculations.

The major disadvantages of Bjerrum's method are the limits placed on the data used to calculate each K_n. One cannot use data for which $\bar{n}$ is greater than n, or data for which $\bar{n}$ is very close to n, because the term $(n - \bar{n})$ appears in the denominator of equation 17. Consequently, K_1 is calculated from the data for which $\bar{n}$ is between the limits of 0.3 and 0.7, K_2 is calculated from data for which $\bar{n}$ has the limits 1.3 and 1.7, and similarly for the higher constants. A value of K_n is calculated from each $\bar{n}$ and $[A]$ data set in the appropriate range, and the results are averaged.

Two other similar successive approximation methods are those of Poë (17) and of Rossotti (18).

The Fronaeus method (19) is an example of a graphical integration technique. This method is based on the observation that equation 16 can be rewritten,

$$\bar{n} = \frac{[A]F'}{F}, \tag{18}$$

where

$$F = \sum_{n=0}^{N} \beta_n [A]^n,$$

and

$$F' = dF/d[A].$$

Equation 18 can be integrated to give

$$\ln F(i) = \int_0^{[A]_i} (\bar{n}/[A])d[A],$$

where the lower limits of integration are taken as $[A] = 0$ and $F = 1$, and the upper limits are taken as $[A] = [A]_i$ and $F = F(i)$. One can calculate the value of $F(i)$ for each set of data $(\bar{n},[A])$ using graphical integration. A new function F^1 is defined by the equation

$$F^1 = \frac{F - 1}{[A]} = \beta_1 + \beta_2[A] + \ldots + \beta_N[A]^{N-1}.$$

A set of $F^1(i)$ values can be calculated from the values of $F(i)$ and $[A]_i$; when $F^1(i)$ is plotted against $[A]_i$ the intercept will be β_1. The same procedure is continued to find the remaining stability constants. In general, the function F^n is defined as follows:

$$F^n = \frac{F^{n-1} - \beta_{n-1}}{[A]} = \beta_n + \beta_{n+1}[A] + \ldots + \beta_N[A]^{N-n}.$$

A plot of $F^n(i)$ <u>versus</u> $[A]_i$ will have an intercept equal to β_n.

A disadvantage of the Fronaeus method is the tendency to prejudice the data by smoothing the curves in both the graphical integration and extrapolation steps. Errors will tend to accumulate, since each β_n is calculated from its predecessors.

The least squares method used in this research is based on the method of Sullivan, Rydberg, and Miller (20). This method was first adapted to the calculation of rare-earth carboxylate complex stability constants by Stagg and Powell (21). The method has been further modified by Powell and several of his co-workers.

Equations 15 and 16 are the mathematical starting point of the least squares method. For the sake of notational convenience, the free ligand concentration, hitherto designated $[A]$, will be represented by the symbol X. If equation 15 is set equal to equation 16, the following relation may be derived:

$$\sum_{n=0}^{N} (Y - X - nZ)\beta_n X^n = 0.$$

The residual for a given set of data (X(i),Y(i),Z(i)) will therefore be given by the equation

$$U(i) = \sum_{n=0}^{N} (Y(i) - X(i) - nZ(i))\beta_n X(i)^n. \qquad (19$$

In applying the method of least squares, one minimizes the sum of the squares of the residuals with respect to the desired parameters. If the errors in the data are not of uniform magnitude over the range of measurements under consideration, a weighting factor is introduced: this factor weights the data with the smaller errors more heavily than the data with the larger errors. Hence, the sum to be minimized is written,

$$S = \sum_{i=1}^{I} W(i)U(i)^2, \qquad (20$$

where W(i) is the weighting factor for the ith data set and I is the total number of data sets (X(i),Y(i),Z(i)). When S is minimized with respect to the parameters, N equations of the form

$$\frac{dS}{d\beta_n} = 2\sum_{j=0}^{N}\Big[\sum_{i=1}^{I} W(i)(Y(i) - X(i) - nZ(i)) \\ (Y(i) - X(i) - jZ(i))\beta_j X(i)^{n+j}\Big]$$

are obtained. These N equations are set equal to zero and solved simultaneously using matrix algebra.

Each of the N equations has the form

$$P(n) + R(n,1)\beta_1 + R(n,2)\beta_2 + \ldots + R(n,N)\beta_N = 0,$$

where

$$P(n) = \sum_{i=1}^{I} W(i)(Y(i) - X(i))(Y(i) - X(i) - nZ(i))X(i)^n, \quad (21$$

and

$$R(n,j) = \sum_{i=1}^{I} W(i)(Y(i) - X(i) - nZ(i)) (Y(i) - X(i) - jZ(i))X(i)^{n+j}. \quad (22$$

These N equations can be put in matrix form as

$$[R(n,j)][\beta_n] = [V(n)],$$

where $V(n) = -P(n)$, and $[R(n,j)]$ is a N by N square matrix while $[\beta_n]$ and $[V(n)]$ are N by one column matrices. This matrix equation can be solved for the elements β_n by finding the inverse of the coefficient matrix $[R(n,j)]$, since

$$[\beta_n] = [R(n,j)]^{-1}[V(n)].$$

The elements of the matrix $[R(n,j)]^{-1}$ are found by dividing the transposed matrix of the cofactors of the elements of $[R(n,j)]$ by the determinant of $[R(n,j)]$. As a result, one obtains N equations for the β_n values of the form

$$\beta_n = \frac{\sum_{j=1}^{N} Q(n,j)V(j)}{\mathrm{Det}[R(n,j)]}, \qquad (23$$

where Q(n,j) is an element of the transposed matrix of the cofactors of the elements of [R(n,j)].

The computer program is set up to calculate the elements P(n) and R(n,j) from the data sets (X(i),Y(i),Z(i)) using equations 21 and 22. The program then finds the elements Q(n,j) from the values of R(n,j) using formulas obtained by the cofactor method. Finally, the values of β_n are calculated using equation 23.

The weighting factor appears in equations 21 and 22; therefore, this function must be determined prior to the calculation of P(n) and R(n,j). The weighting factor is related to the errors in the measurements by the expression

$$W(i) = 1/\sigma(i)^2,$$

where $\sigma(i)$ is the standard error in the residual U(i); this quantity reflects the errors in the data X(i), Y(i), and Z(i). Furthermore, $\sigma(i)$ can be equated to dU(i) where this differential is given by the equation

$$dU(i) = (\partial U/\partial X)_i dX(i) - (\partial U/\partial Y)_i dY(i) - (\partial U/\partial Z)_i dZ(i) \qquad (24$$

The partial derivative terms in this equation can be readily found from equation 19. The terms dX(i), dY(i), and dZ(i) are the standard deviations in the quantities X(i), Y(i), and

Z(i) respectively. By means of the usual propagation of random error equations, one can calculate the average relative error in each of these three quantities. As can be seen from the equations used in calculating these quantities, errors in stock solution concentrations, errors in preparing the sample solutions (such as inaccurate pipette and burette readings), and errors in the pH measurements can all give rise to errors in X(i), Y(i), and Z(i). By estimating the possible errors in each experimental step one can calculate the average relative errors in X, Y, and Z. The standard deviations in these three quantities are related to the average relative errors by equations of the form

$$dX(i) = (\sigma_X/X)X(i),$$

where (σ_X/X) is the average relative error in X.

Sullivan, Rydberg, and Miller in their original paper on this subject (20) ignored the last two terms in equation 24; they assumed that most of the error in the residual U(i) was due to errors in X(i). Thus, for the standard deviation in U(i) they wrote

$$\sigma(i) = (\partial U/\partial X)_i m_X X(i),$$

where m_X is the constant (σ_X/X). Consequently, for the weighting factor they used

$$W(i) = 1/[(\partial U/\partial X)_i m_X X(i)]^2 \qquad (25$$

Sullivan, Rydberg, and Miller calculated a value of 0.007 for m_x; Stagg, who used the same weighting factor, found a value of 0.02 for m_x.

In order to check the validity of using the shortened weighting factor defined by equation 25, the author revised the computer program to include all the terms of equation 24 in the weighting factor. For the experimental method described in the previous chapter, the following relative errors were found:

$$(\sigma_x/X) = 0.007,$$
$$(\sigma_y/Y) = 0.004,$$
$$(\sigma_z/Z) = 0.006.$$

Calculations of stability constants made using the complete weighting factor were compared with calculations made using the shorter weighting factor. Several statistical methods were used to compare the results of the two calculations; these methods will be discussed in detail in the next section. The results obtained with the complete weighting factor appeared to give a better fit of the data, and showed smaller standard deviations in the calculated β_n values; consequently, the complete weighting factor was adopted in place of the original shorter one.

The partial differential terms in equation 24 contain the parameters β_n. Therefore, in order to calculate the weighting factor, one must first estimate the values of the desired stability constants. An iterative process, similar to the one in the Bjerrum method, was used to refine the calculations until no difference existed between the parameters used to calculate the weighting factors at the beginning of a computation and the parameters subsequently calculated using those weighting factors. Crude initial estimates of each β_n must be fed into the computer program to calculate the first set of weighting factors; thereafter, the stability constants calculated from equation 23 are used to calculate a new set of weighting factors. The cycle of calculations was repeated until the parameters resulting from two successive calculations differed by less than one part in ten thousand. In practice, with reasonably good data, convergence was obtained within five iterations regardless of the accuracy of the initial estimates.

The use of a weighting factor in the least squares calculation of rare-earth complex stability constants was found to be essential. Stagg attempted to perform the least squares calculation without a weighting factor but could not obtain any meaningful results (15, p. 24). The author attempted the same thing and found that, in the case of the three parameter program, roughly the same results were obtained whether or not a weighting factor was used; however, the results obtained with a weighting factor were statistically more reliable than those obtained without one. For example, the stability constants found without the use of a weighting factor for the cerous α-hydroxyisobutyrate system were as follows:

$$\beta_1 = 4.369 \times 10^2 \pm 1.76 \times 10,$$
$$\beta_2 = 5.226 \times 10^4 \pm 7.33 \times 10^2,$$
$$\beta_3 = 2.599 \times 10^7 \pm 9.02 \times 10^4.$$

The stability constants found for the same system using the weighted least squares program were

$$\beta_1 = 3.980 \times 10^2 \pm 3.02,$$
$$\beta_2 = 5.624 \times 10^4 \pm 1.13 \times 10^3,$$
$$\beta_3 = 2.140 \times 10^6 \pm 8.71 \times 10^4.$$

The method used to calculate the standard deviations of the parameters will be discussed in the next section. With a four parameter system, on the other hand, no reasonable results could be obtained without the use of a weighting factor. The stability constants calculated without the use of a weighting factor in this case differed by as much as 50% from those calculated using a weighting factor; moreover, in terms of standard deviations, the results obtained without the weighting factor were meaningless.

The use of a weighting factor is apparently necessary if acceptable results are to be obtained in a least squares computation of rare-earth stability constants from potentiometric data. This fact may be attributed to the large variation in the standard deviations of the data over the concentration range employed. For the research reported in this dissertation, the standard deviations in both X and Y varied from about 10^{-6} to about 10^{-4} as the concentrations in the sample solutions varied. Because of the differences in the standard deviations of X and Y, all the data sets were not equally reliable. The weighting factor takes these differences into account, since the weighting factor is inversely proportional to the squares of the standard deviations. Consequently, the smaller the standard deviations for a given set of data (X(i), Y(i),Z(i)) the more heavily this set is weighted in the calculation of the stability constants.

The least squares method has several advantages over the successive approximation and graphical integration methods. The entire range of data is used to calculate each of the constants; this is usually impossible in the successive approximation techniques. There is no tendency to prejudice the data by smoothing the curves, as is the case with the graphical integration method. The least squares method allows for a number of statistical checks on the results of the computations, such as the calculation of the standard deviation of each parameter. Finally, the use of a digital computer to perform the least squares calculation permits very rapid computations. The I.B.M. 360 computer used in this research took less than one minute to calculate all fifteen sets of stability constants for each rare-earth carboxylate series.

C. Additional Calculations

After a set of stability constants had been calculated which satisfied the conditions set for ending the iterative process, the computer program then calculated a number of quantities from the stability constants. These additional calculations provided a means of evaluating the reliability of the stability constants and of the data from which they had been derived.

The mean ligand number had been calculated for each data set by means of equation 15; since this value of $\bar{n}$ had been obtained from the experimental quantities X(i), Y(i), and Z(i), it was designated the experimental $\bar{n}$. The same quantity was also calculated from the stability constants and the X(i) values by means of equation 16; this value of $\bar{n}$ is called the calculated $\bar{n}$. The percentage difference between the two values of $\bar{n}$ was also calculated for each individual data set. As a rule, these differences are less than one percent. If for an individual data set a percentage difference much in excess of one percent was found, a significant experimental error was probably involved; this set was dropped from the series and the β_n values recalculated. If in a series of measurements several data sets showed large percentage differences, the entire series was considered to be of poor quality and the measurements were repeated on a new set of sample solutions. Thus, the percentage differences in the two values of $\bar{n}$ provide a means of checking the consistency of each data point with respect to the entire series of measurements. The calculations reported in this dissertation were made using data for which the percentage differences were less than one percent.

A statistical measure of how well the calculated parameters fit the data was obtained by computing S_{min}. This quantity is the value of S in equation 20 that results when the values of U(i) are computed from equation 19 using the newly calculated stability constants. Because of the way in which the weighting factor has been defined, S_{min} has the chi-squared distribution for (I - N) degrees of freedom, where I is the number of data points used in the calculation and N is the number of parameters calculated (22). One can compare the values of S_{min} with the tabulated values of chi-squared for (I - N) degrees of freedom to obtain the probability of achieving a fit, due to chance, as poor or worse than the one obtained. The values of S_{min} found for the systems studied in this dissertation all gave a probability limit greater than 0.80, thereby indicating a reasonably good fit of the data by the parameters.

The standard deviations in the parameters were calculated by the method of external consistency (22). The equation used to calculate σ_n, the standard deviation in β_n, is

$$\sigma_n = \sqrt{\frac{Q(n,)S_{min}}{\mathrm{Det}[R(n,j)](I - N)}} ,$$

where Q(n,n) is the diagonal element in the transposed matrix of the cofactors of the elements of the coefficient matrix [R(n,j)].

The coefficient of variation of β_n was found by the equation

$$V_n = \frac{100\sigma_n}{\beta_n}$$

The coefficient of variation allows for easy comparison of the standard deviations of systems for which the values of β_n differ substantially.

Finally, the amount of $NaClO_4$ stock solution that should have been added to each sample to achieve an ionic strength of 1.000 molar was obtained from equation 3 using the calculated $\bar{n}$ values. The volume of $NaClO_4$ that should have been added to the ith sample is therefore given by the expression

$$V_{sp}(i) = \frac{V_t}{C_{sp}}\left(0.1 - 0.5\left[C_M(3 - \bar{n}_i)^2 + [H]_i + Y(i) - \bar{n}_i C_M + \frac{V_b(i)C_A}{V_t} + \frac{3V_M(i)C_M}{V_t}\right]\right),$$

where the term $C_M(3 - \bar{n}_i)^2$ is used as an approximation for the sum $\sum_{n=0}^{N} [MA_n]_i(3 - n)^2$.

V. REVIEW OF PREVIOUS STUDIES

During the past fifteen years a considerable amount of information has been collected on the complex formation equilibria of the rare-earth ions. A comprehensive review of the literature up to 1964 has been published by Moeller et al. (3).

The reported values of rare-earth complex stability constants vary from 10^{-10} to 10^{22} depending upon the nature of the ligand. For a given ligand, the stability constant values usually increase as the atomic number of the rare-earth ion increases: the value of β_1 for a lutetium complex may be as much as one hundred times larger than the value of β_1 for the corresponding lanthanum complex. The variation of the stability constants with atomic number is usually irregular, and a drop in complex stability is often noted for ions in the middle of the rare-earth series. Many aspects of rare-earth stability constant data have been difficult to interpret, and much remains to be learned about the factors governing rare-earth ion complex formation.

The rare-earth complex systems that have received serious attention in recent years may be divided into several categories depending on the coordinating atoms and dentate character of the ligands. The most widely studied ligands have been simple or substituted carboxylates, aminopolycarboxylates, and polyaminopolycarboxylates. Some hydrolytic and inorganic complex systems have also been studied. Each ligand type will be discussed briefly.

The weakest rare-earth complexes appear to be the hydrolytic complexes. The hydroxo complexes of only a few of the rare-earth ions have been studied in detail (23, 24, 25, 26). The stability constant values reported for these complexes are very small; for example, β_1 for lanthanum is reported to be 10^{-10} (24). Consequently, hydroxo complexes are unlikely to be present in aqueous solution in concentrations large enough to interfere with the study of other rare-earth complexes.

The complexes formed by the rare-earth ions with inorganic ligands such as chloride (27), thiocyanate (28), and nitrate (29) ions are also quite weak. The values of β_1 for complexes of this type are usually between one and ten, indicating little more than ion-pair formation. The information available on inorganic complexes is still rather limited.

Three simple carboxylate ligands, acetate (30, 31, 32), propionate (33, 34), and isobutyrate (21, 34), have received detailed study as rare-earth complexing agents. The values of β_1 for these complexes are between 10^2 and 10^3. As an example, the $\log\beta_1$ values for the acetate complexes, as reported by Kovar (32), are plotted against rare-earth atomic number in Figure 1.

Several hydroxy substituted carboxylate ligands have received serious attention, such as the glycolate (35, 36, 37), lactate (35, 37, 38, 39), glyoxalate (40), ethylglycol-

Figure 1. Logarithms of the first formation constants of some rare-earth complexes
a: acetates (32)
b: glycolates (40)

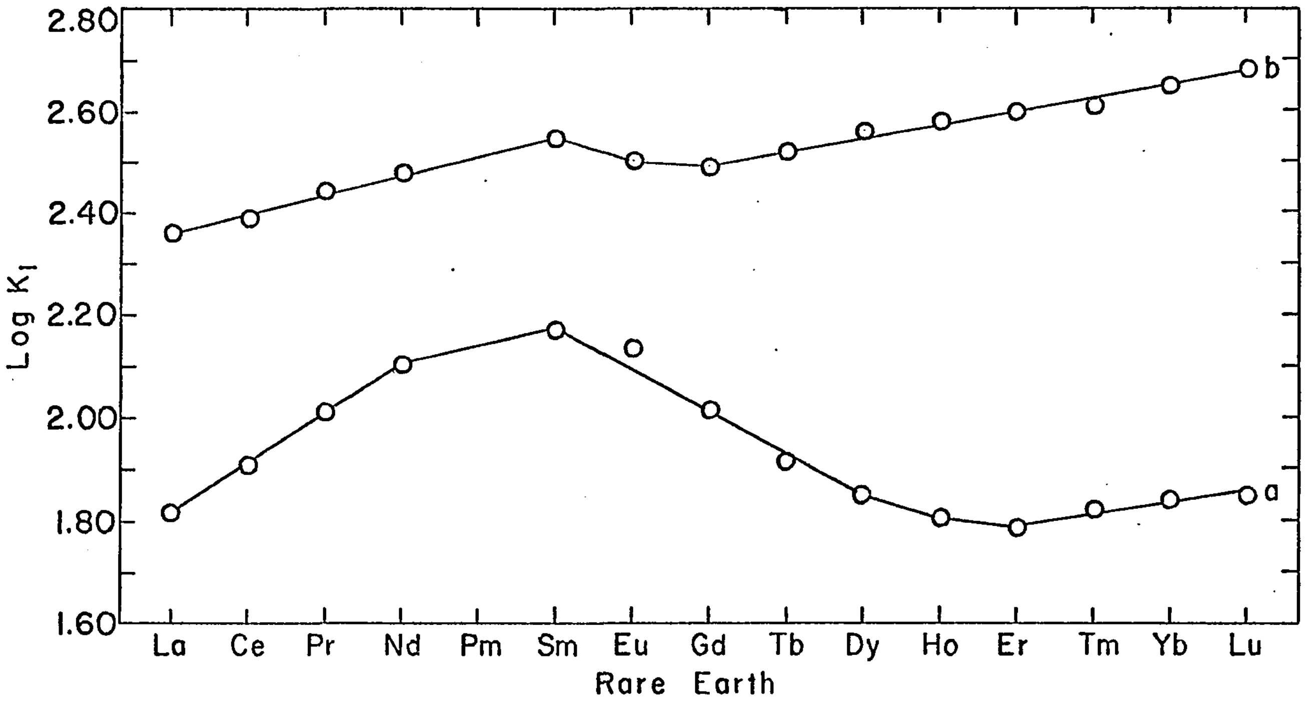
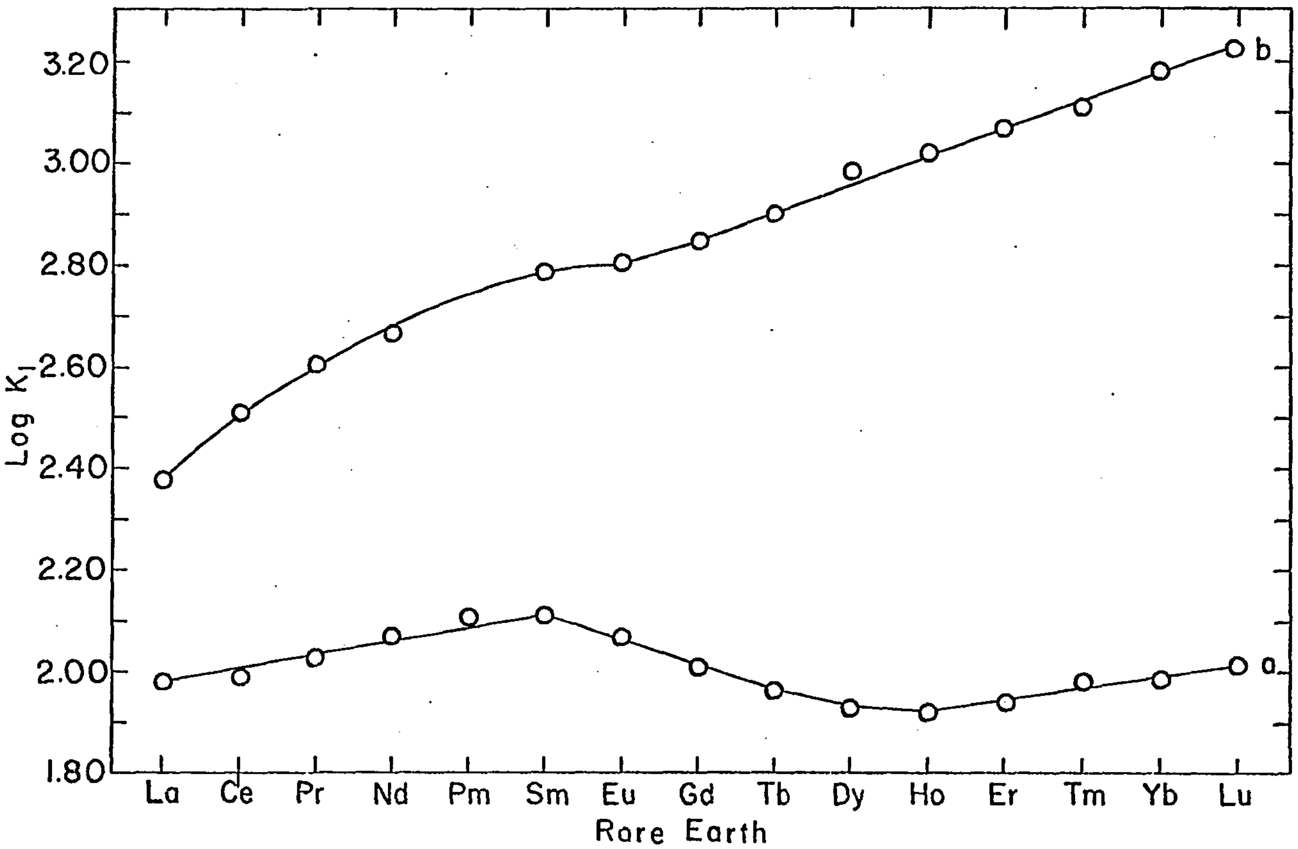

2.80
2.60
2.40
2.20
2.00
1.80
1.60
Log K_1
b
a
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Rare Earth

Figure 2. Logarithms of the first formation constants of some rare-earth complexes
a: mercaptoacetates (47)
b: 1-hydroxycyclopentanecarboxylates (9)


3.20
3.00
2.80
2.60
2.40
2.20
2.00
1.80
Log K_1
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Rare Earth
b
a

ate (41, 42), methylethylglycolate (41, 42, 43), diethylglycolate (41, 42), methylpropylglycolate (43), methylisopropylglycolate (44), t-butylglycolate (44), t-butylmethylglycolate (44), mandelate (45, 46), atrolactate (46), and 1-hydroxycyclopentanecarboxylate (9). The complexes studied in this dissertation belong in this category. The $\log\beta_1$ values reported by Suzuki for the glyoxalates (40) are plotted in Figure 1, and the $\log\beta_1$ values of Powell and Rowlands (9) for the 1-hydroxycyclopentanecarboxylates are plotted in Figure 2.

Other substituted carboxylate ligands which have been studied are the mercaptoacetate (47), methoxyacetate (47), glycinate (48), and picolinate (49, 50). The $\log\beta_1$ values reported by Kolat (47) for the mercaptoacetates are plotted in Figure 2.

The rare-earth complexes of some dicarboxylate ligands such as the diglycolate ion (51) have been studied, as well as those of several aminopolycarboxylate ligands such as the iminodiacetate (52), nitrilotriacetate (53, 54), and dipicolinate (55). These aminopolycarboxylate ligands can coordinate through nitrogen as well as through oxygen and form very strong complexes. As an example, the $\log\beta_1$ values of Moeller and Ferrus (54) for the nitrilotriacetates are plotted in Figure 3.

The strongest rare-earth complexes are formed by polyaminopolycarboxylate ligands such as ethylenediamine-N,N,N',N'-tetraacetate (56), N-hydroxyethylenediamine-N,N',N'-tri-

Figure 3. Logarithms of the first formation constants of the rare-earth nitrilotriacetate complexes (54)

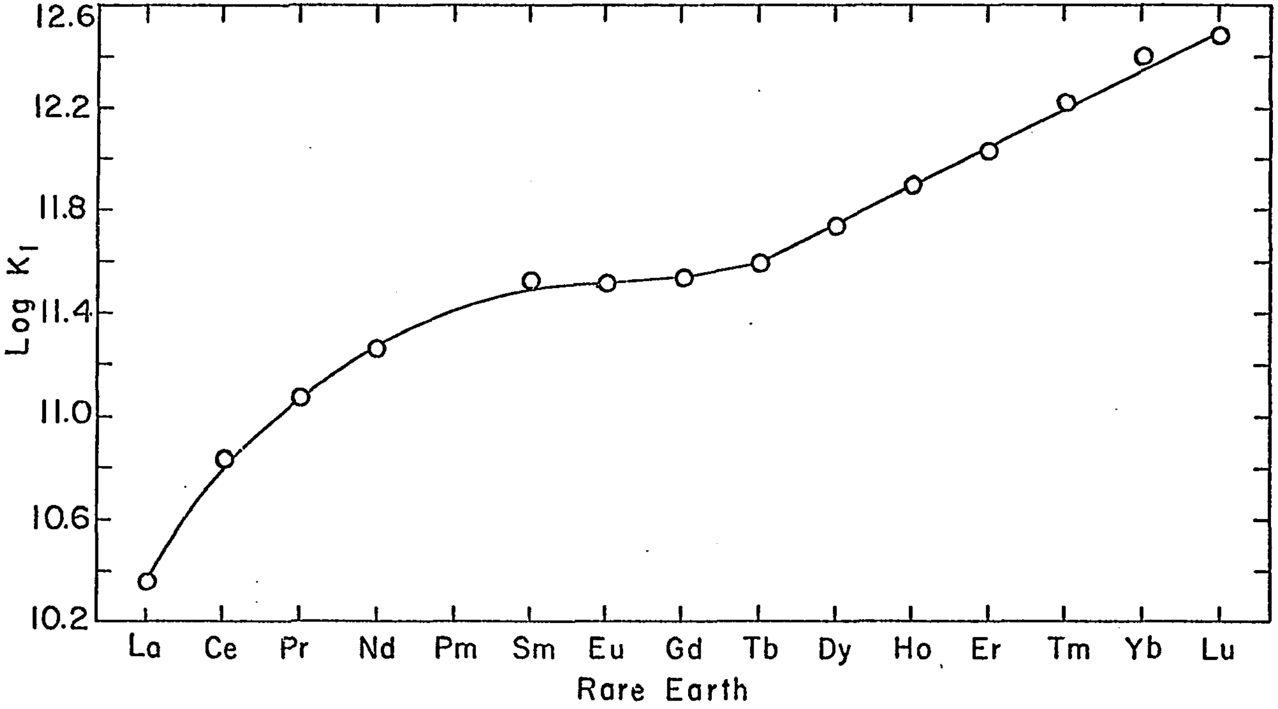
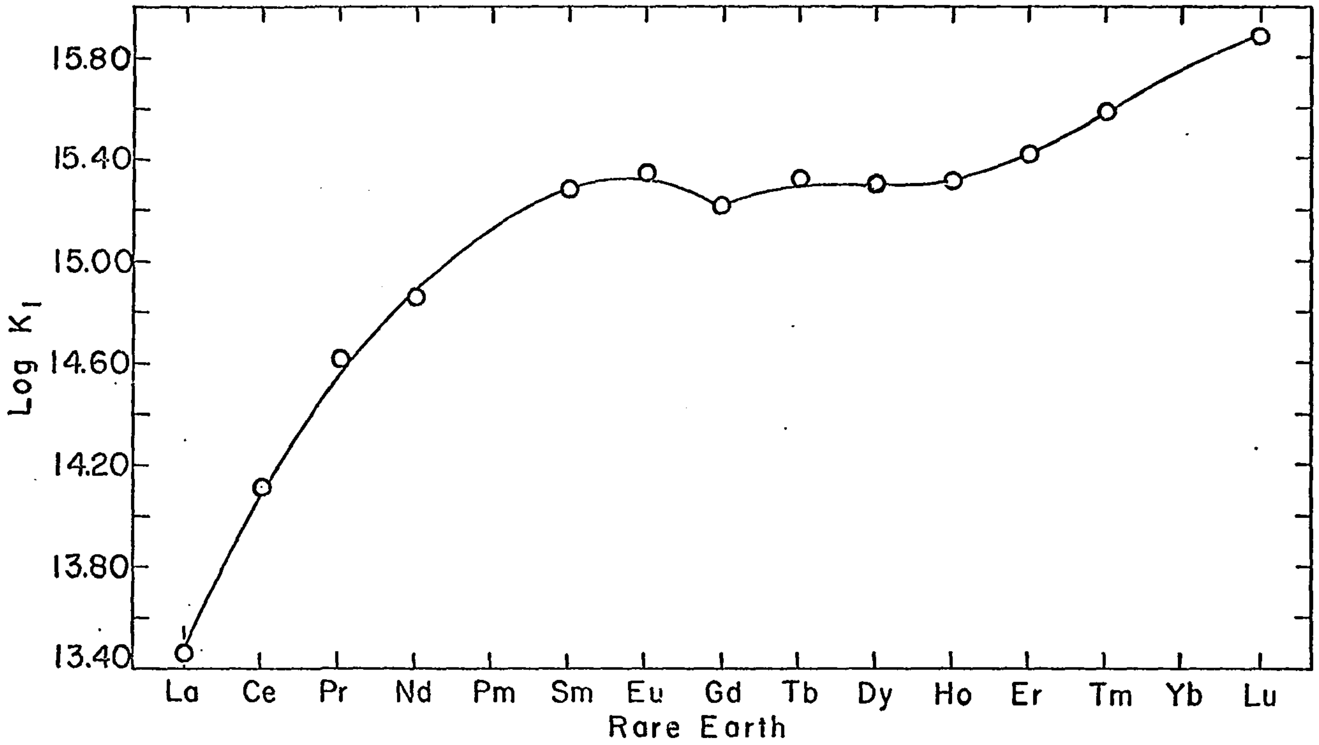

12.6
12.2
11.8
11.4
11.0
10.6
10.2
Log K_1
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Rare Earth

Figure 4. Logarithms of the first formation constants of the rare-earth N-hydroxyethylenediamine-N,N',N'-triacetate complexes (58)


Log K_1
15.80
15.40
15.00
14.60
14.20
13.80
13.40
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Rare Earth

acetate (57, 58), etylenediamine-N,N'-diacetate (52), trans-1,2-diaminocyclohexane-N,N'-tetraacetate (59, 60), and diethylenetriamine-N,N,N',N',N"-pentaacetate (61, 62). The first two of these ligands are the most commonly used complexing agents in large scale ion-exchange separations of the rare-earth elements. As an example, the $\log\beta_1$ values of Moeller and Ferrus (58) for the complexes of the N-hydroxyethylenediamine-N,N',N'-triacetate (HEDTA) ion are plotted in Figure 4.

VI. EXPERIMENTAL RESULTS

The stability constant values obtained for the rare-earth complexes of the α-hydroxyisobutyrate and 2,2-bis-(hydroxymethyl)propionate ligands are tabulated below. The logarithms of the stability constants, the step formation constants, and the step formation constant ratios are also listed. At least two determinations were made for each system studied; the results with the smallest standard deviations are reported here.

Table 1. Stability constants of the rare-earth α-hydroxyisobutyrate complexes

Metal	β_1	$\beta_2 \times 10^{-4}$	$\beta_3 \times 10^{-6}$	$\beta_4 \times 10^{-8}$
La	289.7 ± 4.6	1.78 ± 0.10	0.130 ± 0.064	---
Ce	366.6 ± 4.2	3.51 ± 0.11	0.187 ± 0.075	---
Pr	506.6 ± 2.5	4.637 ± 0.065	0.500 ± 0.046	---
Nd	578.9 ± 4.6	5.882 ± 0.084	0.971 ± 0.057	---
Sm	770.6 ± 7.4	12.73 ± 0.21	3.50 ± 0.19	---
Eu	946 ± 13	19.80 ± 0.58	10.34 ± 0.75	---
Gd	990.5 ± 4.7	22.82 ± 0.29	13.27 ± 0.52	1.64 ± 0.23
Tb	1239.1 ± 7.8	37.47 ± 0.50	26.1 ± 1.0	3.73 ± 0.50
Dy	1360 ± 19	45.1 ± 1.1	32.1 ± 2.9	---
Ho	1592 ± 11	65.09 ± 0.91	56.0 ± 2.5	1.7 ± 1.5
Er	1756 ± 21	95.3 ± 1.8	93.8 ± 5.7	23.3 ± 4.2
Tm	2009 ± 10	111.01 ± 0.89	129.3 ± 2.5	18.9 ± 1.4
Yb	2280 ± 26	148.6 ± 2.2	181.9 ± 7.0	23.6 ± 3.5
Lu	2565 ± 22	188.4 ± 2.0	293.9 ± 8.0	86.8 ± 6.7
Y	1333 ± 12	47.37 ± 0.84	38.0 ± 2.1	2.8 ± 1.3

Table 2. Logarithms of the stability constants of the rare-earth α-hydroxyisobutyrate complexes

Metal	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	$\log\beta_4$
La	2.462	4.253	5.114	---
Ce	2.564	4.545	5.271	---
Pr	2.705	4.666	5.699	---
Nd	2.763	4.770	5.987	---
Sm	2.887	5.105	6.545	---
Eu	2.976	5.297	7.015	---
Gd	2.996	5.358	7.123	8.216
Tb	3.093	5.574	7.417	8.571
Dy	3.134	5.655	7.507	---
Ho	3.202	5.814	7.748	8.251
Er	3.247	5.979	7.972	9.367
Tm	3.303	6.045	8.112	9.277
Yb	3.358	6.172	8.260	9.373
Lu	3.409	6.275	8.468	9.939
Y	3.125	5.676	7.580	8.439

The values of log β_1 for both sets of complexes are plotted <u>versus</u> rare-earth atomic number in Figure 5 and <u>versus</u> rare-earth ionic radius in Figure 6. Several interesting features of these graphs are apparent. The variation of log β_1 with atomic number or ionic radius is remarkably different in each case. In the case of the 2,2-bis(hydroxymethyl)propionate (BHMPA) complexes, two sharp discontinuities appear: there is a maximum at samarium and a minimum at holmium. Also, the value of log β_1 for lanthanum appears to be exceptionally low and out of line with the next four elements. In the case of the α-hydroxyisobutyrate complexes, a nearly

Figure 5. Logarithms of the first formation constants of the rare-earth 2,2-bis-(hydroxymethyl)propionate (a) and α-hydroxyisobutyrate (b) complexes

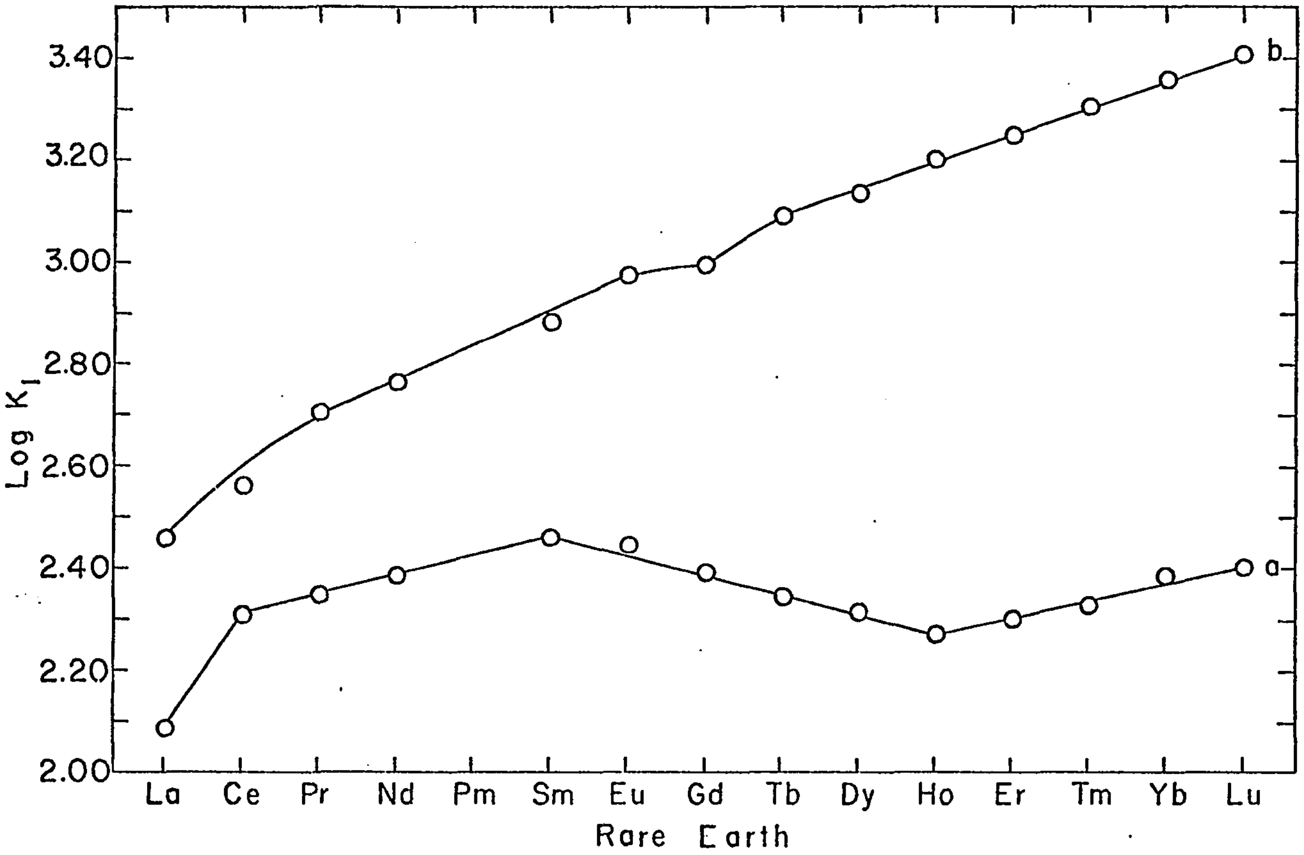

3.40
3.20
3.00
2.80
2.60
2.40
2.20
2.00
Log K_1
b
a
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Rare Earth

Figure 6. Logarithms of the first formation constants of the rare-earth 2,2-bis(hydroxymethyl)propionate (a) and α-hydroxyisobutyrate (b) complexes as functions of cationic radius

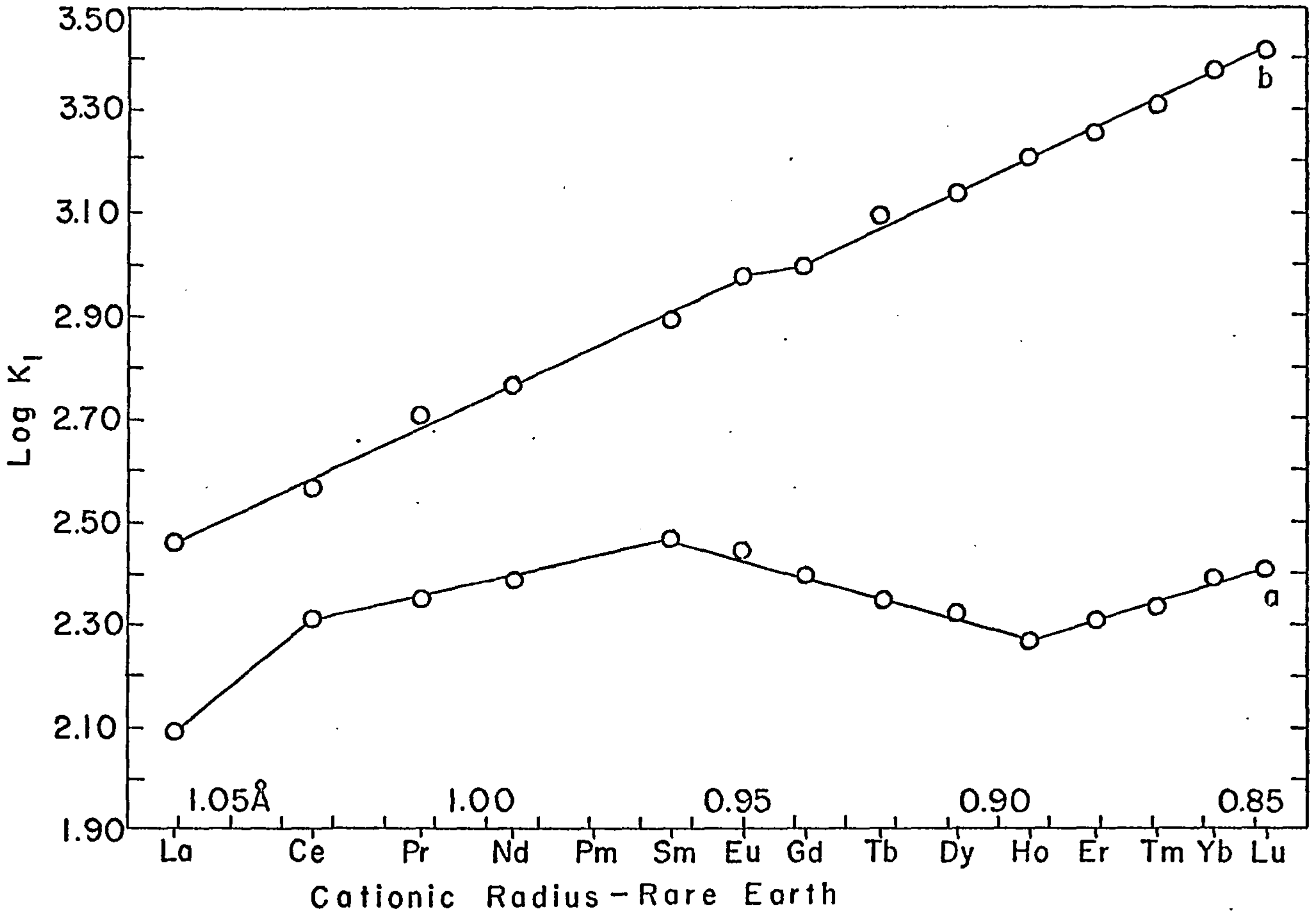

3.50
3.30
3.10
2.90
2.70
2.50
2.30
2.10
1.90
Log K_1
b
a
1.05Å
1.00
0.95
0.90
0.85
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Cationic Radius - Rare Earth

Table 3. Step formation constants and step formation constant ratios of the rare-earth α-hydroxyisobutyrate complexes

Metal	K_2	K_3	K_4	K_1/K_2	K_2/K_3
La	61.8	7.3	---	4.69	8.50
Ce	95.6	5.3	---	3.84	18.0
Pr	91.5	10.8	---	5.53	8.48
Nd	101.6	16.5	---	5.70	6.16
Sm	165.3	27.5	---	4.66	6.01
Eu	209.2	52.2	---	4.52	4.01
Gd	230.4	58.2	12.4	4.30	3.96
Tb	302.4	69.7	14.3	4.10	4.34
Dy	332.0	71.1	---	4.10	4.67
Ho	408.9	86.0	3.2	3.89	4.75
Er	539.6	98.4	24.8	3.27	5.48
Tm	552.5	116.4	14.6	3.64	4.75
Yb	651.7	122.5	13.0	3.50	5.32
Lu	734.4	156.0	29.5	3.49	4.71
Y	355.4	80.3	7.2	3.75	4.43

linear curve is obtained, although a small discontinuity appears at europium. In both cases the plot _versus_ ionic radius is smoother than the plot _versus_ atomic number.

The variation in log β_1 with increasing atomic number shown by the BHMPA complexes is similar to that obtained by Kovar with the acetate complexes (Figure 1). The variation in log β_1 with atomic number shown by the αHIB complexes is roughly the same as that found by Powell and Rowlands with the 1-hydroxycyclopentanecarboxylate complexes (Figure 2).

No previous work has been reported on the rare-earth BHMPA complexes. However, a few studies have previously been

Table 4. Stability constants of the rare-earth 2,2-bis-(hydroxymethyl)propionate complexes

Metal	β_1	$\beta_2 \times 10^{-3}$	$\beta_3 \times 10^{-4}$
La	123.3 ± 0.5	3.00 ± 0.07	1.95 ± 0.25
Ce	204.2 ± 0.8	8.84 ± 0.07	23.23 ± 0.99
Pr	221.0 ± 0.7	7.78 ± 0.12	6.52 ± 0.59
Nd	242.5 ± 0.7	9.60 ± 0.15	3.66 ± 0.71
Sm	290.4 ± 1.1	13.18 ± 0.24	5.1 ± 1.2
Eu	278.9 ± 0.9	12.27 ± 0.18	5.33 ± 0.93
Gd	247.5 ± 0.9	12.50 ± 0.19	13.6 ± 1.0
Tb	220.4 ± 1.1	10.16 ± 0.23	12.9 ± 1.2
Dy	206.8 ± 1.0	8.62 ± 0.18	2.65 ± 0.85
Ho	186.8 ± 1.4	8.18 ± 0.25	2.2 ± 1.1
Er	199.5 ± 0.5	8.04 ± 0.11	3.11 ± 0.57
Tm	212.5 ± 0.8	8.96 ± 0.16	4.66 ± 0.77
Yb	243.2 ± 0.9	12.78 ± 0.16	17.96 ± 0.89
Lu	251.5 ± 1.0	13.60 ± 0.22	23.4 ± 1.3
Y	172.6 ± 0.7	5.86 ± 0.13	5.36 ± 0.59

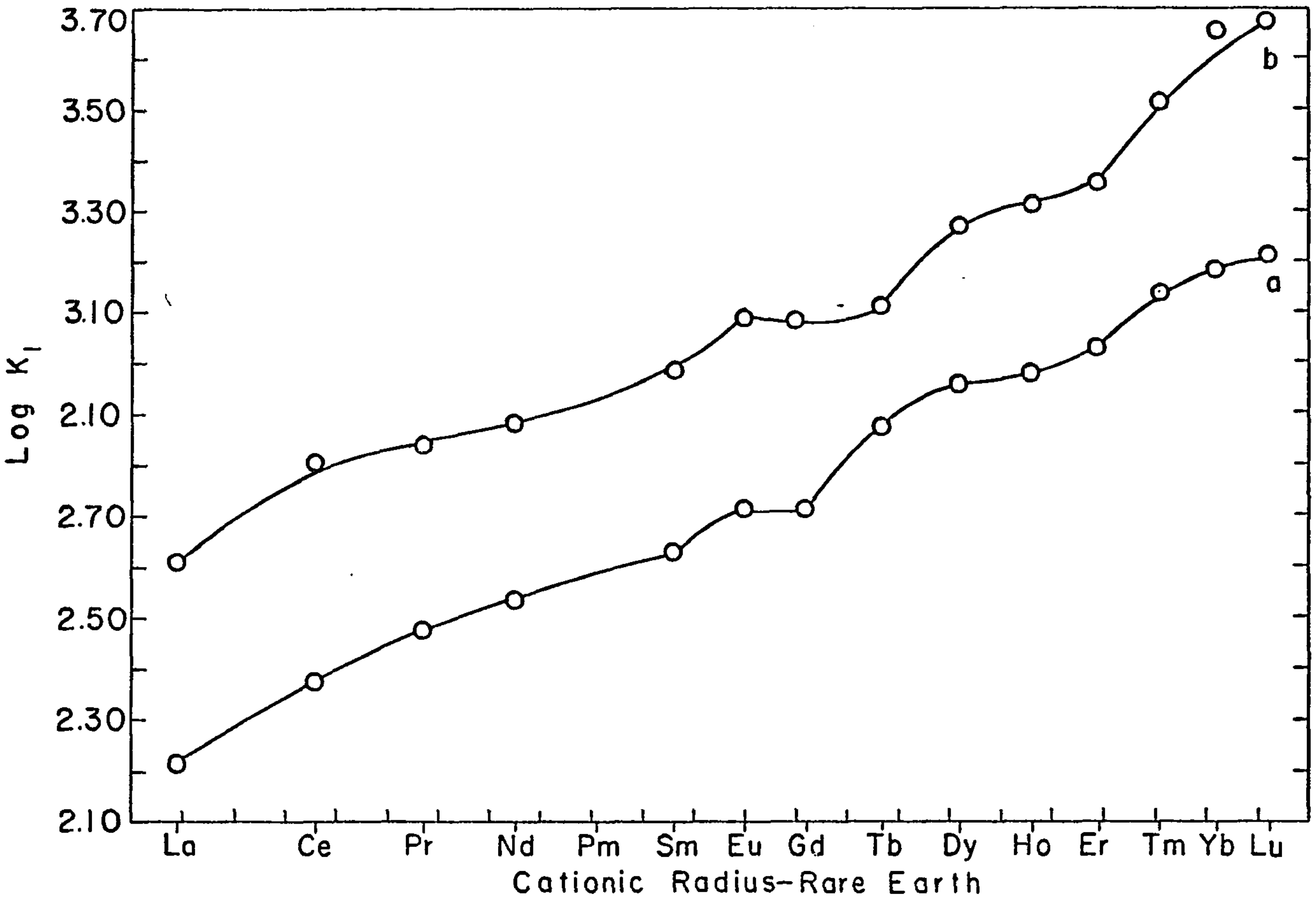
made on the rare-earth αHIB complexes.

Two previous studies of the rare-earth αHIB system have been made by members of Dr. J. E. Powell's research group. In 1963 Kolat reported a set of stability constants which had been measured at 20° and an ionic strength of 0.10 molar (47). His data had been obtained with a Beckman model GS pH meter, and the results had been calculated by hand using the method of Fronaeus. The values of $\log\beta_1$ reported by Kolat are plotted *versus* ionic radius in Figure 7. The irregular features of this curve were not readily explicable in terms of current theory.

Figure 7. Logarithms of the first formation constants of the rare-earth α-hydroxyisobutyrate complexes as functions of cationic radius

a: data of Stagg and Powell (21)

b: data of Kolat (47)



3.70
3.50
3.30
3.10
2.10
2.70
2.50
2.30
2.10
Log K$_1$
b
a
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Cationic Radius-Rare Earth

Figure 8. Logarithms of the first formation constants of the rare-earth α-hydroxy-isobutyrate complexes as functions of cationic radius
a: data of Deelstra and Verbeek (39)
b: data of Suzuki (63)

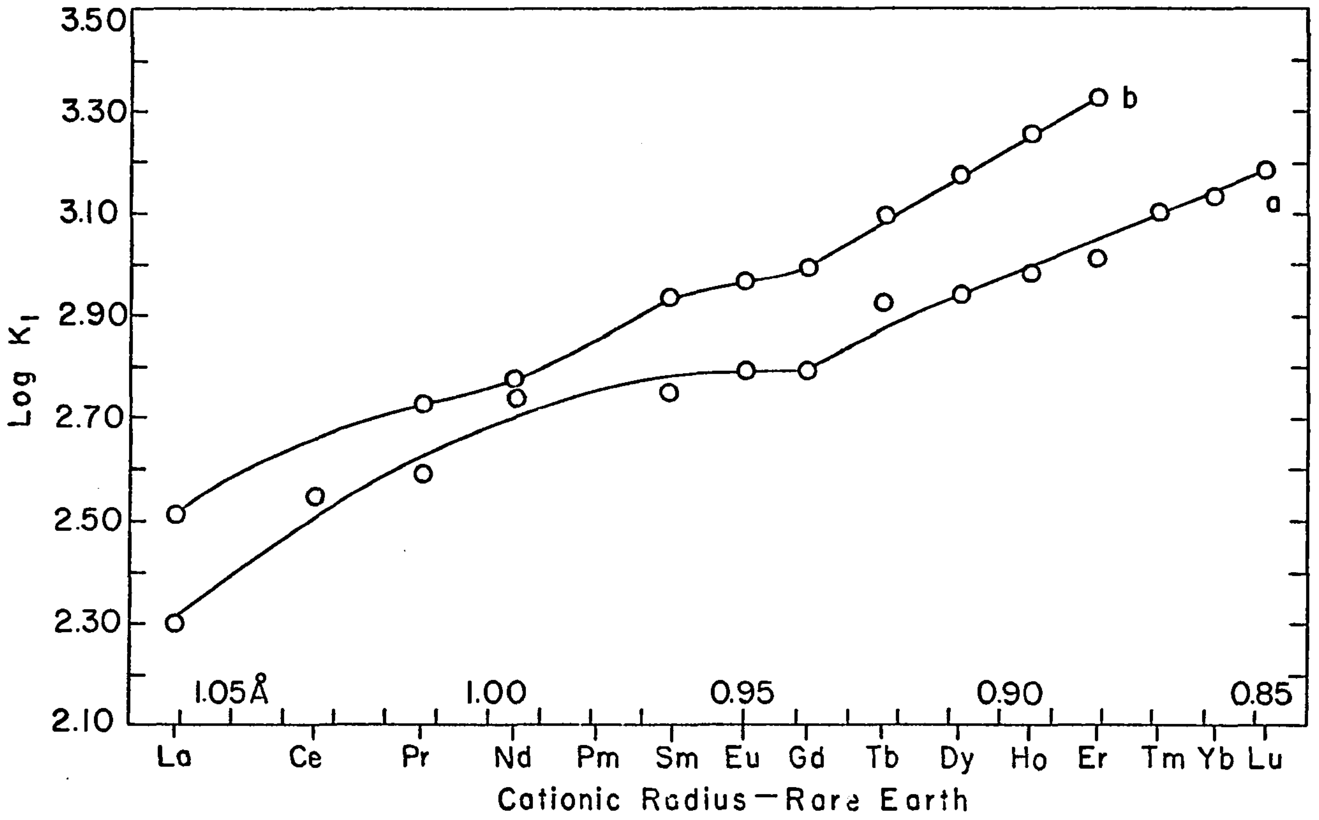

Log K_1
3.50
3.30
3.10
2.90
2.70
2.50
2.30
2.10
b
a
1.05Å
1.00
0.95
0.90
0.85
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Cationic Radius—Rare Earth

Table 5. Logarithms of the stability constants, step formation constants, and step formation constant ratios of the rare-earth 2,2-bis(hydroxymethyl)propionate complexes

Metal	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	K_2	K_3	K_1/K_2	K_2/K_3
La	2.091	3.477	4.290	24.3	6.5	5.07	3.74
Ce	2.310	3.946	5.366	43.3	26.3	4.72	1.65
Pr	2.344	3.891	4.814	35.2	8.4	6.28	4.20
Nd	2.385	3.983	4.563	39.6	3.8	6.12	10.4
Sm	2.463	4.120	4.710	45.4	3.9	6.40	11.7
Eu	2.445	4.089	4.727	44.0	4.4	6.34	10.1
Gd	2.394	4.097	5.136	50.5	10.9	4.90	4.62
Tb	2.343	4.007	5.110	46.1	12.7	4.78	3.64
Dy	2.316	3.936	4.424	41.7	3.1	4.96	13.6
Ho	2.271	3.913	4.338	43.8	2.7	4.27	16.4
Er	2.300	3.905	4.493	40.3	3.9	4.95	10.4
Tm	2.328	3.952	4.668	42.1	5.2	5.05	8.10
Yb	2.386	4.107	5.255	52.6	14.1	4.63	3.73
Lu	2.401	4.134	5.370	54.1	17.2	4.65	3.14
Y	2.237	3.768	4.729	34.0	9.2	5.08	3.71

Subsequent improvements in experimental technique prompted a re-examination of the rare-earth α-hydroxyisobutyrate system. In 1964 Stagg and Powell reported a new set of stability constants which had been measured at a temperature of 25° and an ionic strength of 0.50 molar (21). Their data had been obtained with a Beckman model 76 expanded scale pH meter, and the least squares method had been used to compute the results. The values of log β_1 reported by Stagg and Powell are also plotted in Figure 7. A number of irregularities are present in this curve which still do not lend themselves to easy interpretation.

In order to secure an even more reliable set of data on the rare-earth α-hydroxyisobutyrate system, the present study was undertaken. The most widely used conditions of temperature and ionic strength, 25° and 0.1000 molar, were employed. Further improvements in the experimental method, such as the use of the Beckman model 1019 pH meter, were adopted. The preparation of twenty individual samples for each metal-ligand system allowed for a more exact control of ionic strength than was possible with the titration method employed in the previous studies. Also, a number of improvements were made in the least squares computation method which led to more precise results and a better evaluation of errors than were obtainable with the program originally employed by Stagg.

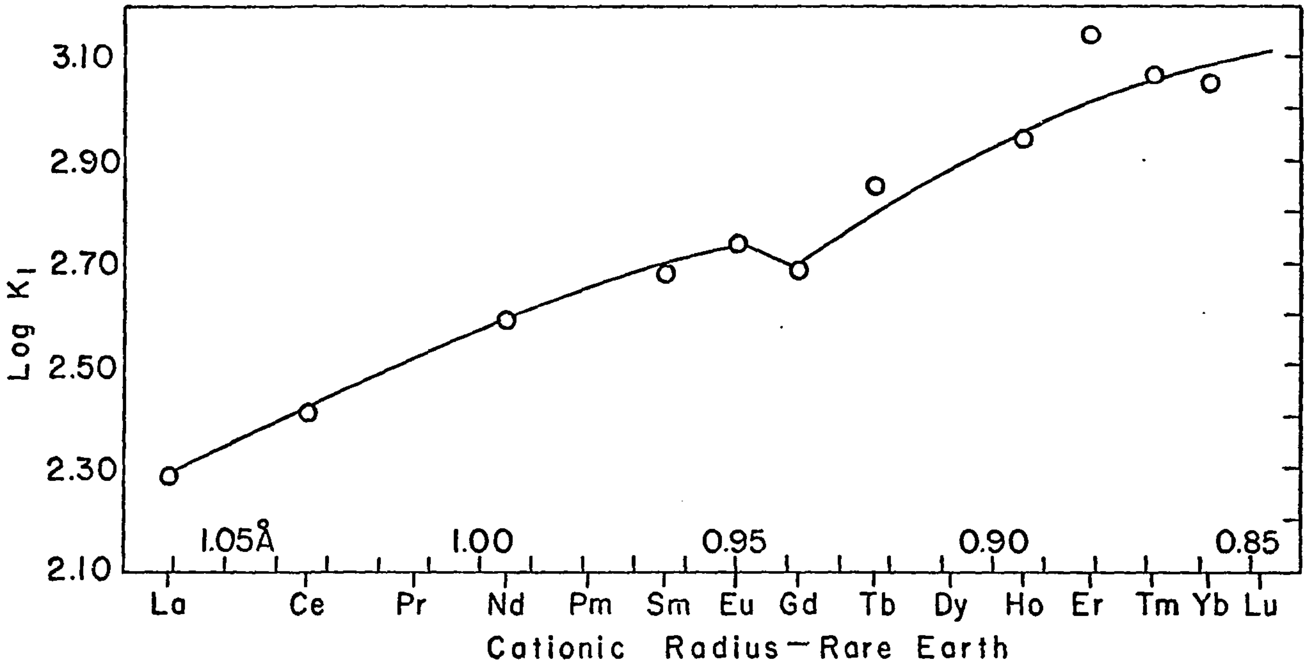
A study of the rare-earth α-hydroxyisobutyrate complexes similar to the one described in this dissertation was begun simultaneously by Y. Suzuki, a former member of Dr. Powell's research group. The experimental method used by Suzuki is similar to the one described in chapter II with one significant exception: a double-junction reference electrode was used to minimize the errors due to the formation of insoluble potassium perchlorate at the electrode tip. Essentially the same computer program as the one described above in chapter III was used by Suzuki. The preliminary results obtained by Suzuki are listed in Table 6. Comparison of these values with the author's results in Tables 2 and 3 shows good agreement from lanthanum to samarium, close agreement from europium to dysprosium, and less satisfactory agreement for the remaining elements. The values of log β_1 reported by Suzuki are plotted versus ionic radius in Figure 8.

Table 6. Logarithms of the stability constants and step formation constant ratio of the rare-earth α-hydroxyisobutyrate complexes as reported by Suzuki (63)

Metal	logβ_1	logβ_2	logβ_3	K_1/K_2
La	2.511	4.16	5.48	7.38
Pr	2.724	4.76	5.91	4.91
Nd	2.772	4.78	5.86	5.80
Sm	2.930	5.15	6.71	5.18
Eu	2.966	5.23	6.79	5.04
Gd	2.990	5.34	7.05	4.33
Tb	3.095	5.49	7.33	5.01
Dy	3.174	5.72	7.68	4.27
Ho	3.252	5.88	8.04	4.21
Er	3.324	5.98	8.26	4.67
Y	3.206	5.74	7.90	4.77

Two other sets of rare-earth α-hydroxyisobutyrate complex data have been reported. Choppin and Chopoorian in 1961 published a set of data obtained at 25° and an ionic strength of 2.000 molar (37), and Deelstra and Verbeek in 1964 published a set of stability constant values obtained at 25° and an ionic strength of 0.200 molar (39). In both cases the experimental and computational methods used by these authors differ widely from the ones used in this dissertation. The values

Figure 9. Logarithms of the first formation constants of the rare-earth α-hydroxyisobutyrate complexes as a function of cationic radius from the data of Choppin and Chopoorian (37, 84)


Log K$_1$
3.10
2.90
2.70
2.50
2.30
2.10
1.05Å
1.00
0.95
0.90
0.85
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Cationic Radius—Rare Earth

of log β_1 obtained by Deelstra and Verbeek are plotted in Figure 8, and those of Choppin and Chopoorian are plotted in Figure 9.

VII. DISCUSSION

A. A Proposed Model of Rare-Earth Complex Formation

The graphs of the previous two chapters illustrate the relation between the logβ_1 values for a given series of complexes and increasing atomic number (or decreasing ionic radius). Although these graphs exhibit several distinct patterns, the same characteristic trends are often observed with chemically similar ligands. For example, the data for the BHMPA complexes (Figures 5 and 6) show the same trends as the logβ_1 data for simple carboxylate ligands such as acetate (30, 31, 32), propionate (33, 34), and isobutyrate (21, 34) and for other ligands such as mercaptoacetate (47) and methoxyacetate (47). Also, the logβ_1 data for the αHIB complexes (Figure 5 and 6) show a similar relation to rare-earth ionic radius as the data for other α-hydroxycarboxylate ligands such as glycolate (35, 36, 37), lactate (35, 37, 38, 39), glyoxalate (40), ethylglycolate (41, 42), and 1-hydroxycyclopentanecarboxylate (9).

Several attempts to provide theoretical explanations for the unusual features of rare-earth stability constant data have been made. Most of the early attempts were limited in scope and capable of explaining only a few facts. In the last few years, general theories of rare-earth complex formation have been developed by J. E. Powell and co-workers and by G. R. Choppin and co-workers. T. Moeller, L. A. K. Stavely, and I. Grenthe and their co-workers have also contributed to the development of this subject. The theory of rare-earth complex formation presented below is a synthesis of the views of all these authors; however, it primarily reflects the approach of Dr. J. E. Powell.

The starting point of any interpretation of stability constant data is the resolution of the step formation constants into their enthalpy and entropy contributions by means of the equation

$$\log K_n = \frac{-\Delta H_n + T\Delta S_n}{2.303RT} \qquad (26$$

Secondly, it is necessary to postulate a model of the complex formation process.

The aqueous rare-earth cations are known to be heavily hydrated: they exert a strong attraction for the negative ends of the dipoles of several water molecules and they are surrounded by two or more layers of oriented water molecules known as the hydration sphere. The hydration sphere consists of two regions: the inner hydration sphere made up of water molecules in direct contact with the ion; and the outer hydration sphere, which consists of water molecules more distant from the ion but oriented to it and whose motion is restricted by their attraction to the rare-earth ion. The number of water molecules in the inner hydration sphere is equal to the coordination number of the rare-earth ion; this value is thought to be eight, nine, or ten. The number of water molecules in the outer hydration sphere is difficult to ascertain; nevertheless, some properties of rare-earth salt solutions, such as transference numbers and partial molar volumes, give an indication of the overall size of the hydration sphere.

Carboxylate ions are also hydrated in aqueous solution; however, because of their lower charge and nonspherical shape, their hydration spheres are no doubt much smaller and much less strongly oriented than those of the rare-earth cations.

When a carboxylate ligand complexes a rare-earth cation, one can visualize the process as taking place in three steps: first, a number of water molecules are displaced from the inner hydration sphere of the cation, along with several additional water molecules from the outer hydration sphere; secondly, the ligand loses all of its hydrated water; and thirdly, an ionic bond is formed between the cation and the ligand. On the basis of this model, one can divide the enthalpy and entropy of complex formation into three parts. Thus for the formation of the first complex,

$$\Delta H_1 = \Delta H_{1a} + \Delta H_{1b} + \Delta H_{1c},$$

and

$$\Delta S_1 = \Delta S_{1a} + \Delta S_{1b} + \Delta S_{1c}.$$

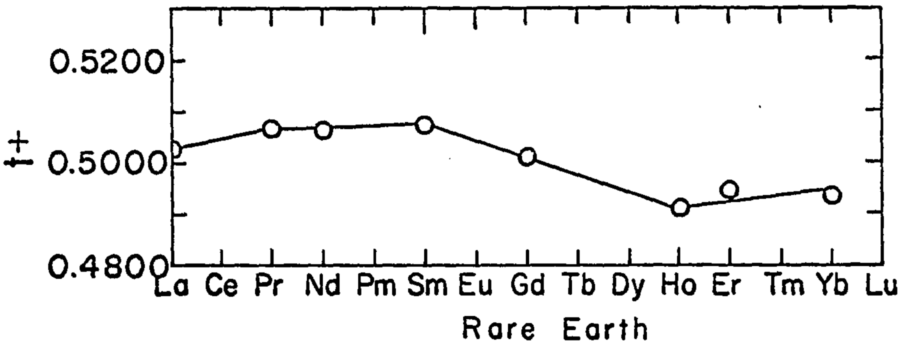
These three steps will now be considered individually from a thermodynamic point of view.

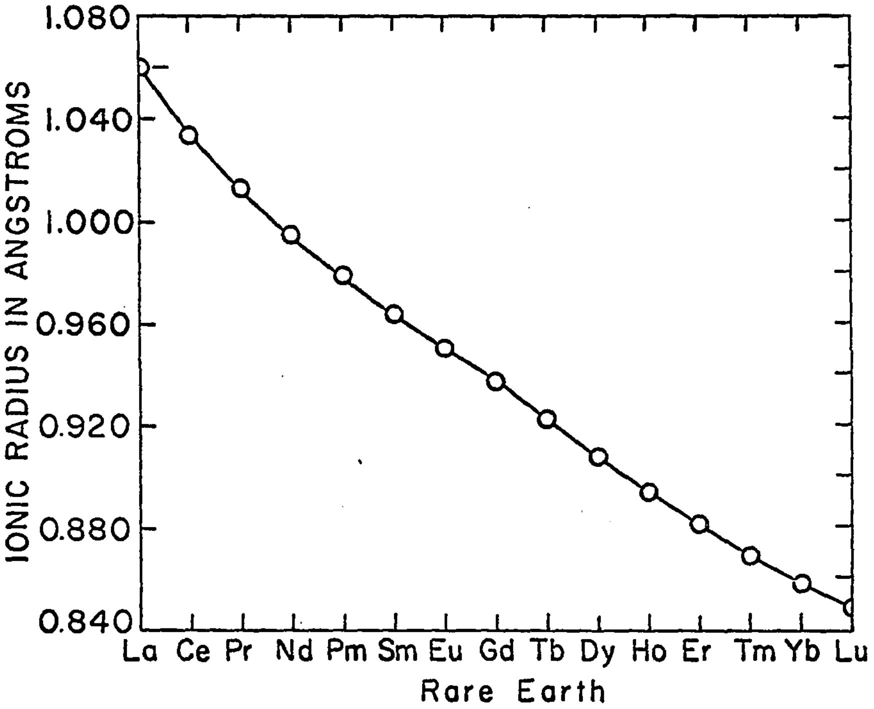
The loss of water of hydration by the cation will be an endothermic process. The hydrated water molecules will have to be supplied with sufficient energy to overcome the electrostatic ion-dipole attraction and then acquire the same average kinetic energy as the water molecules in the bulk of the solvent. The enthalpies of hydration of the rare-earth ions appear to be comparatively high. Harvey and Porter (64 p. 326) list a value of -806.3 kcal/mole for the enthalpy of hydration of the lanthanum ion at 25°. A significant portion of this energy must be restored when the lanthanum ion forms a complex.

It is therefore certain that ΔH_{1a}, the enthalpy change due to loss of water of hydration by the cation, will be positive. One must next consider how ΔH_{1a} will vary throughout the rare-earth series. This quantity should increase as the strength of the ion-dipole forces increases and as the number of water molecules in the hydration sphere increases. To a first approximation, one would expect that the decrease in ionic radius, and consequent increase in charge density, from lanthanum to lutetium would result in a more tightly bound hydration sphere and thus a slight progressive increase in ΔH_{1a}. However, studies of rare-earth salt solutions by Spedding and co-workers (65, 66, 67, 68, 69) indicate that the size of the hydration sphere changes irregularly as the rare-earth ionic radius decreases. For example, electrochemical measurements (65) show that the transference numbers of the rare-earth ions increase slightly from lanthanum to samarium,

Figure 10. Transference numbers of rare-earth ions at infinite dilution (65)

Figure 11. Radii of the rare-earth ions (72)


0.5200
0.5000
0.4800
t+
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Rare Earth


1.080
1.040
1.000
0.960
0.920
0.880
0.840
IONIC RADIUS IN ANGSTROMS
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Rare Earth

decrease from europium to holmium, and increase again from erbium to lutetium, as illustrated in Figure 10. Since the larger the transference number, the smaller the effective (or hydrated) ionic radius, the size of the hydration sphere must increase abnormally from europium to holmium. Measurements of the equivalent conductances (65), activity coefficients (65), heats of dilution (66), relative viscosities (67), and apparent molal volumes (68) of rare-earth salt solutions all support the idea of an increase in ionic hydration between samarium and holmium, or in some cases between neodymium and dysprosium.

Spedding and co-workers attributed the unexpected increase in the size of the hydration sphere of the ions between samarium and holmium to a gradual change in the coordination number of the ions. They assumed that, as the ionic radius decreases, the number of water molecules that can be accommodated in the inner hydration sphere may decrease. From structural studies, to be discussed in some detail later, it appears that the coordination number of the lighter rare-earth ions is nine or ten and that of the heavier rare-earth ions is eight or nine. Hence it is thought that between samarium and holmium the coordination number decreases by one. The change does not take place in one step, however, but from europium to holmium the portion of ions having the lower coordination number steadily increases.

The water molecules in the inner hydration sphere shield those in the outer hydration sphere from the ionic charge. If the number of water molecules in the inner hydration sphere is decreased, those in the outer sphere will feel a greater positive charge; thus the number of water molecules in the outer hydration sphere will increase. Consequently, the outer hydration sphere will be larger and the water molecules in it will be more strongly attracted to the metal ion. As the relative number of metal ions with the lower coordination number increases, the portion of ions with the larger hydration sphere will increase. At dysprosium or holmium all the ions will have the lower coordination number and the larger hydration sphere. Between samarium and dysprosium the portion of the ions with the larger hydration sphere will steadily increase.

In terms of enthalpy, the endothermicity of ΔH_{1a} will increase with the size of the hydration sphere and the strength of the forces of attraction between the ion and the water dipoles. From lanthanum to samarium the value of ΔH_{1a} should show a slight increase due to the increase in charge density of the ions. From europium to dysprosium the value of ΔH_{1a} should increase sharply along with the increase in the average size of the hydration sphere. Finally, from holmium to lutetium the value of ΔH_{1a} should show a slight increase along with the increase in charge density of the ions.

The trends in the entropy change for the first step,

ΔS_{1a}, should be similar to the trends in ΔH_{1a}. The hydration sphere of a rare-earth cation is a highly ordered system; this fact is indicated by the large negative entropy of hydration listed by Harvey and Porter (64, p. 326) for the lanthanum ion at 25°, -96.6 eu/mole. The loss of water of hydration by a rare-earth cation will result in an increase in the disorder of the system. The value of ΔS_{1a} should increase with the size of the hydration sphere and the number of water molecules displaced therefrom. Consequently, the value of ΔS_{1a} should be roughly constant from lanthanum to samarium and from holmium to lutetium, since the size of the hydration sphere is roughly constant for each of these two groups of ions. Between samarium and holmium there should be a large increase in ΔS_{1a} as the average size of the hydration sphere increases.

For the first step in the formation of a rare-earth complex the value of ΔH_{1a} is always endothermic and discourages complex formation; on the other hand, the value of ΔS_{1a} is always positive and encourages complex formation.

In the discussion above, it was assumed that the behavior of the ligand remained constant throughout the entire series of rare-earth complexes. Obviously the size and dentate character of the ligand will have a significant effect on the magnitude of ΔH_{1a} and ΔS_{1a}. The dentate character is the number of sites at which the ligand can bond to the cation. For most ligands that form rare-earth complexes, the dentate character is greater than one; it may be as high as six, as is the case with EDTA. As the dentate character of the ligand increases, the necessary disruption of the cationic hydration sphere increases, and consequently so do ΔH_{1a} and ΔS_{1a}. Furthermore, it is clear that, regardless of dentate character, a bulky ligand will require more disruption of the outer hydration sphere than a smaller ligand; this in turn gives rise to higher values for ΔH_{1a} and ΔS_{1a}.

Since the decrease in the radii of the rare-earth ions results in a decrease in the coordination number of the ions, it is reasonable to assume that the same effect might also give rise to a decrease in the effective dentate character of a given ligand. As the ionic radius decreases, it may no longer be possible for all the coordination sites on the ligand to attach to the rare-earth ion without causing significant distortion of the ligand. Evidence will be presented later which suggests that such a change in dentate character does indeed take place with a number of ligands. Therefore, it is appropriate at this time to consider the effect of such a change on the values of ΔH_{1a} and ΔS_{1a}. A decrease in dentate character will result in less disruption of the hydration sphere than occurs with those ions for which a higher dentate character is possible. Thus the expected values of ΔH_{1a} and ΔS_{1a} will be lower for those metals which require the ligand to exhibit a lower dentate character.

The relation between rare-earth stability constant values and entropy increases due to the displacement of water of hydration from rare-earth ions has been known for some time. This idea was developed by Schwarzenbach in 1952 (70), who introduced the term "chelate effect" to describe the exceptionally high stability of complexes formed with polydentate ligands. The relation between the enthalpy of complex formation and the size of the hydration sphere, and consequently the similarity between certain rare-earth stability constant data and the electrochemical properties of the rare-earth ions, was first noted in 1964 in two papers published almost simultaneously by Grenthe (31) and by Edelin de la Praudiere and Stavely (71). Their ideas were elaborated in 1965 by Choppin and Strazik (29) and Choppin and Graffeo (34).

The second step in the formation of a rare-earth complex is the loss of hydrated water molecules by the ligand. This step will also be an endothermic process for the same reasons that the loss of water by the cation was an endothermic process. No data appears to be available on the values of the hydration energies of the carboxylate ions. However, one may safely assume that, because of the lower charge and irregular shape, the hydration energies of the carboxylate anions are much smaller than the hydration energies of the rare-earth cations. Moreover, one can assume that the extent of hydration of a ligand is related to its basicity: the more basic the ligand, the greater the probable degree of hydration.

The entropy change for the second step, ΔS_{1b}, will be positive, since the ordered water structure in the vicinity of the anion will be destroyed.

The values of ΔH_{1b} and ΔS_{1b} depend only on the nature of the ligand and should be constant for a given series of rare-earth complexes. Although consideration of ΔH_{1b} and ΔS_{1b} may not contribute to the understanding of stability trends within a given series of rare-earth complexes, differences in these quantities may partially explain the relative stability of different ligands with respect to the rare-earth ions.

The significance of the degree of hydration of the ligand in rare-earth stability constant studies was first pointed out by Powell in 1966 (10).

The third step in the formation of a rare-earth complex is the easiest to understand thermodynamically. The negatively charged ligand bonds to the positively charged rare-earth cation. The enthalpy of this step will be coulombic and depend inversely on the separation of the charges. For a given ligand, the enthalpy of this step will depend only on the ionic radius. The ionic radii of the rare-earth ions are shown plotted against atomic number in Figure 11 (72). The third step will be exothermic, and the exothermicity will increase with decreasing ionic radius.

The relation between rare-earth stability constant values and ionic radii has also been known for some time. In 1955 Jones (73) pointed out the almost linear relation between $\log K_1$ for rare-earth EDTA complexes and rare-earth ionic radius.

A number of authors (37, 74, 75) have considered the possibility of ligand field stabilization energy contributions to the enthalpy of rare-earth complex formation. Since the 4f orbitals are buried beneath the 5s and 5p orbitals, they probably cannot participate in covalent bonding. However, the electric field surrounding a rare-earth ion can remove the degeneracy in the energy of these orbitals.

The electronic properties of crystalline rare-earth compounds have been studied in detail (76, 77), and it has been found that spin-orbit coupling is far more important in determining the energy of the 4f orbitals than crystal field splitting. The spin-orbit couplings for these electrons are of the order of several thousand wave numbers, while the crystal field splittings are only one to two hundred wave numbers (78, p. 114). Consequently the magnetic and spectral properties of crystalline rare-earth compounds primarily reflect spin-orbit coupling and are almost independent of the chemical environment.

Several authors have studied the electronic properties of rare-earth complexes in solution (79, 80, 81). The 4f orbitals appear to be split energetically by the ligand field, and the magnitude of the splitting (100 to 200 cm^{-1}) is approximately the same as in crystals. However, the spectral and magnetic properties of rare-earth complexes in solution have been difficult to interpret quantitatively in terms of ligand field theory. Since the geometry of the complexes is uncertain, one cannot be certain of the symmetry of the ligand field. Without a knowledge of the symmetry of the ligand field, the exact manner in which the 4f orbitals can be split into different energy levels cannot be determined.

Although it is certain that the 4f orbitals are affected by the ligand field in rare-earth complexes, opinion is divided over the comparative significance of ligand field stabilization energy in determining the stability of the complexes. Most workers have ignored this factor entirely and have interpreted all aspects of rare-earth stability constant data in terms of other thermodynamic factors. In support of this attitude Orgel (82) has pointed out that the ligand field produced by a ligand which coordinates through oxygen, such as a carboxylate ion, should not be much stronger than the ligand field produced by the oxygen atoms of the water molecules surrounding the aqueous ion. Of course this observation does not hold for ligands which also coordinate through nitrogen, such as the aminopolycarboxylates.

On the other hand, Stavely and Randall (74) have employed qualitative ligand field theory to explain such features of rare-earth stability constant data as the so-called "gadolinium break", and Yatsimirskii and Kostromina (75) have used semiquantitative ligand field theory in an attempt to explain almost all the features of rare-earth stability constant data.

Stavely and Randall noted that ligand field stabilization would always be absent in the complexes of the lanthanum, gadolinium, lutetium, and yttrium ions. In the lanthanum and yttrium ions the 4f orbitals are empty; in the gadolinium ion they are half filled; and in the lutetium ion they are completely filled. Thus in a plot of $\log\beta_1$ versus atomic number or ionic radius the values of $\log\beta_1$ for lanthanum, gadolinium, and lutetium should be slightly out of line with the other members of the series, assuming that a certain amount of ligand field stabilization energy contributes to the stability of the complexes of all the other rare-earth ions. This phenomenon has been observed in many sets of rare-earth stability constant data and may be seen in some of the graphs in the previous two chapters. The drop in stability at gadolinium was noted early in rare-earth complex studies and was named the "gadolinium break" (83). Another frequently encountered phenomenon is the exceptionally low stability of many yttrium complexes. Since the radius of the yttrium ion is almost the same as that of the erbium ion, it might be expected that the complexes of these two metals would be of similar stability. According to Stavely and Randall, the lack of ligand field stabilization energy accounts for the lower stability of the yttrium complexes.

Yatsimirskii and Kostromina tried to explain nearly all the different patterns observed in $\log\beta_1$ versus atomic number curves of rare-earth stability constant data in terms of the differences in the amount of ligand field stabilization energy that the ions attain in different environments. They explained the shape of the $\log\beta_1$ versus atomic number curve for the HEDTA complexes (Figure 4) by proposing that the value of 14Dq for the complexed ion varied in a different way with increasing atomic number than the value of 14Dq for the hydrated ion. They offered little experimental proof for their proposals, and their assumption of octahedral symmetry for all rare-earth complexes invalidated many of their conclusions. All recent structural studies have ruled out octahedral symmetry for rare-earth complexes, since the coordination number of the rare-earth ions is never less than eight.

In summary, it may be said that ligand field theory is at present of very limited applicability in rare-earth stability constant studies. It may be assumed that ligand field stabilization energy does make a small contribution to the enthalpy of complex formation in the case of all the ions except the four mentioned above. However, one cannot go into any more detail until the geometry of rare-earth complexes is definitely established. It might then be possible to use ligand field theory in a quantitative explanation of some aspects of rare-earth stability constant data. Even then however, ligand field stabilization energy might prove to be of negligible importance in most rare-earth complex systems.

The entropy change for the third step, ΔS_{1c}, is negative, since the order of the system is increased and the configurational entropy of the ligand is decreased. Moeller and co-workers have stressed the role of configurational entropy changes in their explanation of the stability trends in the rare-earth polyaminopolycarboxylate complexes (3, 58). Their data on EDTA and HEDTA complexes indicate that ΔS_1 increases substantially as the atomic number of the rare-earth ion increases; for example, Moeller and Ferrus (58) found ΔS_1 to be 54.2 cal/deg-mole for the lanthanum HEDTA complex and 73.4 cal/deg-mole for the lutetium HEDTA complex at 25° and 0.1000 molar ionic strength. The increase in ΔS_1 was thought by Moeller and Ferrus to be due to the progressive decrease in the loss of configurational entropy by the ligand as the cationic radius decreases. They assumed that, as the ionic radius decreases, the bond strength and steric hindrance increase, thereby loosening the bond and allowing for an increase in the configurational entropy of the ligand. Considerations based on configurational entropy differences, if valid, will be more relevant for complexes of larger ligands, such as polyaminopolycarboxylates, than for complexes of smaller ligands such as simple carboxylates.

The discussion above has considered the thermodynamic factors controlling the value of the first step formation constant. The step formation constants of the higher complexes are governed by the same factors as well as additional kinetic and electrostatic factors. Further discussion of the higher step formation constants will be left for the next section.

B. Interpretation of Experimental Data

In this section experimental evidence will be offered in support of the model of complex formation proposed above, and the new results reported in the previous chapter will be interpreted in terms of this model.

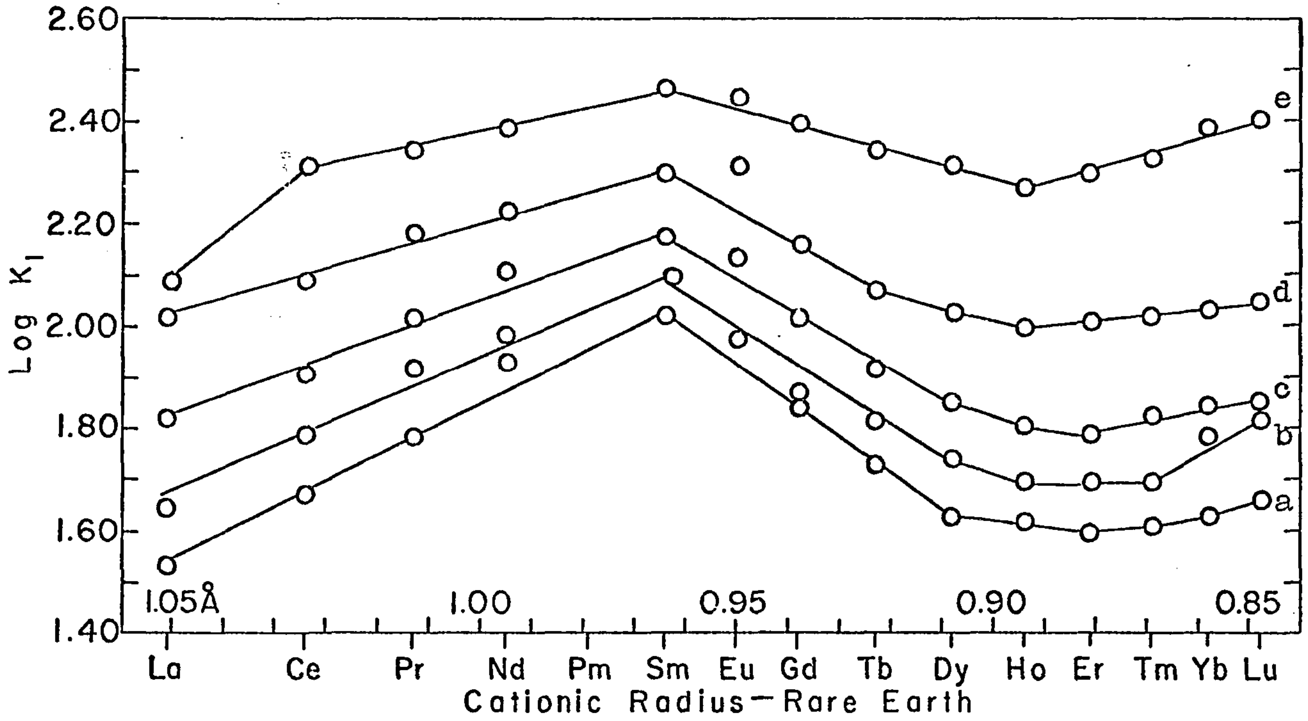
A large amount of data is available on rare-earth stability constants and consequently on the free energies of complex formation. On the other hand, little reliable data is available on the enthalpies and entropies of complex formation. One series of ligands for which all the desired information is available is the acetate, propionate, and isobutyrate series. These data will be used to illustrate the theory of complex formation discussed in the preceding section.

The values of log K_1 reported by several authors for the rare-earth acetate (30, 31, 32), propionate (34), and isobutyrate (21, 34) are plotted against cationic radius in Figures 12 and 13. The values of $-\Delta H_1$ obtained by Grenthe (31) for the rare-earth acetates are plotted in Figure 14 along with the $-\Delta H_1$ values obtained by Choppin and Graffeo (34) for the propionates and isobutyrates. The corresponding values of ΔS_1 for the three sets of complexes are plotted in Figure 15.

It can be seen that the enthalpy of formation of the three simple carboxylates is endothermic and varies from about 2 to 5 kcal/mole. The corresponding values of $T\Delta S_1$ vary from about 4 to 8 kcal/mole. Thus the entropy and enthalpy

Figure 12. Logarithms of the first formation constants of some rare-earth complexes as functions of cationic radius

a: propionates, data of Choppin and Graffeo (34), T = 25°C, I = 2 M
b: isobutyrates, data of Stagg and Powell (21), T = 25°C, I = 0.5 M
c: acetates, data of Kovar (32), T = 25°C, I = 0.1 M
d: acetates, data of Kolat and Powell (30), T = 20°C, I = 0.1 M
e: 2,2-bis(hydroxymethyl)propionates, this work, T = 25°C, I = 0.1 M



2.60
2.40
2.20
2.00
1.80
1.60
1.40
Log K1
e
d
c
b
a
1.05Å
1.00
0.95
0.90
0.85
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Cationic Radius—Rare Earth

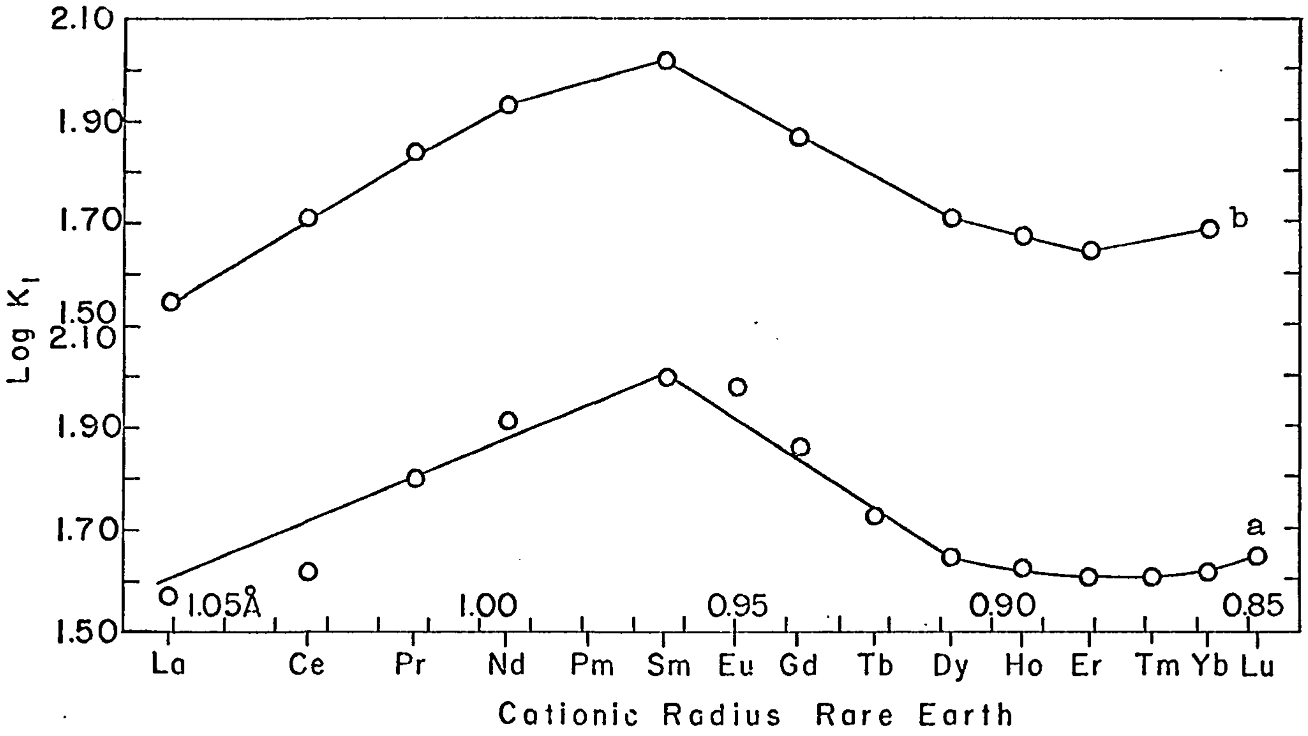


Figure 13. Logarithms of the first formation constants of some rare-earth complexes as functions of cationic radius
a: isobutyrates, data of Choppin and Graffeo (34), T = 25°C, I = 2 M
b: acetates, data of Grenthe (31), T = 25°C, I = 2 M

Figure 14. Enthalpies of formation of some 1:1 rare-earth complexes as functions of cationic radius at T = 25°C and I = 2 M

a: isobutyrates, data of Choppin and Graffeo (34)
b: propionates, data of Choppin and Graffeo (34)
c: acetates, data of Grenthe (31)
d: glycolates, data of Choppin and Friedman (84)
e: α-hydroxyisobutyrates, data of Choppin and Friedman (84)
f: lactates, data of Choppin and Friedman (84)

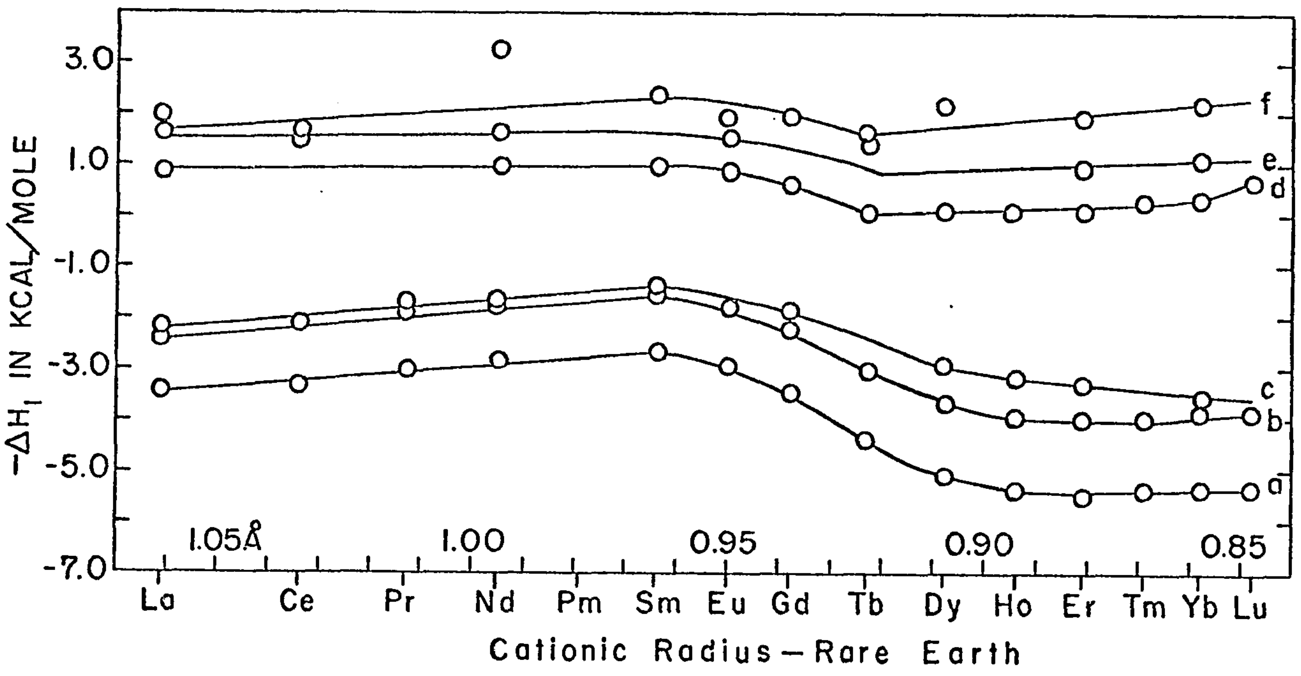
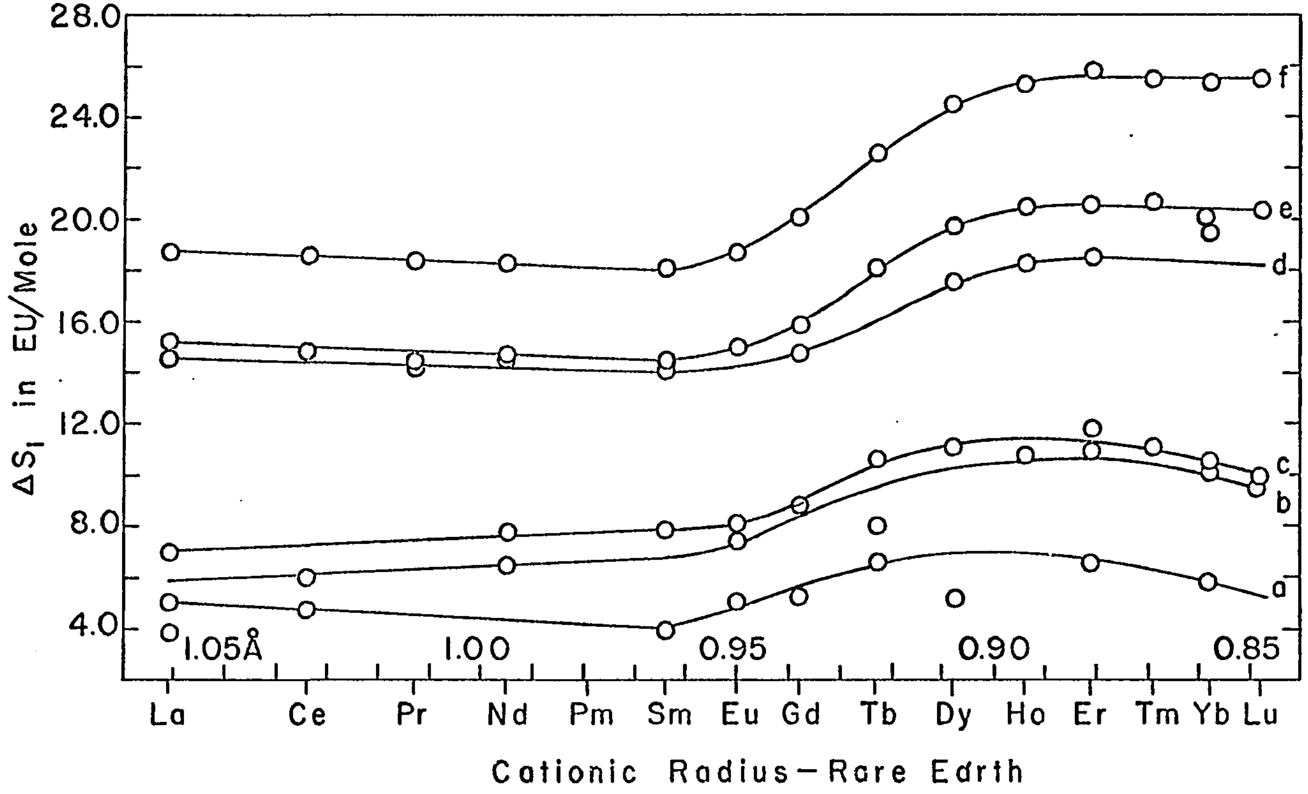

-ΔH₁ IN KCAL/MOLE
3.0
1.0
-1.0
-3.0
-5.0
-7.0
1.05Å
1.00
0.95
0.90
0.85
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
f
e
d
c
b
a
Cationic Radius — Rare Earth

Figure 15. Entropies of formation of some 1:1 rare-earth complexes as functions of cationic radius at T = 25° and I = 2 M

a: lactates, data of Choppin and Friedman (84)
b: α-hydroxyisobutyrates, data of Choppin and Friedman (84)
c: glycolates, data of Choppin and Friedman (84)
d: acetates, data of Grenthe (31)
e: propionates, data of Choppin and Graffeo (34)
f: isobutyrates, data of Choppin and Graffeo (34)


28.0
24.0
20.0
16.0
12.0
8.0
4.0
ΔS_1 in EU/Mole
1.05Å
1.00
0.95
0.90
0.85
f
e
d
c
b
a
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Cationic Radius—Rare Earth

terms are of equal importance in these systems, and the stability of the complexes results from $T\Delta S_1$ always being slightly larger than ΔH_1.

The $\log K_1$ values in Figures 12 and 13 all show the same basic trends: the value of $\log K_1$ increases from lanthanum to samarium, decreases from europium to holmium, and increases again from erbium to lutetium. The values of $-\Delta H_1$ follow the same trends as $\log K_1$, while ΔS_1 decreases slightly from lanthanum to samarium, increases rapidly from europium to holmium, and then remains almost constant from erbium to lutetium.

The endothermicity of the formation of these series of complexes is apparently due to the fact that the exothermicity of ΔH_{1c} is not sufficient to overcome the endothermic nature of ΔH_{1a} and ΔH_{1b}. On the other hand, the positive character of ΔS_{1a} and ΔS_{1b} probably account for the fact that ΔS_1 is positive. With each ligand, ΔH_1 and ΔS_1 should remain roughly constant for the first six rare-earth ions. As the ionic radius decreases, ΔH_{1c} becomes more negative and ΔH_1 becomes less endothermic; therefore $\log K_1$ increases almost linearly with decreasing ionic radius throughout this region of the curve. Since ΔH_{1b}, ΔS_{1b}, and ΔS_{1c} depend primarily on the nature of the ligand, they are not expected to influence the shape of the $\log K_1$ versus ionic radius curve.

The value of ΔH_{1c} should continue to become more negative from europium to holmium; however, the large increase in the endothermicity of ΔH_{1a} which accompanies the increased hydration of these five ions overshadows this factor. Although ΔS_1 also increases, the sharp increase in ΔH_1 (or decrease in $-\Delta H_1$) causes a steady decrease in $\log K_1$.

The hydration sphere reaches its maximum size at holmium. The values of ΔH_{1a} and ΔS_{1a} become nearly constant for the next four ions, and $\log K_1$ again increases almost linearly with decreasing ionic radius.

In several of the $\log K_1$ *versus* ionic radius curves in Figures 12 and 13 there appears to be a slight drop in stability at lanthanum, gadolinium, and lutetium. It is tempting to attribute this to a lack of ligand field stabilization energy for these three ions. The data are not consistent enough in this respect however, to allow for a conclusive interpretation in terms of ligand field theory.

The thermodynamic data of Grenthe and of Choppin and Graffeo indicate that ΔH_1 and ΔS_1 both increase with ligand size. This is to be expected, since the bulkier the ligand, the greater the disruption of the hydration sphere and the greater the relative magnitudes of ΔH_{1a} and ΔS_{1a}.

The values of $\log K_1$ for the 2,2-bis(hydroxymethyl)propionate complexes are also presented in Figure 12. It can easily be seen that the variation in $\log K_1$ with ionic radius for this set of complexes follows the same pattern as the simple carboxylates. One can therefore attribute the variation in $\log K_1$ for these complexes to the same changes in enthalpy and entropy that were shown to underlie the variations in $\log K_1$ for the simple carboxylates. And one can assume that the same model of complex formation is valid. Thus the increase in $\log K_1$ from lanthanum to samarium and from erbium to lutetium is a direct consequence of decreasing ionic radius and increasing $-\Delta H_1$. The decreasing stability from europium to holmium results from the progressive increase in the average size of the hydration sphere which causes a drop in $-\Delta H_1$ for the complexes of the ions in the middle of the rare-earth series.

There appears to be a drop in the stability of the BHMPA complexes of the three ions lanthanum, gadolinium, and lutetium which might be attributed to the absence of ligand field stabilization energy. The value of $\log K_1$ for the lanthanum complex appears to be markedly out of line with the values of $\log K_1$ for the complexes of the next four ions; however, the lanthanum value was checked several times for experimental errors and must be considered as reliable as any of the other values reported. The yttrium complex of the BHMPA ligand is weaker than the erbium complex of the same ligand; this fact might also reflect the absence of ligand field stabilization energy.

The BHMPA ligand is apparently a stronger ligand than the simple carboxylate ions. The greater strength of this ligand may be partially due to its size and the correspondingly larger value of ΔS_{1a}. However, there is evidence that the dentate character of the BHMPA ligand is higher than that of the simple carboxylates. This possibility will be considered later in connection with K_1/K_2 ratios.

When the graphs in Figures 12 and 13 are compared with each other, it can be seen that the discontinuities at samarium and holmium become less pronounced as the stability of the complex series increases. Thus the curve for BHMPA is smoother than those of the other complex systems. It is also to be noted that with very strong ligands, such as EDTA or HEDTA, the discontinuities in $\log K_1$ associated with changes in the size of the hydration sphere are completely absent (Figure 4). An explanation for these phenomena may be found by considering the comparative importance of $-\Delta H_1$ and $T\Delta S_1$ in determining the value of $\log K_1$. As pointed out earlier, the thermodynamic data on the carboxylate complexes indicate that $-\Delta H_1$ and $T\Delta S_1$ are of equal importance; for example, for the lanthanum propionate system $-\Delta H_1$ was found to be -2.47 kcal/mole and $T\Delta S_1$ was found to be 4.56 kcal/mole (34). However, for many strong complexes the entropy term is much more important than the enthalpy term; for example, Mackey, Powell, and Spedding (83) found $-\Delta H_1$ to be 2.93 kcal/mole and $T\Delta S_1$ to be 17.8 kcal/mole for the lanthanum EDTA complex. It appears that with weak ligands the trends in $-\Delta H_1$ govern the trends in $\log K_1$; thus the discontinuities in $-\Delta H_1$ at samarium and holmium usually appear as discontinuities in $\log K_1$. With stronger ligands, the discontinuities in $\log K_1$ at samarium and holmium become attenuated as $T\Delta S_1$ becomes increasingly larger than $-\Delta H_1$. With the strongest ligands, the trends in $T\Delta S_1$ almost completely determine the trends in $\log K_1$.

There are a number of differences between the thermodynamic properties of the rare-earth complexes of the simple carboxylate ligands and those of the α-hydroxycarboxylate ligands. The differences, as well as the similarities, between these two groups of complexes can be explained in terms of the model of complex formation proposed above.

The $\log K_1$ data published by various authors for the glycolate (36, 84), lactate (84), α-hydroxyisobutyrate (84), and 1-hydroxycyclopentanecarboxylate (9) complexes are plotted against ionic radius in Figures 16 and 17. The $-\Delta H_1$ and ΔS_1 values found by Choppin and Friedman (84) for the glycolate, lactate, and α-hydroxyisobutyrate systems are plotted in Figures 14 and 15 respectively. The enthalpy and entropy data published by these authors are reasonably reliable and are in good agreement with a partial set of calorimetric data found by Grenthe (31) under the same experimental conditions. On the other hand, the $-\Delta H_1$ and ΔS_1 values published by Choppin and Friedman for the lactate and α-hydroxyisobutyrate complexes are of limited value: the estimated errors in these quantities are often over 20%, and several of the rare-earth ions were not studied. The $-\Delta H_1$ and ΔS_1 curves for the lactate and α-hydroxyisobutyrate series in Figures 14 and 15 are drawn similar to the curve for the glycolate series;

Figure 16. Logarithms of the first formation constants of some rare-earth complexes as functions of cationic radius

a: glycolates, data of Choppin and Chopoorian (37, 84), T = 25°C, I = 2 M
b: lactates, data of Choppin and Chopoorian (37, 84), T = 25°C, I = 2 M
c: glycolates, data of Powell, Karraker, Kolat, and Farrell (35), T = 20°C, I = 0.1 M
d: lactates, data of Powell, Karraker, Kolat, and Farrell (35), T = 20°C, I = 0.1 M

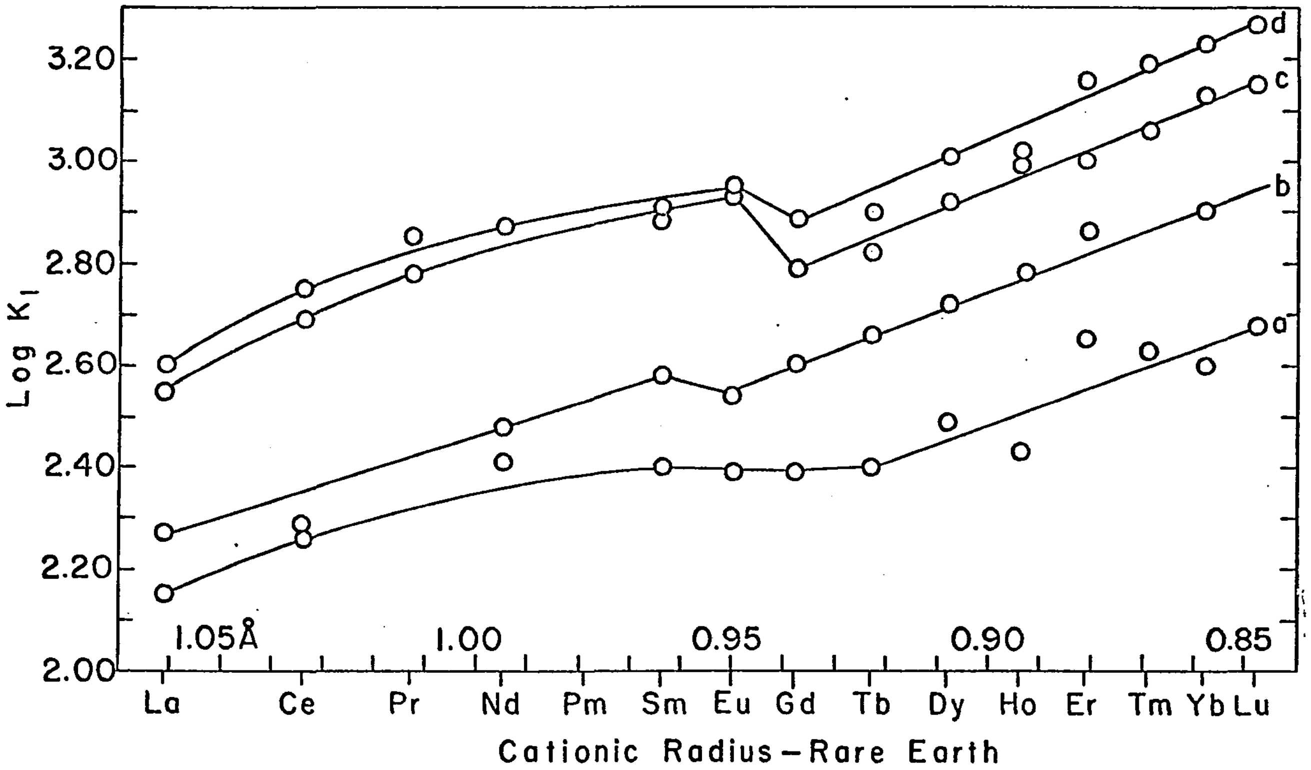
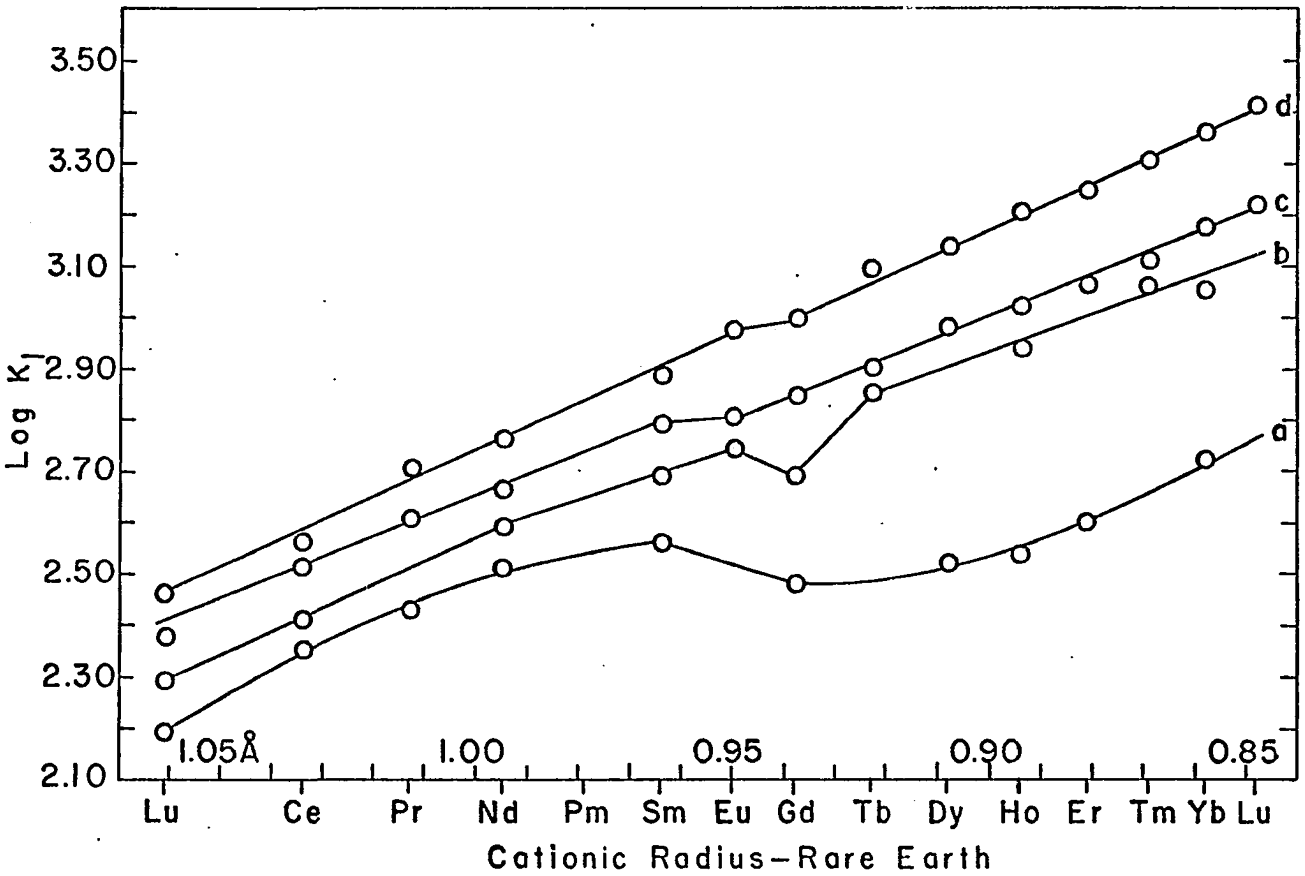

3.20
3.00
2.80
2.60
2.40
2.20
2.00
Log K_1
1.05Å
1.00
0.95
0.90
0.85
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Cationic Radius – Rare Earth
d
c
b
a

Figure 17. Logarithms of the first formation constants of some rare-earth complexes as functions of cationic radius

a: glycolates, data of Sonesson (36), T = 20°C, I = 2 *M*
b: α-hydroxyisobutyrates, data of Choppin and Chopoorian (37, 84), T = 25°C, I = 2 *M*
c: 1-hydroxycyclopentanecarboxylates, data of Powell and Rowlands (9), T = 25°C, I = 0.1 *M*
d: α-hydroxyisobutyrates, this research, T = 25°C, I = 0.1 *M*


Log K1
3.50
3.30
3.10
2.90
2.70
2.50
2.30
2.10
1.05Å
1.00
0.95
0.90
0.85
Lu
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
a
b
c
d
Cationic Radius–Rare Earth

however, as Choppin and Friedman pointed out, a straight line would fit the data as well as the glycolate-type curve.

There are several interesting features of the α-hydroxycarboxylate data which contrast with the data on the simple carboxylate complexes. The ΔH_1 values for the glycolate series of ligands are exothermic, while the ΔH_1 values for the acetate series were endothermic. Also, the ΔS_1 values for the glycolate group are smaller than those for the acetate group. Finally, the plots of $\log K_1$ versus ionic radius for the glycolate group do not show the decrease in stability from europium to holmium that was characteristic of the simple carboxylate complexes.

Since the calorimetric data for the glycolate series are the most reliable, an interpretation of these data in terms of the proposed model of rare-earth complex formation will be undertaken first. Then, these considerations will be extended to similar series of complexes, particularly the α-hydroxyisobutyrate complexes studied in this dissertation.

Two reasons may be advanced for the exothermicity of the rare-earth glycolate complexes as compared with the endothermicity of the acetate complexes. First, the participation of the hydroxyl group in bonding, thereby forming a five-membered chelate ring, will result in a stronger bond and a more negative value of ΔH_{1c}. Secondly, while the acetate ion is hydrated, via hydrogen bonding between the carboxylate oxygens and surrounding water molecules, the glycolate ion probably is not. The α-hydroxycarboxylate ions are thought to form an intramolecular hydrogen bond between a carboxylate oxygen and a hydroxyl group (10). Therefore, energy does not have to be supplied to dehydrate the glycolate ion prior to complex formation, although some energy will be needed to break the hydrogen bond. As a result, ΔH_{1b} will be much smaller for the glycolate ion than for the acetate ion. Thus, for rare-earth acetate complexes, the sum of ΔH_{1a} and ΔH_{1b} is greater than $-\Delta H_{1c}$; whereas for glycolate complexes, $-\Delta H_{1c}$ is greater than the sum of ΔH_{1a} and ΔH_{1b}.

The lower ΔS_1 values for the glycolate complexes as compared with the acetate complexes may be explained in a similar fashion. While ΔS_{1b} is positive in the case of the acetates because of the dehydration of the ligand, ΔS_{1b} is probably much smaller in the case of the glycolates. Some authors (31, 84, 85) have further suggested that the α-hydroxycarboxylates, when forming chelates, incorporate a water molecule between the hydroxyl group and the metal. The consequent formation of a seven-membered ring is assumed to be responsible for the lowering of ΔS_1. The formation of a seven-membered ring rather than a five-membered ring is however rather unlikely because of steric factors. Normally, five-membered rings are far more stable than larger rings, because strains on the bond angles are minimized (86, p. 157).

The trends observed in ΔH_1 and ΔS_1 for the glycolate complexes are more difficult to rationalize than their comparative magnitudes. As can be seen in Figure 14, $-\Delta H_1$ increases very slowly from lanthanum to samarium, decreases smoothly from europium to terbium, and then increases slowly again from dysprosium to lutetium with a slight upward turn for the last two elements. Similarly, ΔS_1 increases gradually from lanthanum to samarium, increases rapidly from europium to terbium, and then remains almost constant for the remaining elements with a slight downward turn for the last two metals. As a result of the trends in $-\Delta H_1$ and ΔS_1, the values of $\log K_1$ increase from lanthanum to samarium, drop from europium to gadolinium, and then increase from terbium to lutetium. As can be seen in Figures 16 and 17, the three plots of $\log K_1$ versus ionic radius for glycolate complexes can be more or less resolved into two separate segments, one from lanthanum to samarium, and the other from gadolinium to lutetium. The increase in $\log K_1$ from lanthanum to samarium is not strictly linear and shows a leveling off at samarium; this feature is apparent in all three sets of data. The values of $\log K_1$ from gadolinium to lutetium show considerable scatter about the straight line drawn through them; however, no consistent deviations from linearity can be observed in all three sets of data, so that the scatter can be attributed to experimental errors.

The changes in $-\Delta H_1$ and ΔS_1 observed in the middle of the glycolate series are much less pronounced than those exhibited by the simple carboxylate series. Moreover, the changes in these quantities appear to level off at terbium rather than at holmium. The increase in the size of the cationic hydration sphere known to take place between samarium and holmium should be independent of the nature of the ligand present; therefore, ΔH_{1a} and ΔS_{1a} might still be expected to increase substantially from samarium to holmium. Apparently an additional factor enters the picture with the glycolate complexes which partially overcomes the expected drop in stability in the samarium to holmium region: this factor is most likely a change in the dentate character of the ligand.

The effect of a decrease in dentate character on the expected values of ΔH_{1a} and ΔS_{1a} was discussed in the previous section. It was pointed out that a lower dentate character would require less disruption of the hydration sphere and consequently lower the values of ΔH_{1a} and ΔS_{1a}. Of course, a lower dentate character would mean a less exothermic ΔH_{1c}, but at the same time it might allow for an increase in the configurational entropy of the ligand, thereby increasing ΔS_{1c}. It is therefore possible that in the middle of the rare-earth series, where the average size of the hydration sphere is rapidly increasing, the lower dentate character becomes energetically more favorable, and a drop in stability throughout the europium to holmium region is avoided. Such a decrease in dentate character might be gradual and follow the gradual decrease in coordination number and consequent increase in hydration of the rare-earth ions that is known to take place in the middle of the series. The variation of $\log K_1$ with ionic radius should be smoother than otherwise, if a change in dentate character gradually compensates for the increase in hydration of the metal ion.

Two pieces of experimental evidence suggest that the glycolate ion exhibits a different dentate character in the complexes of the lighter rare-earth ions than it does in the complexes of the heavier rare-earth ions. Powell and Farrell (87) have found that the rare-earth triglycolates from lanthanum to europium separate from solution as anhydrous salts, while those from gadolinium to lutetium separate as dihydrates. More significant however, is the fact that K_1/K_2 ratios for the lighter rare-earth glycolates are larger than those of the heavier rare-earth glycolates. Because of kinetic factors, the K_1/K_2 ratios are directly related to the dentate character of the ligand. The significance of K_1/K_2 ratios will be considered in more detail presently.

Assuming that the above interpretation of the rare-earth glycolate data is valid, the same analysis can be extended to other α-hydroxycarboxylate systems for which reliable calorimetric data are unavailable. If one examines the $\log K_1$ *versus* ionic radius curves for the lactate, α-hydroxyisobutyrate, and 1-hydroxycyclopentanecarboxylate complexes as presented in Figures 16 and 17, one can see that each of these curves may be resolved into straight line segments with the break between the two segments occurring between samarium and gadolinium.

The two linear segments are usually parallel. The drop in stability between samarium and gadolinium varies in magnitude from one complex series to another: it is most pronounced with the glycolates and barely perceptible with the α-hydroxyisobutyrates.

The relation between $\log K_1$ and ionic radius for the αHIB complexes studied by the author is almost linear throughout. One straight line would fit all fourteen data points almost as well as the curve drawn in Figure 17. Although the $\log K_1$ data published by other workers (21, 37, 39, 47, 63) for the αHIB complexes show more scatter, one straight line could be drawn that would fit each of these data sets reasonably well. If $\log K_1$ for αHIB complexes were a strictly linear function of rare-earth ionic radius, it would be tempting to conclude that only an electrostatic factor (interionic charge separation) governs the stability of the complexes. However, when the αHIB data are considered in relation to the data found for similar ligands and the known properties of the rare-earth ions, it is evident that the apparent linearity of the $\log K_1$ _versus_ ionic radius curve is the result of several competing trends in ΔH_1 and ΔS_1 and that several factors must govern the stability of the complexes.

On the basis of the explanation proposed above for the trends in the rare-earth glycolate data, the following explanation for the trends in $\log K_1$ of the αHIB complexes may be suggested. First, the increase in stability from lanthanum to samarium no doubt results from the increase in $-\Delta H_{1c}$ which accompanies decreasing ionic radius. The slight drop in stability at europium and gadolinium reflects the increase in the average size of the hydration sphere that accompanies the gradual decrease in the coordination number of the ions from europium to holmium. The fact that $\log K_1$ begins to increase again after gadolinium may be due to a decrease in dentate character brought on by the increasing degree of hydration. The formation of a complex with a lower dentate character may be energetically more favorable for those ions which have the larger hydration sphere and lower coordination number; on the other hand, formation of a complex with higher dentate character may be energetically more favorable for those ions which have the smaller hydration sphere and larger coordination number. Since it is often assumed that two types of aqueous ions, differing in coordination number, exist for the rare earths from europium to dysprosium, it is not impossible that two types of complex can coexist in varying amounts for these ions. Finally, the complexes of the last five rare-earth ions all have the same lower dentate character, and $\log K_1$ will again increase with decreasing ionic radius.

The most questionable aspect of this discussion is the assumption of the change in dentate character. The principal experimental support for this assumption comes from consideration of the K_1/K_2 ratios. It is therefore necessary to discuss the theory and application of K_1/K_2 ratios in detail.

The statistical dependence of the ratios of the successive dissociation constants of polyprotic acids was first pointed out by Ostwald in 1889 (88). N. Bjerrum (89) subsequently developed a quantitative theory of successive dissociation constants that utilized concepts from the Debye-Huckel theory of electrolytic solutions. J. Bjerrum (16) later extended this theory to the study of the successive formation constants of transition metal complexes.

According to J. Bjerrum, the ratio of two successive formation constants is given by the ratio,

$$*K_n/*K_{n+1} = S \times E \times R. \qquad (27$$

The term S is called the statistical factor; it takes into account the extent to which K_n is kinetically favored over K_{n+1}. The quantity E is defined as the coulombic factor; it takes into consideration the degree to which K_n is electrostatically favored over K_{n+1} when the ligand bears a negative charge. The term R is called the rest factor and includes any other relevant factors such as steric hindrance.

The value of S may be derived directly from consideration of the two formation constants, K_n and K_{n+1}. Each of these constants is equal to the rate constant of the forward step over the rate constant of the reverse step. The rate constant of the forward step, in each case, is proportional to the number of sites at which the ligand can bond to the preexisting complex. The rate constant of the reverse step, in each case, is proportional to the number of ways in which the product complex can lose a ligand to re-form the original complex.

If the ligand is monodentate and the coordination number of the cation is N, it can easily be seen that

$$S = \frac{(N - n + 1)(n + 1)}{n(N - n)}.$$

If the ligand is polydentate, in order to find the factors proportional to the forward rate constants one must examine the geometry of each reactant complex to determine the number of sites available to the ligand. This step is facilitated by the use of structural models. The reverse rate constants will always be proportional to the number of ligands present in the product complex.

Before one can determine the values of S for rare-earth complexes, one must consider the possible geometric structures of these complexes.

Many X-ray crystallographic studies have been made on rare-earth compounds, and a coordination number of nine has been found in most cases. In the compound $Nd(H_2O)_9(BrO_3)_3$ (90) and in the compounds $M(C_2H_5OSO_3)_3(H_2O)_9$ (91), where M is lanthanum, praseodymium, erbium, or yttrium, the cation is surrounded by nine water molecules, six of which are at the apices of a right triangular prism with the other three situated beyond each rectangular face of the prism. The same coordination number and geometric arrangement is found for rare-earth cations, according to Wells (92, pp. 74, 340, 553), in the following compounds: the trihydroxides of lanthanum, praseodymium, neodymium, samarium, gadolinium, dysprosium, erbium, and ytterbium; the trichlorides of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, and gadolinium; and in the tribromides of lanthanum, cerium, and praseodymium. A similar but slightly distorted 9-coordinate array of donor atoms has recently been found (93) in solid EDTA complexes of the type $[M(EDTA)(H_2O)_3]^-$, where M represents all the rare-earth ions from lanthanum to terbium. However, in complexes of the type $HM(EDTA)(H_2O)_4$ a coordination number of ten has been found (93).

An X-ray diffraction study of the aqueous gadolinium ion (94) indicated a coordination number of eight or nine for this ion. A coordination number of eight has also been found for the gadolinium ion in crystals of $GdCl_3 \cdot 6H_2O$, where the $[Cl_2Gd(H_2O)_6]$ ion has been shown to be present (95).

The statistical ratios calculated by Powell (10) for all possible geometries of complexed rare-earth cations are listed in Table 7.

The term E in equation 27 takes into account the electrostatic factors which influence the K_n/K_{n+1} ratio when the ligand bears a negative charge. The presence of one or more negatively charged ligands in a complex reduces the overall charge of the complex and inhibits the approach of additional

Table 7. Statistical ratios of successive formation constants

coordination number	geometric configuration	dentate character	S
10	archimedian antiprism + 2	tridentate	4.92
		bidentate	3.13
		monodentate	2.22
9	triangular prism + 3	tridentate	4.92
		bidentate	3.27
		monodentate	2.25
8	dodecahedron	tridentate	7.11
		bidentate	3.64
		monodentate	2.29
8	archimedian antiprism	tridentate	5.33
		bidentate	3.56
		monodentate	2.29
8	cube	tridentate	7.33
		bidentate	3.43
		monodentate	2.29
7	pentagonal bipyramid	tridentate	10.00
		bidentate	4.09
		monodentate	2.33
6	octahedron	tridentate	16.00
		bidentate	4.80
		monodentate	2.40

ligands.

J. Bjerrum (16) developed an equation for calculating E from Coulomb's law. Unfortunately, because of the oversimplifications in his model, Bjerrum's equation is of little practical use. For rare-earth complexes with uninegative ligands, Bjerrum's equation would predict a value of about 4 for E; this result is much too large, since many experimental K_1/K_2 ratios are themselves less than 4.

Since E cannot, as a rule, be calculated theoretically, it must be obtained experimentally (96). If stepwise enthalpies of formation are available, one can use equation 26 to obtain the relation

$$\log E = \frac{\Delta H_2 - \Delta H_1}{2.3RT}, \qquad (28$$

assuming that only electrostatic factors are responsible for the differences in successive enthalpies. The most reliable set of calorimetric data on rare-earth complexes with uninegative ligands is probably Grenthe's data on the glycolate system (31). Nevertheless, his values of ΔH_2 show a number of apparently random fluctuations, and the values of E that one can calculate from his data using equation 28 vary from 0.43 to 1.45. Other sets of ΔH_2 data (34, 84) are so unreliable that calculations of E from them would be pointless. The calculations of E from Grenthe's data probably reveal the approximate magnitude of E, even though they do not yield an unequivocal value for this constant.

The only remaining course is to employ values of E which have been found for other complex systems involving uninegative ligands. This procedure is justifiable since E is basically a ligand effect and depends primarily on the charge of the ligand and not on the nature of the metal cation.

Manning (97, 98, 99) has found a value of 1.6 for E in many complex systems involving uninegative ligands. A study by Larson and Folkeson (100) indicated a value of 1.4 for this constant. Thus one can assume that E for rare-earth complexes with uninegative ligands is approximately 1.6 ± 0.1. When more accurate values of stepwise enthalpies of formation are available for rare-earth complexes, the value of E can be found with more certainty.

The rest factor (R) in equation 27 is usually ignored. It is only taken into consideration when such factors as steric hindrance, due to very large ligands, or strong ligand field effects influence the value of the K_1/K_2 ratio.

The thermodynamic K_1/K_2 ratio is related to the experimental K_1/K_2 ratio by means of the equation

$$\frac{{}^*K_1}{{}^*K_2} = \frac{K_1}{K_2}F'(f),$$

where

$$F'(f) = \frac{f_{MA}{}^2}{f_M f_{MA_2}}.$$

Applying the conventional form of the Debye-Hückel equation (equation 4), one finds

$$\log F'(f) = \frac{2AI^{\frac{1}{2}}}{1 + B\mathring{a}I^{\frac{1}{2}}}.$$

Substituting the average value of the ion-size parameter for rare-earth ions reported by Spedding and Atkinson (65) and the appropriate values of A and B at 25°, one obtains an estimated value of 1.56 for F'(f) at an ionic strength of 0.1000 molar. The value of the ion-size parameter depends to some extent on the particular rare-earth ion in question and on the anion of the background electrolyte. If the value of the ion-size parameter is varied within reasonable limits, F'(f) at 0.1000 molar ionic strength will vary by ±0.05.

Since the value of F'(f) at 0.1000 molar ionic strength is approximately the same as the coulombic factor for uninegative ligands, the experimental value of K_1/K_2 at 0.1000 molar ionic strength should be approximately equal to S, the statistical factor.

Powell and Rowlands studied the rare-earth complexes of the 1-hydroxycyclopentanecarboxylate (HCPC) ligand at an ionic strength of 0.1000 molar (9). They found that the average K_1/K_2 ratio from lanthanum to neodymium was 4.93 and that from terbium to lutetium the average K_1/K_2 ratio was 3.29. The K_1/K_2 ratios from samarium to gadolinium took on intermediate values. The ratio 4.93 is very close to the statistical factor of 4.92 for tridentate ligandcy on a nine- or ten-coordinate cation. The ratio 3.29 is very close to the statistical factor of 3.27 for bidentate ligandcy on a nine-coordinate cation and not too far removed from the statistical factors for bidentate ligandcy on an eight-coordinate cation (3.43, 3.56, and 3.64). Powell and Rowlands therefore concluded that the lighter rare-earth ions were bonded tridentately by the HCPC ligand, while the heavier rare-earth ions were bonded bidentately. The intermediate ratios found for samarium, europium, and gadolinium were thought to imply that mixtures of both types of complex were present with these ions. Although the data seemed to indicate that the drop in coordination number in the middle of the rare-earth series was from ten to nine, the possibility of a drop from nine to eight could not be excluded.

The question then arose as to how the HCPC ligand could bond tridentately. Geometric considerations precluded the possibility of both carboxylate oxygens bonding directly to the rare-earth ion. However, it might be possible for one of the carboxylate oxygens to bond indirectly, via a hydrogen bond to a coordinated water molecule, while the other carboxylate oxygen bonds directly. This postulate is similar to the one advanced by Grenthe concerning indirect bonding, via water, by the hydroxyl group (31). If both carboxylate oxygens participated in bonding, one directly and the other indirectly, a six-membered chelate ring would be formed. The drop in dentate character from tridentate to bidentate could involve either rupture of the indirect bond to one of the carboxylate oxygens, or rupture of the bond between the metal and the hydroxyl group.

An alternative explanation of the apparent tridentate character of the HCPC ligand is possible. Actually, the statistical factor, and hence K_1/K_2, is related to the dentate character of the ligand only insofar as the dentate character represents the number of coordination sites blocked by each ligand. It is possible that the second carboxylate oxygen, while not forming any bond to the cation, does block an additional coordination site from being occupied by another ligand.

Powell and co-workers have extended the study of K_1/K_2 ratios to several other sets of rare-earth stability constant data collected at 0.1000 molar ionic strength. The same values of K_1/K_2 found with the HCPC ligand have been encountered with quite a few other ligands.

The data reported by Fleischer (42) for the rare-earth ethylglycolates showed an average ratio of 4.8 for the lighter rare-earth ions and an average ratio of 3.3 from holmium to lutetium with intermediate values from gadolinium to dysprosium. The rare-earth ethylglycolates appear to follow the same pattern as the HCPC complexes.

A study of the rare-earth methylisopropylglycolates (10) indicated a ratio of 4.9, and therefore tridentate ligandcy, throughout the series. The somewhat less precise data of Fleischer on the methylethylglycolates seemed also to indicate tridentate ligandcy throughout the series, although the average K_1/K_2 ratio was only 4.5 (42).

The K_1/K_2 ratios found by Kovar (32) for the rare-earth acetates tend to indicate that the acetate ligand behaves bidentately throughout the series, since the average K_1/K_2 ratio is 3.77. Bidentate ligandcy for the acetates could only come about by means of the six-membered ring involving both carboxylate oxygens and a water molecule. However, if acetate behaved as a monodentate ligand, a K_1/K_2 ratio of 2.2 to 2.3 would be expected.

The K_1/K_2 ratios found by the author for the BHMPA complexes are listed in Table 5. If the ratios for praseodymium, neodymium, samarium, and europium are ignored, the other ten ratios have an average value of 4.84 ± 0.19. This value obviously suggests tridentate ligandcy, and tridentate behavior is conceivable with a β,β'-dihydroxycarboxylate ligand. The ratios for the ions from praseodymium to europium average 6.29 ± 0.29; this number is not close to any of the possible statistical factors. No explanation of these four values is apparent at this time, and one would hesitate to attribute them to experimental errors in view of their mutual consistency.

The K_1/K_2 ratios found by the author for the rare-earth αHIB complexes are listed in Table 3. The average value of K_1/K_2 from lanthanum to samarium is 4.89; this value is close to the statistical factor of 4.92 associated with tridentate bonding on a nine- or ten-coordinate cation. The average value of K_1/K_2 from holmium to lutetium is 3.55; this value is in the vicinity of the statistical factors for bidentate ligandcy on an eight-coordinate cation (3.43, 3.56, or 3.64), but it is not too far removed from the value of 3.27 associated with bidentate ligandcy on a nine-coordinate cation. The K_1/K_2 values from europium to dysprosium gradually drop from 4.52 to 4.10, suggesting that a mixture of both types of complexes is present. Hence, the αHIB ligand appears to follow almost the same pattern as the HCPC ligand.

Considerable support for the above interpretation of the αHIB stability constant ratios comes from a recent study by Matkovich (101). In this study the stability constants of the neodymium and thulium αHIB complexes were measured at several ionic strengths ranging from 0.05 to 0.70 molar. Aside from the use of KNO_3 as the supporting electrolyte and the use of rare-earth nitrate stock solutions, Matkovich employed the same experimental method and computational technique as used by the author. The relation between K_1/K_2 and $I^{\frac{1}{2}}$ was found to be almost linear; however, an exponential least squares curve showed smaller deviations than a straight line least squares curve. The exponential least squares curve found for the neodymium complexes was

$$\frac{K_1}{K_2} = 7.49e^{-0.573I^{\frac{1}{2}}},$$

and that for the thulium complexes was

$$\frac{K_1}{K_2} = 4.79e^{-0.713I^{\frac{1}{2}}}.$$

The intercepts of these curves at zero ionic strength should equal the thermodynamic step formation constant ratio $^*K_1/^*K_2$.

The thermodynamic stability constant ratio will equal the statistical factor S multiplied by the coulombic factor 1.5. The statistical factor for tridentate bonding on a ten-coordinate cation (4.92) multiplied by 1.5 equals 7.38; the statistical factor for bidentate bonding on a nine-coordinate cation (3.27) multiplied by 1.5 is 4.91. The thermodynamic K_1/K_2 ratio of 7.49 for the neodymium complex is fairly close to the predicted value of 7.38; likewise the value of $^*K_1/^*K_2$ for the thulium complex, 4.79, is close to the predicted value of 4.91. Considering the experimental errors in Matkovich's K_1/K_2 ratios, the agreement is quite satisfactory. These results lend strong support to the proposed difference in dentate character between the lighter and the heavier rare-earth αHIB complexes. The specific values of $^*K_1/^*K_2$ imply that the change in coordination number from ten to nine brings on a change in dentate character from three to two. A possible change in coordination number from nine to eight is not completely ruled out by the data, although the agreement between theoretical and experimental values of $^*K_1/^*K_2$ would be poorer if this were the case.

The use of K_1/K_2 ratios to predict the structure of rare-earth complexes involves several assumptions that might be open to question. More studies of the type undertaken by Matkovich, as well as more structural studies of solid rare-earth complexes, will be necessary before the relationship between experimental K_1/K_2 ratios and complex structure can be firmly established. Nevertheless, the conclusions based on K_1/K_2 data presented in this dissertation can be regarded as plausible in view of the present knowledge of this subject.

The step formation constants of higher order complexes are often more difficult to interpret than the K_1 values, because of the larger experimental errors involved. For a given complex series, K_n rapidly decreases as n increases; the kinetic and electrostatic factors responsible for this decrease have already been described. Otherwise, the same thermodynamic factors govern the formation of the higher complexes as govern the formation of the first complex.

The $\log K_2$ values found for the rare-earth BHMPA complexes are plotted in Figure 18. This curve shows the same trends as the corresponding $\log K_1$ values, although the scatter of points is greater. The K_3 values for the BHMPA system listed in Table 5 show such random fluctuations that no significance can be attributed to the variations in this quantity.

The $\log K_2$ values found by the author for the rare-earth αHIB complexes are plotted in Figure 18, and the $\log K_3$ values for this system are plotted in Figure 19. The first four values of $\log K_2$ are out of line with the remaining values, and there appears to be an increase in stability between neodymium and samarium. The first five values of $\log K_3$ are out of line with the succeeding values, and in this case an increase in stability appears between samarium and europium. This behavior is not easy to explain, but it is probably related to the

Figure 18. Logarithms of the second formation constants of the rare-earth 2,2-bis-(hydroxymethyl)propionate (a) and α-hydroxyisobutyrate (b) complexes as functions of cationic radius

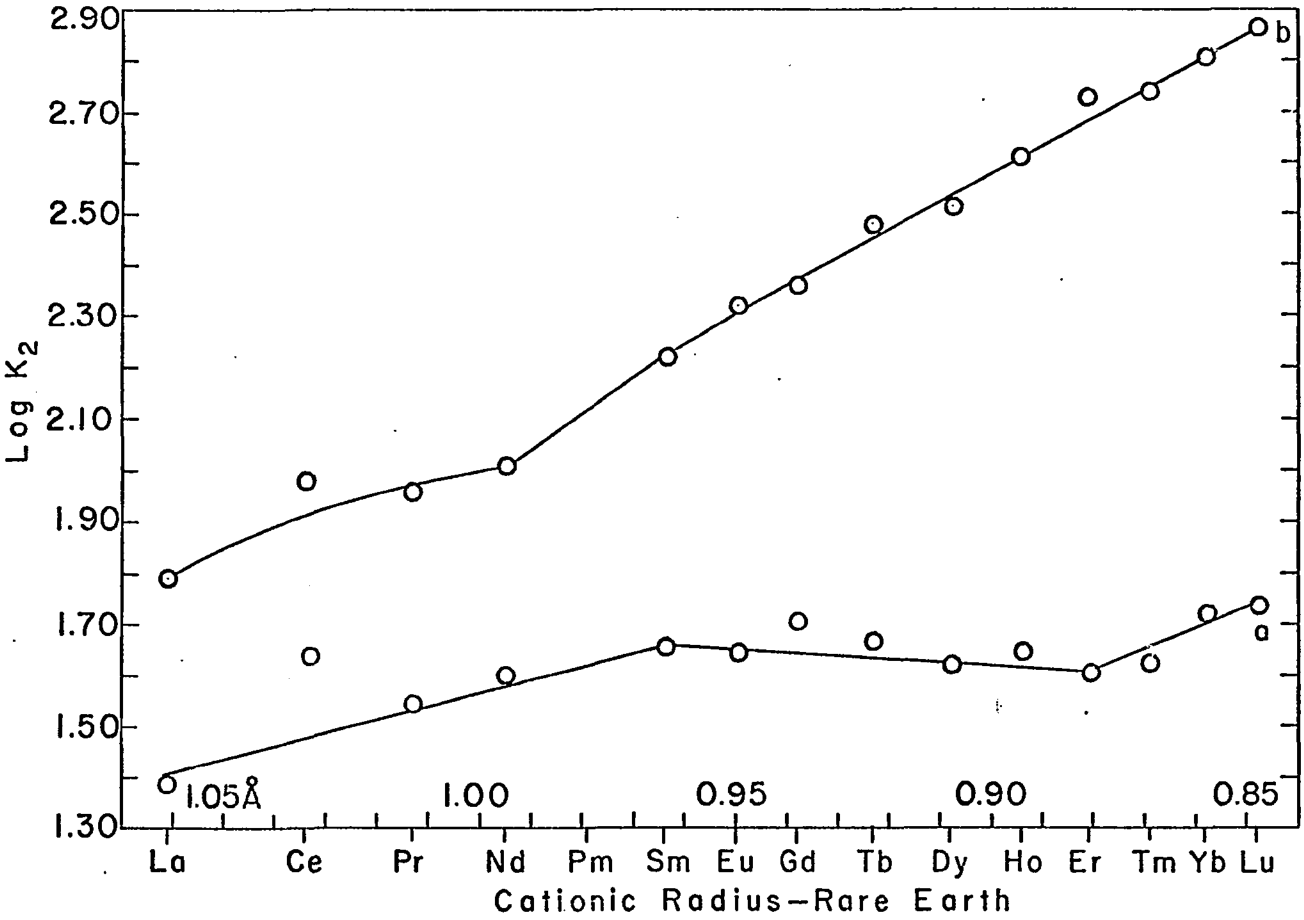
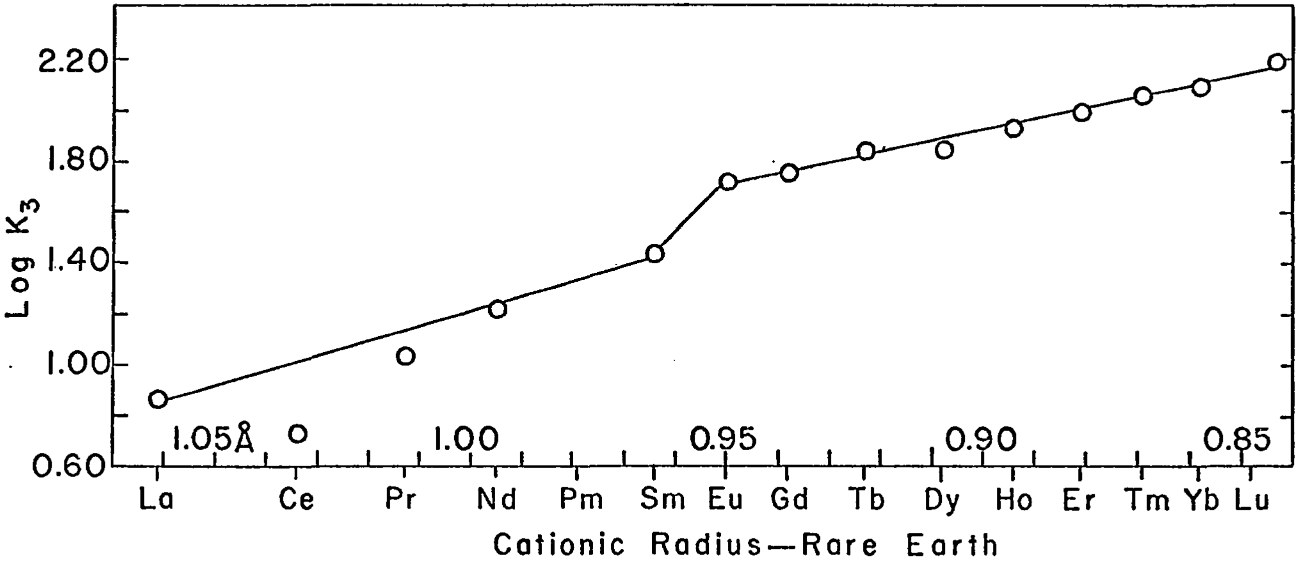

2.90
2.70
2.50
2.30
2.10
1.90
1.70
1.50
1.30
Log K_2
b
a
1.05Å
1.00
0.95
0.90
0.85
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Cationic Radius—Rare Earth

Figure 19. Logarithms of the third formation constants of the rare-earth α-hydroxyisobutyrate complexes as a function of cationic radius


Log K$_3$
2.20
1.80
1.40
1.00
0.60
1.05Å
1.00
0.95
0.90
0.85
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Cationic Radius—Rare Earth

difference in dentate character between the complexes of the lighter rare-earth ions and those of the heavier rare-earth ions. Little information can be inferred from the K_4 values for the αHIB complexes reported in Table 3. It may be significant that a fourth complex appears only with those ions for which bidentate ligandcy is thought to occur.

VIII. SUMMARY

The stoichiometric stability constants of the complexes formed by the trivalent rare-earth ions with the 2,2-bis(hydroxymethyl)propionate and α-hydroxyisobutyrate anions were measured at 25° and an ionic strength of 0.1000 molar using $NaClO_4$ as a supporting electrolyte. The method of competing reactions was used for this study, and twenty sample solutions were prepared for each metal-ligand system studied. The pH of each sample was measured with a Beckman model 1019 pH meter. The stability constants were calculated by means of a weighted least squares program using an I.B.M. 360 computer. A variable acid dissociation constant was used in these calculations. The relation between the stability constants and rare-earth ionic radius was found to be remarkably different for each of the ligands studied. In order to account for this fact and for other features of the data, a theory of rare-earth complex formation was proposed. It was suggested that the trends in the stability of the rare-earth BHMPA complexes primarily reflected the varying degress of hydration of the rare-earth ions. The trends in the stability of the rare-earth αHIB complexes were thought to result from a change in the dentate character of the ligand as well as from changes in the degree of cationic hydration. The ratios of successive step formation constants were used to predict the structure of the complexes. The αHIB ligand appeared to bond the

lighter rare-earth ions tridentately and the heavier rare-earth ions bidentately, while the BHMPA ligand appeared to bond tridentately throughout the rare-earth series.

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XI. APPENDIX A: EXPERIMENTAL DATA FOR THE RARE-EARTH 2,2-BIS(HYDROXYMETHYL)PROPIONATES

Reagent concentrations:

C_A = 0.1000 M except for Ce, Yb, and Lu

C_A = 0.09255 M for Ce, Yb, and Lu

C_{HA} = 0.1099 M except for La, Ce, Yb, Lu, and Y

C_{HA} = 0.1052 M for Ce, Yb, and Lu

C_{HA} = 0.1055 M for La

C_{HA} = 0.1011 M for Y

C_M = 0.1000 M except for La, Sm, Er, and Yb

C_M = 0.09785 M for La

C_M = 0.1042 M for Sm

C_M = 0.1021 M for Er

C_M = 0.09255 M for Yb

C_{MH} = 0.0000 M except for Ce

C_{MH} = 0.002604 M for Ce

C_{sp} = 1.066 M

Dissociation Constant

V_b, ml.	pH
1.00	4.4246
1.00	4.4239
1.50	4.4139
2.00	4.4090
2.50	4.4053
3.00	4.4038
3.50	4.4027
4.00	4.4021
4.50	4.4019
5.00	4.4019
6.00	4.4003
7.00	4.4000
8.00	4.3987
9.00	4.3945
10.00	4.3996
11.00	4.3996
12.00	4.4024
15.00	4.4012
20.00	4.4021
25.00	4.4048

Lanthanum

V_b, ml.	pH
1.00	4.3104
1.50	4.2981
2.00	4.2935
2.50	4.2907
3.00	4.2921
3.50	4.2922
4.00	4.2938
4.50	4.2944
5.00	4.2980
6.00	4.3019
7.00	4.3056
8.00	4.3094
9.00	4.3135
10.00	4.3161
11.00	4.3190
12.00	4.3223
16.00	4.3342
20.00	4.3441
24.00	4.3537
26.00	4.3610

Cerium

V_b, ml.	pH
1.00	4.1057
1.00	4.1077
1.50	4.1178
2.00	4.1273
2.50	4.1338
3.00	4.1418
3.50	4.1462
4.00	4.1515
4.50	4.1564
5.00	4.1601
6.00	4.1683
7.00	4.1763
8.00	4.1828
9.00	4.1905
10.00	4.1976
11.00	4.2001
12.00	4.2077
16.00	4.2253
20.00	4.2400
24.00	4.2517

Praseodymium

V_b, ml.	pH
1.00	4.1879
1.50	4.1775
2.00	4.1743
2.50	4.1782
3.00	4.1798
3.50	4.1836
4.00	4.1860
4.50	4.1916
5.00	4.1960
6.00	4.2038
7.00	4.2127
8.00	4.2200
9.00	4.2267
10.00	4.2342
11.00	4.2415
12.00	4.2458
16.00	4.2664
20.00	4.2820
24.00	4.2948

Neodymium

V_b, ml.	pH
1.00	4.1737
1.00	4.1737
1.50	4.1630
2.00	4.1600
2.50	4.1618
3.00	4.1659
3.50	4.1700
4.00	4.1739
4.50	4.1795
5.00	4.1844
6.00	4.1941
7.00	4.2038
8.00	4.2123
9.00	4.2202
10.00	4.2279
11.00	4.2344
12.00	4.2421
16.00	4.2640
20.00	4.2819
24.00	4.2947

Samarium

V_b, ml.	pH
1.00	4.1299
1.00	4.1319
1.50	4.1233
2.00	4.1198
2.50	4.1244
3.00	4.1280
4.00	4.1420
4.50	4.1458
6.00	4.1634
7.00	4.1742
8.00	4.1857
9.00	4.1960
11.00	4.2125
12.00	4.2210
15.00	4.2423
20.00	4.2701
25.00	4.2873

Europium

V_b, ml.	pH
1.00	4.1462
1.00	4.1495
1.50	4.1384
2.00	4.1363
2.50	4.1399
3.00	4.1445
3.50	4.1498
4.00	4.1544
4.50	4.1597
5.00	4.1650
6.00	4.1761
7.00	4.1867
8.00	4.1980
9.00	4.2075
10.00	4.2162
11.00	4.2243
12.00	4.2322
15.00	4.2502
20.00	4.2756
25.00	4.2930

Gadolinium

V_b, ml.	pH
1.00	4.1674
1.00	4.1678
1.50	4.1545
2.00	4.1540
2.50	4.1539
3.00	4.1570
3.50	4.1582
4.00	4.1632
4.50	4.1689
5.00	4.1717
6.00	4.1823
7.00	4.1909
8.00	4.1983
9.00	4.2059
10.00	4.2133
11.00	4.2216
12.00	4.2277
15.00	4.2476
20.00	4.2669
25.00	4.2841

Terbium

V_b, ml.	pH
1.00	4.1839
1.00	4.1878
1.50	4.1761
2.00	4.1733
2.50	4.1735
3.50	4.1765
4.00	4.1798
4.50	4.1827
5.00	4.1901
6.00	4.1967
7.00	4.2026
8.00	4.2088
9.00	4.2178
10.00	4.2220
11.00	4.2293
12.00	4.2359
15.00	4.2490
20.00	4.2709
25.00	4.2868

Dysprosium

V_b, ml.	pH
1.00	4.1982
1.00	4.1995
1.50	4.1856
2.00	4.1827
2.50	4.1841
3.00	4.1858
3.50	4.1901
4.00	4.1917
4.50	4.1940
5.00	4.2002
6.00	4.2047
7.00	4.2144
8.00	4.2211
9.00	4.2266
10.00	4.2348
11.00	4.2415
12.00	4.2478
15.00	4.2621
20.00	4.2821
25.00	4.3002

Holmium	
V_b, ml.	pH
1.00	4.2158
1.00	4.2145
1.50	4.1999
2.00	4.1952
2.50	4.1935
3.00	4.1981
3.50	4.1997
4.00	4.2022
4.50	4.2054
5.00	4.2078
6.00	4.2123
7.00	4.2210
8.00	4.2284
9.00	4.2364
10.00	4.2416
11.00	4.2435
12.00	4.2483
15.00	4.2639
20.00	4.2835
25.00	4.3007

Erbium	
V_b, ml.	pH
1.00	4.2000
1.00	4.2000
1.50	4.1884
2.00	4.1839
2.50	4.1850
3.00	4.1873
3.50	4.1902
4.00	4.1932
4.50	4.1961
5.00	4.1999
6.00	4.2082
8.00	4.2210
9.00	4.2278
10.00	4.2339
11.00	4.2401
12.00	4.2459
16.00	4.2660
24.00	4.2947

Thulium	
V_b, ml.	pH
1.00	4.1932
1.00	4.1932
1.50	4.1822
2.00	4.1790
2.50	4.1795
3.00	4.1821
3.50	4.1843
4.00	4.1881
4.50	4.1919
5.00	4.1946
6.00	4.2026
7.00	4.2118
8.00	4.2179
9.00	4.2253
10.00	4.2319
11.00	4.2379
12.00	4.2435
16.00	4.2654
20.00	4.2818
24.00	4.2922

Ytterbium

V_b, ml.	pH
1.00	4.1600
1.00	4.1618
1.50	4.1477
2.00	4.1416
2.50	4.1418
3.00	4.1439
3.50	4.1447
4.00	4.1462
4.50	4.1519
5.00	4.1545
6.00	4.1630
7.00	4.1703
8.00	4.1782
9.00	4.1858
10.00	4.1922
11.00	4.1970
12.00	4.2040
15.00	4.2205
20.00	4.2423
25.00	4.2600

Lutetium

V_b, ml.	pH
1.00	4.1550
1.00	4.1538
1.50	4.1401
2.00	4.1354
2.50	4.1353
3.00	4.1358
3.50	4.1398
4.00	4.1421
4.50	4.1467
5.00	4.1500
6.00	4.1589
7.00	4.1660
8.00	4.1738
9.00	4.1801
10.00	4.1866
11.00	4.1924
12.00	4.2000
16.00	4.2205
17.00	4.2269
24.00	4.2517

Yttrium

V_b, ml.	pH
1.00	4.2610
1.50	4.2481
2.00	4.2459
2.50	4.2459
3.00	4.2463
3.50	4.2497
4.00	4.2521
4.50	4.2558
5.00	4.2579
6.00	4.2624
7.00	4.2678
8.00	4.2757
9.00	4.2799
10.00	4.2860
11.00	4.2892
12.00	4.2940
16.00	4.3118
20.00	4.3239
24.00	4.3381
28.00	4.3446

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

Reagent concentrations:

C_A = 0.1000 M

C_{HA} = 0.09561 M for Pr, Nd, Sm, Eu, Gd, Yb, and K_a

C_{HA} = 0.09700 M for La, Ce, Tb, and Dy

C_{HA} = 0.1010 M for Ho, Tm, Lu, and Y

C_{HA} = 0.1009 M for Er

C_M = 0.1000 M except for La, Sm, Er, and Yb

C_M = 0.09785 M for La

C_M = 0.1042 M for Sm

C_M = 0.1021 M for Er

C_M = 0.09255 M for Yb

C_{MH} = 0.0000 M except for Ce

C_{MH} = 0.002604 M for Ce

C_{sp} = 1.012 M for La, Ce, Gd, Tb, Dy, and K_a

C_{sp} = 1.066 M for Pr, Nd, Sm, Eu, and Yb

C_{sp} = 0.9864 M for Ho, Er, Tm, Lu, and Y

Dissociation
Constant

V_b, ml.	pH
1.00	3.9190
1.00	3.9239
1.50	3.8874
2.00	3.8690
2.50	3.8567
3.00	3.8502
3.50	3.8453
4.00	3.8408
4.50	3.8387
5.00	3.8346
6.00	3.8337
7.00	3.8291
8.00	3.8278
9.00	3.8247
10.00	3.8241
11.00	3.8222
12.00	3.8239
15.00	3.8201
20.00	3.8217
25.00	3.8253

Lanthanum	
V_b, ml.	pH
1.00	3.6794
1.05	3.6711
1.50	3.6275
2.00	3.6139
3.00	3.5992
3.50	3.5910
4.00	3.5942
4.50	3.5935
5.05	3.5995
6.05	3.5990
7.00	3.6041
8.00	3.6158
9.00	3.6162
10.00	3.6188
11.05	3.6359
12.00	3.6342
25.00	3.6965

Cerium	
V_b, ml.	pH
1.00	3.5734
1.00	3.5751
1.50	3.5350
2.00	3.5323
3.00	3.5261
3.50	3.5236
4.50	3.5264
5.00	3.5323
6.00	3.5382
7.00	3.5577
8.00	3.5658
9.00	3.5723
10.00	3.5818
11.00	3.5858
12.00	3.5987
15.00	3.6243
20.00	3.6575

Praseodymium	
V_b, ml.	pH
1.00	3.5981
1.00	3.5961
1.50	3.5495
2.00	3.5292
2.50	3.5185
3.00	3.5120
3.50	3.5142
4.00	3.5158
4.50	3.5179
5.00	3.5236
6.00	3.5323
7.00	3.5460
9.00	3.5696
10.00	3.5821
11.00	3.5935
12.00	3.6006
15.00	3.6260
20.00	3.6599
25.00	3.6839

Neodymium

V_b, ml.	pH
1.00	3.5761
1.50	3.5290
2.00	3.5036
2.50	3.4933
3.00	3.4905
3.50	3.4918
4.50	3.4961
5.00	3.5032
6.00	3.5119
7.00	3.5294
8.00	3.5399
9.00	3.5540
10.00	3.5654
11.00	3.5782
12.00	3.5861
15.00	3.6158
20.00	3.6478
25.00	3.6757

Samarium

V_b, ml.	pH
1.00	3.5139
1.00	3.5178
2.00	3.4317
2.00	3.4308
3.00	3.4138
3.50	3.4103
4.00	3.4121
4.60	3.4183
5.00	3.4235
6.00	3.4367
7.00	3.4539
8.00	3.4690
9.00	3.4839
10.00	3.5021
11.00	3.5177
12.00	3.5321
15.00	3.5712
20.00	3.6119
27.50	3.6544

Europium

V_b, ml.	pH
1.00	3.4838
1.00	3.4858
1.50	3.4259
2.00	3.3952
2.50	3.3770
3.00	3.3727
3.50	3.3723
4.00	3.3723
4.50	3.3766
5.10	3.3796
6.00	3.3939
7.00	3.4064
8.00	3.4243
9.00	3.4399
10.00	3.4579
11.00	3.4654
12.00	3.4841
15.00	3.5265
20.00	3.5730
25.00	3.6078

Gadolinium		Terbium		Dysprosium	
V_b, ml.	pH	V_b, ml.	pH	V_b, ml.	pH
1.00	3.4741	1.00	3.4272	1.00	3.4092
1.00	3.4741	1.00	3.4276	1.00	3.4052
1.50	3.4158	1.50	3.3639	1.50	3.3483
2.00	3.3855	2.00	3.3356	2.00	3.3125
2.50	3.3772	2.50	3.3182	2.50	3.2919
3.00	3.3596	3.00	3.3139	3.00	3.2919
3.50	3.3647	3.50	3.3074	3.50	3.2895
4.00	3.3710	4.00	3.3081	4.00	3.2908
4.50	3.3699	4.50	3.3125	4.50	3.2895
5.00	3.3759	5.00	3.3180	5.00	3.3008
6.00	3.3883	6.00	3.3336	6.00	3.3154
7.00	3.4058	7.00	3.3538	7.00	3.3361
8.00	3.4225	8.00	3.3722	8.00	3.3615
9.00	3.4434	9.00	3.3958	9.00	3.3886
10.00	3.4567	10.00	3.4135	10.00	3.4077
11.00	3.4710	11.00	3.4318	11.00	3.4255
12.00	3.4882	12.00	3.4510	12.00	3.4461
15.00	3.5272	15.00	3.4989	15.00	3.4970
20.00	3.5785	20.00	3.5533	20.00	3.5619
25.00	3.6141	25.00	3.5964		

Holmium		Erbium		Thulium	
V_b, ml.	pH	V_b, ml.	pH	V_b, ml.	pH
1.00	3.3699	1.00	3.3445	1.00	3.3270
1.00	3.3670	1.00	3.3487	1.00	3.3270
1.50	3.2983	1.50	3.2687	1.50	3.2518
2.00	3.2605	2.00	3.2349	2.00	3.2090
2.50	3.2447	2.50	3.2039	2.50	3.1858
3.00	3.2349	3.00	3.1972	3.00	3.1749
3.50	3.2315	3.50	3.1894	3.50	3.1705
4.00	3.2290	4.00	3.1963	4.00	3.1710
4.50	3.2383	4.50	3.1940	4.50	3.1768
5.00	3.2439	5.00	3.2001	5.00	3.1853
6.00	3.2662	6.00	3.2171	6.00	3.2025
7.00	3.2844	7.00	3.2409	7.00	3.2278
8.00	3.3098	8.00	3.2682	8.00	3.2522
9.00	3.3357	9.00	3.2994	9.00	3.2819
10.00	3.3584	10.10	3.3219	10.00	3.3074
11.00	3.3825	11.00	3.3449	11.00	3.3308
12.00	3.4106	12.00	3.3660	12.00	3.3598
15.00	3.4600	15.00	3.4263	15.00	3.4237
20.00	3.5322	20.00	3.5028	20.00	3.5022
				25.00	3.5554

Ytterbium	
V_b, ml.	pH
1.00	3.3162
1.00	3.3143
1.50	3.2290
2.00	3.1862
2.50	3.1638
3.00	3.1473
3.50	3.1394
4.00	3.1402
4.50	3.1399
5.00	3.1499
6.00	3.1700
7.00	3.1924
8.00	3.2218
9.00	3.2497
10.00	3.2738
11.00	3.3015
12.00	3.3290
15.00	3.3982
20.00	3.4840
25.00	3.5554

Lutetium	
V_b, ml.	pH
1.00	3.2868
1.00	3.2841
1.50	3.2019
2.00	3.1599
2.50	3.1315
3.00	3.1169
3.50	3.1138
4.00	3.1083
4.50	3.1163
5.00	3.1187
6.00	3.1418
7.00	3.1656
8.00	3.1972
9.00	3.2233
10.00	3.2539
11.00	3.2832
12.00	3.3133
15.00	3.3825
20.00	3.4720

Yttrium	
V_b, ml.	pH
1.00	3.3978
1.00	3.3994
1.60	3.3221
2.00	3.2959
2.50	3.2783
3.00	3.2690
3.50	3.2657
4.00	3.2688
4.50	3.2687
5.00	3.2816
7.00	3.3124
8.00	3.3342
9.00	3.3535
10.00	3.3820
11.00	3.3968
12.00	3.4166
15.00	3.4687
20.00	3.5341