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STABILITY CONSTANTS OF
SOME RARE-EARTH-METAL CHELATES

by

Robert Harreld Karraker

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INTRODUCTION

This dissertation is concerned with the measurement of the stability constants of several rare-earth complexes. Two separate types of complexes were studied in order to elucidate this phase of lanthanide chemistry. The complexes of glycolic acid and lactic acid with the rare-earths were studied as examples of weak complexes and the complexes of rare-earths with 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (DCTA), where only the 1:1 chelate is formed, were studied as examples of strong complexes.

The separation of large amounts of pure rare-earths and yttrium by ion exchange was developed recently at Ames Laboratory (1,2,3) and has increased the availability of pure rare earths. The process involves the use of ion-exchange resins in conjunction with chelating agents. The basis of the separation is the exchange of metal ions between a cation-exchange resin and an aqueous phase. The ability of the aqueous phase to compete with the resin for a rare-earth ion is due mainly to the complexing ability of the chelating agent used. Chelate stability constants, then, permit an estimation of the separation possible and the elution distance required (3). Powell (4) has reviewed the application of chelating agents to the ion-exchange separation of rare-earth mixtures.

Aminopolyacetic acids have proven to be excellent chelating agents for use as eluants in the rare-earth separation process (3,4) and stability constants have been determined previously for the rare-earth chelates of ethylenediamine-N,N,N',N'-tetraacetic acid (EDTA) (5,6), N'(hydroxyethyl)-ethylenediamine-N,N,N'-triacetic acid (HEDTA) (5,7), 1,2-bis-[2-di(carboxymethyl)aminoethoxy]ethane (DE) (7,8), 2,2'-bis[di(carboxymethyl)amino]diethyl ether (ME) (7,8), and carboxymethyl-bis-]2-di(carboxymethyl)-aminoethyl]amine (DETPA) (9). Stability constants for most of the rare-earth chelates of DCTA have also been reported (6). However, the holmium-DCTA constant was not reported, and there appeared to be a discrepancy in the relationship of the yttrium to the rest of the rare earths when the values were compared with the stability constant sequence obtained with EDTA.

Glycolic and lactic acids have not been used for the separation of rare earths in macro-quantities; however, both have been used effectively for the separation of tracer quantities of the rare earths and actinides. Freiling and Bunney (10) have reported optimum conditions for rare-earth separations with ammonium lactate as the eluting agent. Cunninghame et al. (11) have also reported separations of the rare earths with lactate solutions. Stewart (12) reported separations of rare-earth tracers with an ammonia-buffered solution of glycolic acid. Choppin, Harvey and Thompson (13) compared the separation factors of glycolic, lactic, and α-hydroxyisobutyric acid for the actinides. They found that the separation factors improved in the order glycolic acid

$<$ lactic acid $<$ α-hydroxyisobutyric acid.

Numerous theoretical studies have been made regarding the way in which stability constants of strong chelates of the EDTA type depend on the nature of the central metal ion and on the structure of the chelating agent (14). Fewer studies have been made involving weak complexes of metal ions with organic monocarboxylic acids, but some variations have been noted and reported (15). The rare earths provide a unique opportunity for adding to such studies. They comprise a series of fourteen trivalent metal ions that differ from one another only in nuclear charge and in the number of electrons in the inner 4f shell. The increasing charge density of the nucleus causes a decrease in ionic radius from lanthanum to lutetium generally referred to as the lanthanide contraction. Variations in properties across this series are intriguing phenomena of rare-earth chemistry.

RARE-EARTH GLYCOLATE AND LACTATE STABILITY CONSTANTS

Review

Methods of determining stability constants of metal complexes with organic acids

There are several methods of determining very strong stability constants of metal chelates with aminopolycarboxylic acids. These methods are summarized in the section dealing with the stability constants of the rare-earth chelates with DCTA. Most of them are not applicable to the weak complexes formed between metal ions and monocarboxylic acids. There are two major reasons for this. First, with monocarboxylic acids it is necessary to consider several successive constants rather than one. Second, the chemical properties of the free metal ion and the complexed metal ion are often not sufficiently different to enable them to be distinguished from one another by the usual techniques.

All methods that have been used for the determination of weak stability constants depend upon determining one of the species present in the equilibrium mixture. The equilibrium can be written as:

$$MA_a^{+m-a} + A^- \rightleftharpoons MA_{a+1}^{+m-a-1} \quad .$$

Knowing the overall composition, if any of the species

M^{+m}, MA^{+m-1}, MA_2^{+m-2}, ... MA_n^{+m-n}, A^-, can be determined independently, the various complex-formation constants can be calculated.

The most common methods of determining weak stability constants make use of one of the several ways of determining hydrogen-ion concentration. The hydrogen electrode, quinhydrone electrode, glass electrode and the colorimetric determination of indicators have been used for this purpose. In general, an excess of the ligand acid is titrated in the presence of the particular metal ion using standard base. The hydrogen-ion concentration is then related to the free-ligand-ion concentration by the ionization constant of the ligand acid. Thus, the determination of the hydrogen-ion concentration is in reality a determination of the ligand-ion concentration. The methods of carrying out the calculations involved have varied with various researchers. The equations may be solved simultaneously, of course, but this is tedious when several successive constants are to be evaluated. Therefore, Bjerrum (16) has shown how the constants may be estimated closely and refined by successive approximations. Fronaeus (17) developed the technique of graphical integration used in this dissertation. The mathematical methods of both Bjerrum and Fronaeus, as well as that of Leden (18) which requires determination of the free metal ion, have been reviewed and discussed by Sullivan and Hindman (19). A recent paper by Watkins and Jones (20) has shown how relaxation techniques may be applied to the methods of Bjerrum and Fronaeus. The relaxation techniques are simple to program on a computer.

The solubility of iodate salts in solutions of the sodium salts of monocarboxylic acids has been used to determine stability constants of divalent metal salts (21,22). The procedure is to measure the solubility of the metal iodate in the presence of a simple salt of the organic acid, then, to calculate the amount of metal ligand ion, (MA^+), necessarily present to bring the results into harmony with those for normal salts. Workers using this method found only one stability constant

$$M^{++} + A^- \rightleftharpoons MA^+$$

because the ionic strength correction factors for solubility had not been tested and could not be trusted at the higher ligand concentrations needed for the formation of appreciable amounts of more complex species. This technique has been studied sufficiently so that results obtained by it are very reliable. This method yields the thermodynamic stability constant rather than the apparent stability constants at known ionic strength which most other researchers report.

A cation-exchange technique for measuring stability constants has been developed by Schubert (23). This technique requires that the complexes formed have zero or negative net charge. The method is based on the fact that, in a system consisting of a metal cation, the chelating agent, and a cation-exchange resin, the amount of cation sorbed by a definite amount of resin is proportional to the concentration of free cation over a wide concentration range. The distribution coefficient, K_d, must be determined in the presence of the chelating agent, and in the absence of the chelating agent ($K_d{}^o$) in solutions of matching ionic strengths. The stability constant is then determined from the equation

$$K_n = \frac{(K_d{}^o/K_d)-1}{(A^-)^n} .$$

Fronaeus (24) has developed a method of treating data from ion-exchange experiments which permits the calculation of successive formation constants including those of cationic species. This elegant technique is quite complicated, but is applicable to the first type of complex studied in this dissertation. The results obtained generally check very well with those of other methods.

Another technique of determining stability constants employs a rather unique electrode. Joseph has described an amalgam electrode of the third kind, $PbHg(PbC_2O_4,CaC_2O_4)Ca^{+2}$, as well as similar barium and strontium electrodes (25). Lead amalgam is in contact with a mixture of solid lead oxalate and alkaline-earth oxalate. The $Pb^{+2}+2e^- \rightleftharpoons Pb^o$ potential at the electrode depends on the potential of the alkaline-earth ion in the solution. This electrode has been used in conjunction with a silver-silver chloride electrode in saturated KCl to determine stability constants of calcium, strontium, and barium complexes with organic acids (26). The voltage obtained is shown by the following equation

$$E = E^{o} + \frac{2.303RT}{2F}\, pM \quad .$$

The results were calculated assuming that only the 1:1 complex was formed; and, as a result, only the first stability constant was reported. However, the variation of the stability constant with ligand-ion concentration which Joseph observed might have warranted some investigation of a second complex.

Solvent partition has been used by Day and Stoughton (27) for determining the stability constants of thorium complexes and by Connick and McVey (28) to determine stability constants of zirconium complexes. The non-aqueous phase used by these investigators was a benzene solution containing thenoyl trifluoroacetone (TTA) and a number of inorganic and organic ligands were investigated. TTA complexes the metal cation yielding a neutral complex which is absorbed by the organic phase. If R_o represents the distribution ratio between the aqueous and organic phases in the absence of complexing agent, and R_b the distribution ratio in the presence of complexing agent, the following equation can be derived

$$\frac{R_b}{R_o} = 1 + K_1\frac{(HX)}{(H^+)} + K_2\frac{(HX)^2}{(H^+)^2} \quad .$$

Thus the stability constants K_1 and K_2 may be determined by measuring the ratio of metal in the aqueous and organic phases as a function of concentration of the complexing agent, while holding the hydrogen-ion and other activities constant.

The use of extinctiometric measurements to determine stability constants is possible if there is a change in absorption of the solution upon complexing. This method has been found to be applicable to the copper nitrate system (29,30) and to the uranyl monochloroacetate system (31). The method accounts for the absorbance of a solution as being due to the summation of absorbances of the individual species.

$$e = E_m^{\,o}[M] + \sum_{j=1}^{N} E_j[MA_j] + E_A^{\,o}[A]$$

Two techniques have been employed in the calculations. One of these (29) uses an extrapolation to zero ligand concentration to determine the first stability constant and the extinction coefficient associated with it. Then, the remaining constants are determined by obtaining the best fit of the above equation to the experimental data. The second method (30) makes use of the equation

$$\left(\frac{\partial C_A}{\partial C_M}\right)_{E_M} = \bar{n} \qquad \text{from} \qquad C_A = [A] - \bar{n}\, C_M$$

where C_A, C_M, and $\bar{n}$ are as described in the experimental part of this dissertation and

$$E_M = \frac{e - E_A{}^{o} C_A}{C_M} \quad .$$

If C_A is plotted against C_M at constant E_M, a straight line is obtained with the intercept [A] and slope $\bar{n}$. Knowing these values, a $\bar{n}$/[A] versus [A^-] curve is plotted and the procedure is the same as in this dissertation.

One of the more interesting and unique methods of determining stability constants is the frog's heart method. McLean and Hastings (32) noted that the amplitude of the beat of the ventricle of an isolated frog's heart is related to the concentration of calcium ions present in the chambers of the heart. By matching the heart beat obtained with an unknown solution with the heart beat obtained with standard solutions they were able to determine the calcium-ion concentration of their unknown. With other associates (33) they used this measure of calcium ions to evaluate the calcium citrate stability constants. The frog's heart was found to react in a similar manner with strontium ions and the method was used for strontium citrate also. When it was found that magnesium ions had little or no effect upon the heart, the magnesium citrate stability constant was determined by allowing magnesium and calcium to compete for the citrate ion. The results of this method have been checked potentiometrically and by ion exchange, and have been found to be accurate.

Conductivity measurements have been used to measure some stability constants when the complex formed is not charged (34). This technique has been found applicable to the complexes of oxalate and malonate with bivalent metals. Unfortunately, this is not applicable to the successive constants studied in this thesis.

Observed variations of some organic acid stability constants with metal and ligand

According to the theory of Sidgwick and Lowry, a coordinate bond (and hence, a coordination compound) can be formed between any atom or ion which can accept a share in a pair of electrons and any atom or ion which can furnish a pair of electrons. Therefore, the complexes of the monocarboxylic acids are coordination compounds and should follow the rules developed for coordination compounds (35). Much of the data on stability has been correlated, with varying success, with these properties of the metals:

1. The ionization potentials of the metals;
2. The (charge)^2/radius ratios for the various ions; and
3. The electronegativities of the metals.

In general, the stabilities of the metal complexes increase with a large electron affinity of the metal ion, a small radius of the central ion, and a high charge on the central ion.

The characteristics of the ligand which are generally recognized as influencing the stability of complexes are:

1. The basicity of the ligand;
2. The size of the chelate ring;
3. The number of metal chelate rings per ligand;
4. The atom of coordination on the ligand;
5. Steric effects; and
6. Resonance effects.

A number of investigations have shown that for the first transition series, regardless of the nature of the donor group, the "natural order" of the stability of the complexes of bivalent transition metals is $Mn < Fe < Co < Ni < Cu > Zn$. The order is due to a constantly increasing electronegativity up to and including zinc, and a ligand-field correction increasing to a maximum at nickel and copper and falling off abruptly to zero for zinc (36). Perrin (37) has shown that this order holds with the complexes of salicylic acid (Table 1.) The complexes of these ions with acetic, glycolic, and lactic acids are reported in Table 2. The ionic strengths of the individual measurements are not the same, but the order is apparent in spite of this except for the nickel acetate. The ionic strength correction could easily be

Table 1. Stability constants of divalent metal salicylates, $\mu = 0.15$

	Mn	Fe	Co	Ni	Cu	Zn
log K_1	5.90	6.55	6.75	6.95	10.60	6.85
log K_2	3.9	4.7	4.7	4.8	7.85	----

Table 2. Stability constants of some divalent metal acetates, glycolates, and lactates (log K's)

Ligand	Mn (38) (μ=0.16)	Co (38) (μ=0.16)	Ni (39) (μ=1.0)	Cu (40) (μ=0)	Zn (41) (μ=0.2)
Acetate	0.16	0.91	0.67	2.24	1.03
Glycolate	1.06	1.61		2.92	1.92
Lactate	1.19				1.86

enough to put the nickel acetate in line with the rest.

Tervalent ions have not been studied extensively. In general, it can be said that their complexes are more stable than those of divalent ions. The order of stability of acetylacetonates is Fe > Ga > Al > Sc > In > Y > Pr > Ce > La (42). The complexes of tervalent cobalt and chromium are generally much more stable than those of iron (43). Recent publications by Sonesson on yttrium and the rare-earth acetates and glycolates have shown two differing trends (44,45,46,47). Table 3 contains the constants determined by Sonesson. For the acetates the stability constants rise with increasing atomic number and decreasing ionic radii to samarium. Then there is a gradual decrease until ytterbium rises slightly above erbium. For the glycolates the stability constants rise to samarium, drop with gadolinium and rise from there on with the rest of the series.

Table 3. Logarithms of the rare-earth and yttrium acetate and glycolate stability constants, $\mu = 2.0$ ($NaClO_4$)

Rare earth	Acetates				Glycolates			
	K_1	K_2	K_3	K_4	K_1	K_2	K_3	K_4
La	1.57	0.92	0.51	-0.05	2.19	1.57	1.06	0.25
Ce	1.68	1.01	0.45	0.14	2.35	1.67	1.12	0.40
Pr	1.81	1.00	0.46	0.00	2.43	1.76	1.21	0.56
Nd	1.90	1.11	0.44	0.08	2.51	1.84	1.23	0.53
Sm	2.01	1.25	0.59	0.00	2.56	1.97	1.35	0.59
Gd	1.84	1.28	0.59	0.00	2.48	1.95	1.36	0.62
Dy	1.67	1.30	0.82	0.11	2.52	1.96	1.42	0.58
Ho	1.63	1.23	0.89	-0.15	2.54	1.93	1.43	0.52
Er	1.60	1.23	0.82	-0.05	2.60	1.98	1.42	0.49
Yb	1.64	1.19	0.71	0.04	2.72	2.10	1.51	0.46
Y	1.53	1.13	0.72	-0.08	2.47	1.93	1.30	0.56

Kolat and Powell (48) have studied the complete series of rare-earth acetates and yttrium acetate at ionic strength 0.1. Their data, Table 4, agree with Sonesson in the trends

Table 4. Rare-earth acetate stability constants, $\mu = 0.10$ ($NaClO_4$) (data of R. S. Kolat)

Rare-earth	log K_1	log K_2
La	2.02	1.24
Ce	2.09	1.44
Pr	2.18	1.45
Nd	2.22	1.54
Sm	2.30	1.58
Eu	2.31	1.60
Gd	2.16	1.60
Tb	2.07	1.59
Dy	2.03	1.61
Ho	2.00	1.59
Er	2.01	1.59
Tm	2.02	1.59
Yb	2.03	1.64
Lu	2.05	1.64
Y	1.97	1.63

of the stability constants among the rare earths, and show the increase in strength of the complex with decreasing ionic strength.

Although much less quantitative data is available on the stabilities of complex ions of the second and third transition metal series, there is little doubt from their general behavior that stabilities increase within any group as one passes from the first to the second to the third transition series. One non-transition series group which has been studied is the alkaline-earth metals. Some of the stability constants of the alkaline-earth metals and copper have been collected in Table 5. The order of the stability constants of the alkaline-earth complexes is Ca > Sr > Ba. This order shows greater stability for the smaller ionic radii, and with higher ionization potentials.

Table 5. Logarithms of the first stability constant of some divalent metal complexes and the formation constants of the acids, $\mu = 0$

Ligand	Ca	Sr	Ba	Cu	H
Formate (15, 22)	0.80	0.66	0.60	1.98	3.77
Acetate (15, 22)	0.77	0.44	0.41	2.24	4.76
Propionate (15, 22)	0.68	0.24	0.15	2.22	4.87
n-butyrate (15, 22)	0.54	0.15	0.00	2.14	4.82
Bromoacetate (15, 22)	0.41	0.28	0.24	1.59	2.86
Lactate (15, 22)	1.47	0.96	0.77	2.92	3.86
Glycolate (15, 22)	1.58	1.31	1.04	2.92	3.88
Glycine (15, 40)	1.35	0.91	0.77	8.29	2.35
α-aminopropionate (15, 49, 50, 51)	1.24	0.74	0.77	8.40	2.34
β-hydroxybutyrate (22)	0.83				4.39
Methoxyacetate (22)	1.12				
Pyruvate (22)	1.08				

Some ligand effects can be shown in Table 5. The basicity of the ligand is a major factor in the stability of complexes. This is to be expected since the hydrogen ion and the metal ion react in the same way with the ligand. The bromoacetates agree with this theory in that their stability constants with alkaline-earth ions and with hydrogen ion are both weak. The order of the aliphatic monocarboxylic acids stability constants, however, is inversely related to the ionization constants of the acids. The alkaline-earth formates are stronger complexes than the acetates, and the acetates stronger than the propionates even though the affinities of the ligands for hydrogen ions are in the reverse order. With acids which have a coordinating group on the α-carbon, the stability constants are much larger due to the formation of chelates. Apparently, the five-membered-ring chelates are much more stable than the six-membered-ring chelates formed by acids with a coordinating group on the β-carbon. The order of increasing stability for the substituents on the α-carbon with calcium salts is: $-OH > -NH_2 > -OCH_3 > -COCH_3 > -CH_3 > -Br$. This order does not hold for transition metal ions, possibly due to ligand-field effects. If a molecule can form more than one chelate ring with a metal ion, as in the complexes of nitrilotriacetic acid, the stability constants of the complex will be significantly larger for each ring which can form. This is known as the "chelate effect".

Vickery (52) has studied the stability constants of neodymium with a number of organic acids. Some of his data has been reported in Table 6. Vickery's data is of interest to indicate trends in rare-earth complex sequences, but the absolute values he reports may not be accurate. He apparently did not adjust his pH readings to hydrogen-ion concentrations

Table 6. Stability constants of neodymium complexes, $\mu \approx 0.1$ (KNO_3)

Ligand	log K_1	log K_2	log K_3
formate	2.4	1.9	1.7
acetate	2.6	2.1	1.9
propionate	2.5	2.1	1.8
butyrate	2.5	2.0	1.8
iso-butyrate	2.5	2.1	1.6
glycolate	3.4	2.3	1.4
lactate	4.0	2.3	1.7
malate	4.5	3.9	

and he indicated that he used thermodynamic ionization constants of the acids rather than apparent values at 0.1 ionic strength. This could change the ionization constant of the acid by a factor of nearly two and have a still larger effect upon the stability constants. Vickery was attempting to correlate spectral band shifts with stability constants. He found that with monocarboxylic acids the shift of the band to a lower frequency was paralleled by a decrease in log $\overline{K}$ ($\overline{K} = K_1 K_2 \ldots K_n$). This conformed with the energy requirements for complex formation with these ligands. With dibasic acids and chelate-forming ligands, the shift of the band to lower frequency was paralleled by an increase in log $\overline{K}$. Vickery did not give a detailed explanation of these phenomena.

A very complete collection of stability constants was published in 1957 by Bjerrum, Schwarzenbach, and Sillén (53) This work covered all of the data published up to that time, but this field, like all other chemical fields, has been so active that a revision will soon be needed.

Experimental

Derivation of the experimental methods

The methods used for the determination of the rare-earth glycolate and lactate stability constants are essentially those of Bjerrum (16). The methods have been elaborated by Leden (18) and Fronaeus (17). A presentation of Fronaeus's method by Sonesson (44) is the exact method used in this work.

If it is assumed that only mononuclear complexes MA_1, $MA_2, \ldots, MA_n$ are formed, we have the following equilibrium for the formation of the complex MA_n:

$$MA_{n-1}^{+(4-n)} + A^{-} \rightleftharpoons MA_n^{+(3-n)} \quad .$$

The corresponding stability constant is defined as:

$$K_n = \frac{[MA_n^{+(3-n)}]}{[MA_{(n-1)}^{+(4-n)}][A^{-}]} \quad .$$

The corresponding complexity constant β_n is defined as:

$$\beta_n = \prod_{n=1}^{i} K_n = \frac{[MA_n^{+(3-n)}]}{[M^{+3}][A^-]^n} \quad .$$

The total concentration of metal ion (C_M) and the total concentration of ligand (C_A) can be expressed as functions of $[A^-]$ and $[M^3]$:

$$C_M = [M^{+3}] \cdot X \tag{1a}$$

$$C_A = [A^-] + [M^{+3}] \cdot [A^-] \cdot X' \tag{1b}$$

where $X = X([A^-])$ is defined by the equation

$$X = 1 + \sum_{n=1}^{N} \beta_n \cdot [A^-]^n$$

and

$$X' = \frac{d\, X([A])}{d\, [A]} \quad .$$

The ligand number, $\bar{n}$, is a quantity invented by Bjerrum (16) that is defined as the average number of ligands attached to each metal atom.

$$\bar{n} = \frac{\sum_{n=1}^{N} n \beta_n [A^-]^n [M^{+3}]}{[M^{+3}] + \sum_{n=1}^{N} \beta_n [A^-][M^{+3}]} = \frac{C_A - [A^-]}{C_M} \tag{2}$$

A combination of equations 1 and 2, and the elimination of $[M^{+3}]$ will give

$$\frac{\bar{n}}{[A^-]} = \frac{X'}{X} \quad , \tag{3}$$

which is, after integration

$$\mathrm{Ln}X([A]j) = \int_{0}^{[A]_j} \frac{\bar{n}}{[A^-]} \cdot d[A^-] \quad . \tag{4}$$

With this integration there is a value of X for each value of $[A^-]$.

The complexity constants β_1, β_2, etc. can now be calculated by successive extrapolation to $[A^-] = 0$ of the functions X_1, X_2, etc.

$$X_1 = \frac{X-1}{[A^-]} = \beta_1 + \beta_2 \cdot [A^-] + \beta_3 \cdot [A^-]^2 + \ldots.$$

$$X_2 = \frac{X_1 - \quad 1}{[A^-]} = \beta_2 + \beta_3 \cdot [A^-] + \ldots. \tag{5}$$

The calculations require a knowledge of $[A^-]$ both for $\bar{n}$ and for $\bar{n}/_{[A^-]}$. This can be determined from the ionization constant of the ligand acid.

$$K_c = \frac{[H^+][A^-]}{[HA]} \tag{6}$$

When the solution contains only the ligand acid and its sodium salt, the following relationships can be written.

$$[A^-] = C_A' + [H^+]$$

$$[HA] = C_{HA}' - [H^+]$$

C_{HA}' and C_A' are the stoichiometric concentrations of ligand acid and its sodium salt. The ionization constant may then be written

$$K_c = \frac{[H^+](C_A' + [H^+])}{(C_{HA}' - [H^+])} \quad . \tag{7}$$

This equation was used to determine the ionization constants.

For solutions containing rare-earth ions, equation 6 still holds, only now it is used to determine the free-ligand-ion concentration $[A^-]$.

$$[A^-] = \frac{K_c[HA]}{[H+]} = \frac{K_c(C_{HA} - [H^+])}{[H^+]} \tag{8a}$$

$\bar{n}$ can now be calculated

$$\bar{n} = \frac{C_A + [H^+] - [A^-]}{C_M} \quad . \tag{9a}$$

The cerium solutions used contained some excess acid (C_H) which necessitated an adjustment in equations 8a and 9a to account for it.

$$[A-] = \frac{K_c(C_{HA} + C_H - [H^+])}{[H^+]} \tag{8b}$$

$$\bar{n} = \frac{C_A - C_H + [H^+] - [A^-]}{C_M} \tag{9b}$$

Thus all of the calculations may be made with the knowledge of C_A, C_M, K_c, and pH.

Calculation of the margins of error

The major possible source of error in this work lies in the determination of the hydrogen-ion concentration. Feldman (54) has reviewed the possible sources of error and the range of accuracy of the pH meter in determining hydrogen-ion concentration.

Although the Beckman Model G. S. pH meter with an extended range is capable of giving pH readings to ±0.003 pH unit, there are some uncertainties which are unavoidable. The first is that the buffer with which the meter is standardized has a known range of uncertainty. The second is that with a glass electrode and a calomel electrode there is a liquid-junction potential.

Mackey (7) has given a review of the basis of the pH scales and a discussion of the inherent errors in defining a single activity of the hydrogen ion. Feldman (54) has shown that at ionic strength 0.1 all the different assumptions for obtaining the hydrogen-ion activity coefficient agree to ±0.01 pH unit. He found a value for the activity coefficient of the hydrogen ion near the mean for all the assumptions by assuming that the activity coefficient of hydrogen ion in the solution measured was equal to the ratio of the mean activity coefficient squared of hydrochloric acid in a HCl-NaCl mixture to the mean activity coefficient of KCl in pure KCl solution provided all solutions were at the same ionic strength,

$$f_{H^+} = \frac{f^2_{\pm HCl}(HCl\text{-}NaCl)}{f_{\pm KCl}(KCl)} .$$

The National Bureau of Standards has set up a number of standard buffers which have known pH values accurate to ±0.01 pH unit. The Beckman buffers used in this dissertation were based on the NBS standards.

Thus, if a glass electrode pH meter and NBS standard buffer has been used to measure pH, the maximum possible error inherent in the method would be ±0.02 pH unit at ionic strength 0.1.

The liquid-junction potential is the potential that exists at the boundary of two solutions which differ in composition. It is due to a difference in the rates of diffusion of ions of opposite charge. The potential at a solution boundary would be expected to be a function of pH, ionic strength, the nature of the diffusing ions, solvents, temperature, and, in fact, of anything which affects the mobility of ions in solution. Since the pH of the NBS standard buffer is based on cells without liquid junction, the standardization of a glass-electrode pH meter with this standard buffer is subject to an error due to the junction potential term. This error is partially compensated by the junction potential that is present when the electrodes are placed in the solution to be tested. The error due to junction potentials cannot be calculated accurately, but indications of its magnitude have been obtained. Bates, Pinching, and Smith (55) determined the apparent pH_j for a number of test solutions in a cell with liquid junctions. Their results showed that ΔpH (pH_j-pH) did not exceed ±0.02 unit for any of the buffers having pH's between 2.15 and 10.

From these considerations one might conclude that; using the glass electrode pH meter for determining hydrogen-ion concentrations in aqueous solutions at pH's between 2 and 12, and standardizing with a NBS buffer; C_{H^+} could be calculated to an accuracy of ±0.04 pH unit. This is a margin of error in the hydrogen-ion concentration of ±10%.

From this value for the margin of error for the hydrogen-ion concentrations and the standard deviation of the calculation of the acid ionization constants, the errors were calculated for the $\bar{n}/[A^-]$ terms. The errors were calculated by the technique and formulas given by Kolthoff and Sandell (56). With this margin of error an estimate was made of the errors in the first stability constants. The margin of error thus calculated for the lactates varied from ten per cent of the reported value for lanthanum lactate to twenty per cent for lutetium lactate.

After determining the absolute error, the margin of error relative to the other rare earths was calculated. For this determination, the errors were considerably reduced by several factors. Since a stock solution of buffer was used to standardize the pH meter throughout this work, there was no deviation in the pH of the buffer solution. All assumptions with regard to the determination of a single ion activity are the same in each solution and, therefore, should cancel when comparing one rare earth to another. The junction potential also should not vary significantly between solutions of different rare earths because it is unlikely that the mobility of the rare-earth ions differ significantly from each other, and the solutions are identical otherwise. Therefore, the relative margin of error between individual rare earths should depend upon the accuracy of the pH meter and, as stated before, the accuracy of the pH meter used in this work was ± 0.003 pH unit. This is an error in the hydrogen-ion concentration of ± 0.7%. The relative margin of error of the first stability constants of the rare-earth lactates was then calculated and found to be about three to four per cent. This same figure was obtained for the rare-earth glycolates. The margins of error for the second and third stability constants were estimated from the extrapolation curves and the errors in the first stability constants. The margins of error relative to the other rare earths are given in Tables 7 and 8.

Materials and equipment

Rare-earth perchlorate solutions The rare-earth oxides were supplied by the rare-earth separation group under the direction of Dr. J. E. Powell at the Ames Laboratory of the Atomic Energy Commission. All were equal to or greater than 99.9% pure. The oxides were dissolved in excess perchloric acid, and the excess acid removed by boiling to dryness. This process decomposed some of the perchlorate salt, and when the salt was dissolved in water, it was basic with respect to its equivalence point. An aliquot of each solution was then titrated potentiometrically to find the pH of the neutral point of each rare-earth perchlorate. Each solution was then adjusted to its neutral equivalence point. The solutions were then analyzed gravimetrically by precipitation of the insoluble oxalate and ignition to the oxide. The boiling to dryness of the cerium solution oxidized the cerium as well as decomposed it. The solution obtained by dissolving this mass was found to be still on the acid side of the equivalence point. Therefore, a cerium solution was prepared by evaporating down as far as possible on a steam bath and then making it up to volume. The excess acid was titrated with carbonate-free potassium hydroxide and an allowance was made for the excess acid in the calculations of the data. From these solutions tenth-molar solutions were prepared of all of the rare-earth perchlorates, except cerium, which was already too dilute and was left at a molarity of 0.0974.

Glycolic and lactic acid solutions   Reagent grade glycolic and lactic acids were dissolved in water and treated with activated charcoal. The solutions were filtered and passed through a Dowex-50 cation-exchange column in the acid form. The solutions were titrated with standardized carbonate-free sodium hydroxide. From these stock solutions, solutions were prepared which were one-tenth molar in glycolic or lactic acid and one-tenth molar in the sodium salt, by half neutralizing an appropriate amount of either acid with carbonate-free sodium hydroxide.

Carbonate-free sodium hydroxide and potassium hydroxide Carbonate-free sodium hydroxide was prepared by the method suggested by Diehl and Smith (57). Carbonate-free potassium hydroxide was prepared by the method of Powell and Hiller (58). Both solutions of base were standardized against cadmium acid N'-hydroxyethyl-ethylenediamine-N,N,N'-triacetate (59), were stored in a Pyrex bottle and protected against the atmosphere.

Sodium perchlorate   One-molar sodium perchlorate for adjusting the ionic strengths was prepared from reagent grade sodium perchlorate.

pH meter   All pH measurements were made with a Beckman G. S. pH meter using the extended scale. An activity correction of -0.100 unit was applied to the readings of the pH meter to convert hydrogen-ion activity to hydrogen-ion concentration. A short discussion of this activity correction was given in the previous section.

pH-4 buffer   A stock of 2 liters of Beckman pH-4 buffer was prepared and used for each series of rare-earth chelate determinations.

Procedure

The rare-earth glycolate and lactate stability constants were run as follows. A series of fifteen solutions was prepared containing 0.004M rare-earth perchlorate; varying concentrations of the buffer mixture, which was made up of equal concentrations of ligand acid and its sodium salt, between 0.002M and 0.088M in total ligand acid and its sodium salt; and enough sodium perchlorate to adjust the ionic strength to 0.1. Rough measurements were made of the stability constants with solutions in which the ionic strength was adjusted without considering the effect of the complex formation upon the ionic strength. These rough measurements gave information as to the amount of complexing taking place; and solutions were again prepared, this time with the correct amount of sodium perchlorate present to adjust the ionic strength to 0.1.

The solutions were all equilibrated for twenty-four hours in a constant temperature bath set at 20±0.02° C. After that time, the pH of each solution was read with the pH meter while the solutions were still suspended in the constant temperature bath. Figure 1 shows the hydrogen-ion concentration of the solutions plotted against the initial lactic-acid concentration.

In order to take advantage of similar conditions, the ionization constants of glycolic and lactic acids were determined in the same manner except that the rare-earth salt was left out of the solutions and fewer solutions were run. The ionization constants were found to be $2.33 \pm 0.04 \times 10^{-4}$ for lactic acid and $2.72 \pm 0.04 \times 10^{-4}$ for glycolic acid. Each ionization constant was rerun and the values obtained were found to agree within the margin of error reported.

Tables 7 and 8 give the stability constants as determined by this work. The experimental data is given in the appendix. Although Sonesson (44,45,46,47) reports up to four constants for the acetate and the glycolate systems at an ionic strength of 2.0, the low ionic strength of this work did not permit the ligand-ion concentration to attain a high enough value to allow the formation of an appreciable concentration of any anionic species. If only three stability constants are considered, the equation for X_2 (equation 5) is a straight line with β_2 as its intercept and β_3 as its slope.

$$X_2 = \beta_2 + \beta_3[A^-]$$

Figure 1. $[H^+]$ released by 0.004M rare-earth perchlorates in lactic acid-sodium lactate solution

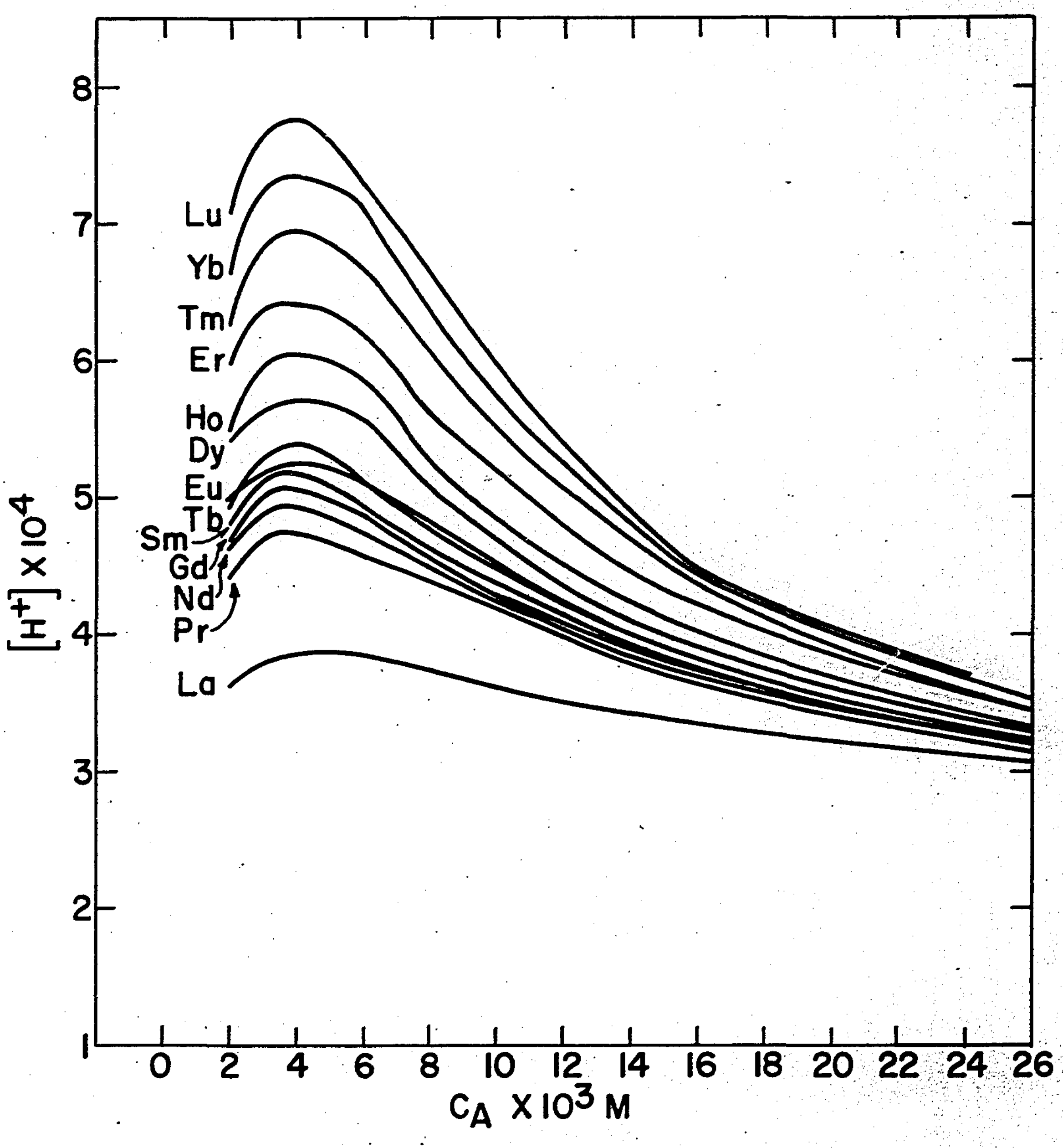

Lu
Yb
Tm
Er
Ho
Dy
Eu
Tb
Sm
Gd
Nd
Pr
La
$[H^+] \times 10^4$
1
2
3
4
5
6
7
8
0
2
4
6
8
10
12
14
16
18
20
22
24
26
$C_A \times 10^3$ M

Table 7. The stability constants of the rare-earth-glycolate systems, $\mu = 0.1\text{m}$ ($NaClO_4$)

Rare-earth	K_1	K_2	K_3
La	355±12	49±6	6±2
Ce	495±15	71±8	7±2
Pr	600±20	80±9	15±4
Nd	780±25	92±10	18±5
Sm	820±25	126±14	36±9
Eu	860±25	137±15	28±7
Gd	620±20	116±13	14±4
Tb	660±20	123±13	13±3
Dy	840±25	111±12	38±10
Ho	980±30	112±12	34±9
Er	1010±30	153±17	46±12
Tm	1135±35	188±21	47±12
Yb	1350±40	174±20	55±14
Lu	1400±45	214±23	63±16
Y	610±20	123±13	8±2

Since the plots of X_2 against ligand-ion concentration did give a straight line, β_3 was computed from the slope rather than from an extrapolation to zero ligand-ion concentration as described in the derivation of equations.

A check of the constants was made by calculating $\bar{n}$'s from the stability constants and comparing with the experimental $\bar{n}$'s. Figure 2 shows the calculated formation curve (smooth curve) and the experimentally determined $\bar{n}$'s (circles) for ytterbium lactate.

Sonesson investigated the possibility of forming polynuclear complexes with both acetate ion and glycolate ion.

Figure 2. Comparison of $\bar{n}$'s calculated from β's (smooth curve) to experimental $\bar{n}$'s (circles) for ytterbium lactate

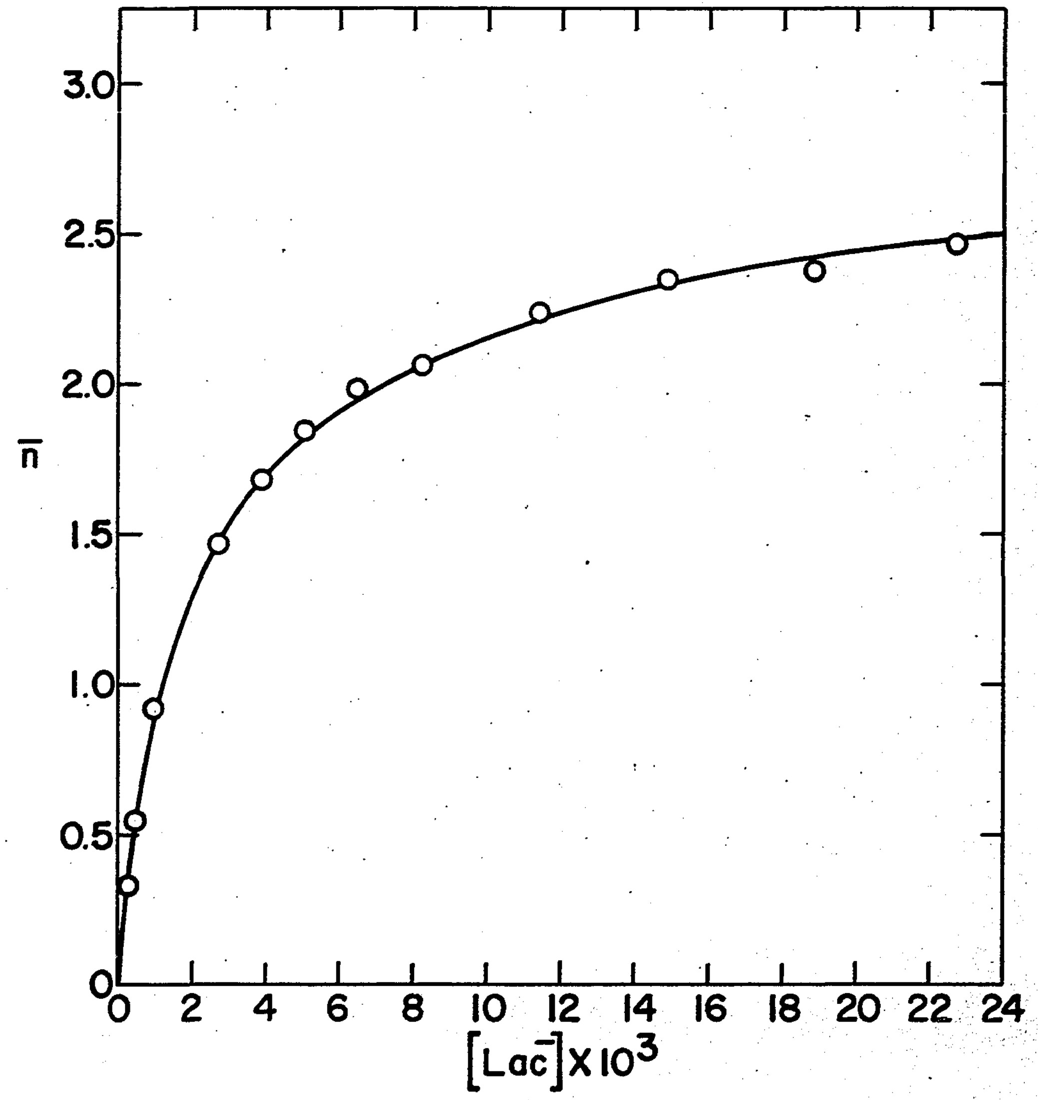

3.0
2.5
2.0
1.5
1.0
0.5
0
$\bar{n}$
0
2
4
6
8
10
12
14
16
18
20
22
24
$[Lac^-] \times 10^3$

Table 8. The stability constants of the rare-earth-lactate systems, $\mu = 0.1m$ ($NaClO_4$)

Rare-earth	K_1	K_2	K_3
La	400±13	55±6	20±5
Ce	570±20	93±10	17±5
Pr	705±24	113±12	16±4
Nb	740±25	126±14	26±7
Sm	760±25	162±18	18±5
Eu	890+30	169+19	18+5
Gd	780±26	141±16	16±4
Tb	790±26	203±22	14±4
Dy	1020±35	220±24	21±5
Ho	1050±35	250±27	26±7
Er	1460±50	288±32	38±10
Tm	1550±52	329±36	53±13
Yb	1700±57	388±42	58±15
Lu	1875±60	405±44	79±20
Y	1040±35	216±24	42±11

He found that the tendency toward dinuclear complexes with acetate ion was very slight and considered the existence of any such complexes as uncertain. With the glycolate ion he was unable to find any concrete evidence for such complexes. Since in this work the metal-ion concentration was kept considerably lower than in Sonesson's work, the existence of polynuclear complexes was completely disregarded.

Discussion

The values of the rare-earth lactate and glycolate stability constants are given in Tables 7 and 8. In general, the rare-earth lactates are more stable than the corresponding rare-earth glycolates. This can be explained as a result of chelation and the influence of the electron donating methyl group on the hydroxyl group. The hydroxyl group should have a higher electron density as a result of the methyl group and should complex more readily with the electropositive metal. This same methyl group could have a similar effect upon the carboxylic acid, but it would be operating through such a distance that its effect would probably be very small. Induction forces are generally believed to be short-ranged forces.

Both the glycolates and lactates are stronger complexes than the acetates reported by Sonesson (45), and Kolať and Powell (48). This fact indicates that some other factors affect the stability constants than just the acid-dissociation constants. The affinities of the ligands for hydrogen ion is in the order of acetate > glycolate > lactate, just the opposite of the order of affinities of the ligands for rare-earth-metal ions.

The activity correction for converting from the ionic strength that Sonesson used (2.0) to the ionic strength used in this work (0.1) can be estimated from the differences in the values of the glycolate stability constants reported by Sonesson and those in this work. It is quite unlikely that this correction should change significantly in the rare-earth series, since the activity coefficients of the rare-earth ions do not change significantly within the series (60). The logarithm of the activity coefficient correction should be the difference in the log values of the stability constants at each ionic strength. A value of between 0.35 and 0.41 for the logarithm of this activity coefficient correction would compensate for most of the difference between the two ionic strengths. This is a reasonable value for such an activity coefficient correction.

Bjerrum (16) has shown that, according to statistical calculations, the stability constants for systems with simply bound ligands ought to have the following relation

$$K_1:K_2:K_3:K_4:K_5:K_6 \ = \ 6:5/2:4/3:3/4:2/5:1/6 \quad .$$

It could be expected from statistical reasons that the quotients K_n/K_{n+1} should have greater values in systems of chelating ligands than in systems with simply bound ligands, since the chelating ligand leaves fewer sites vacant for coordination, where the next ligand can be bound, than does the simply bound ligand. According to Bjerrum, if the metal ion has six octahedrally arranged coordination sites and if the ligand is a bidentate molecule occupying adjacent coordination sites, the stability constants ought to have the following relation

$$K_1:K_2:K_3 \ = \ 12:2:1/3 \quad .$$

Table 9 gives the K_n/K_{n+1} values for the rare-earth glycolates and lactates. The K_1/K_2 values for the glycolates are all near to or greater than a value of six in keeping with Bjerrum's theories. Sonesson (46) did not find values this large for K_1/K_2 at ionic strength 2.0, and also he noted that the ratios did not differ greatly from the ratios observed for the non-chelating acetate systems for the light rare earths.

Table 9. K_n/K_{n+1} values for the rare earth glycolates and lactates at 0.1m ionic strength

Rare-earth	Glycolates		Lactates	
	K_1/K_2	K_2/K_3	K_1/K_2	K_2/K_3
La	7.2	8.2	7.3	2.7
Ce	7.0	10.1	6.1	5.6
Pr	7.5	5.3	6.2	6.9
Nd	8.5	5.1	5.9	4.8
Sm	6.5	3.5	4.7	9.0
Eu	6.3	4.9	5.3	9.4
Gd	5.3	8.3	5.5	8.6
Tb	5.4	9.5	3.9	14.1
Dy	7.6	2.9	4.6	10.5
Ho	8.7	3.3	4.2	9.6
Er	6.6	3.3	5.1	7.6
Tm	6.0	4.0	4.7	6.2
Yb	7.8	3.2	4.4	6.7
Lu	6.5	3.4	4.6	5.1
Y	5.0	15.4	4.8	5.1

For the heavy rare earths his K_1/K_2 ratios for the acetates were lower and near the expected 2.4. Kolat and Powell found the K_1/K_2 ratios for the rare-earth acetates at ionic strength 0.10 varied in a similar manner. The lactate K_1/K_2 values are near six for the light rare earths but are lower for the heavy rare earths. The errors in K_2 are so large as to make the K_1/K_2 ratios inconsistent and somewhat unreliable. The errors in K_3 are so large that the K_2/K_3 ratios are very unreliable. Therefore, the K_2/K_3 ratios will not be discussed, although they are reported here. In general, because of the relatively high values of the stability constants compared to values of stability constants of simple carboxylic acid ligands with other metal ions, it can be said that the glycolate and lactate ions act as chelating ligands.

The relative values of the stability constants across the series of rare-earths is of interest. Figures 3 and 4 show the logarithm of the first stability constants plotted against atomic number. The values of the stability constants with both ligands increase in value with increasing atomic number between lanthanum and europium, and between gadolinium and lutetium. The gadolinium stability constant, however, is lower than the europium stability constant. Thus, the lower series overlaps the higher series. With the tighter lactate complexes, the light-rare-earth series overlaps the heavy series enough to make the samarium and gadolinium lactate systems very similar. With the glycolate complexes, the overlap is much more pronounced, and the gadolinium glycolate stability constants lie in value between the praseodymium and neodymium glycolate stability constants.

Figure 3. First stability constants of the rare-earth glycolates

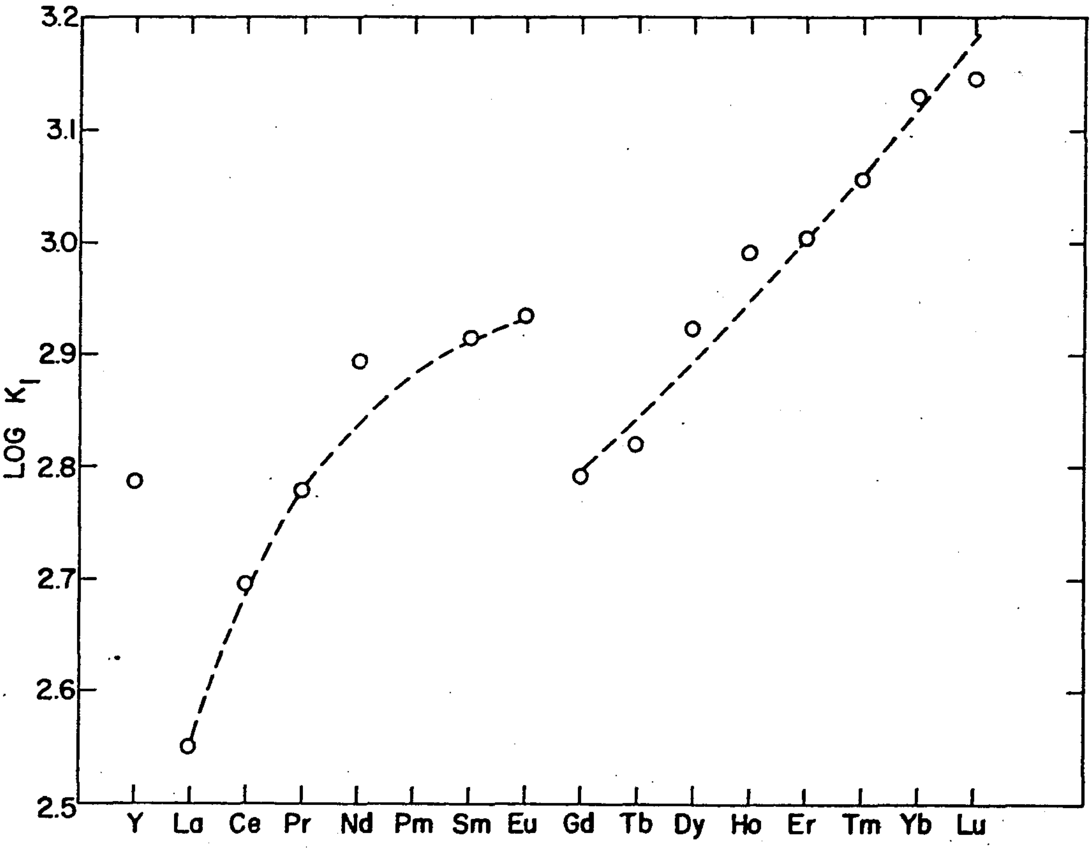
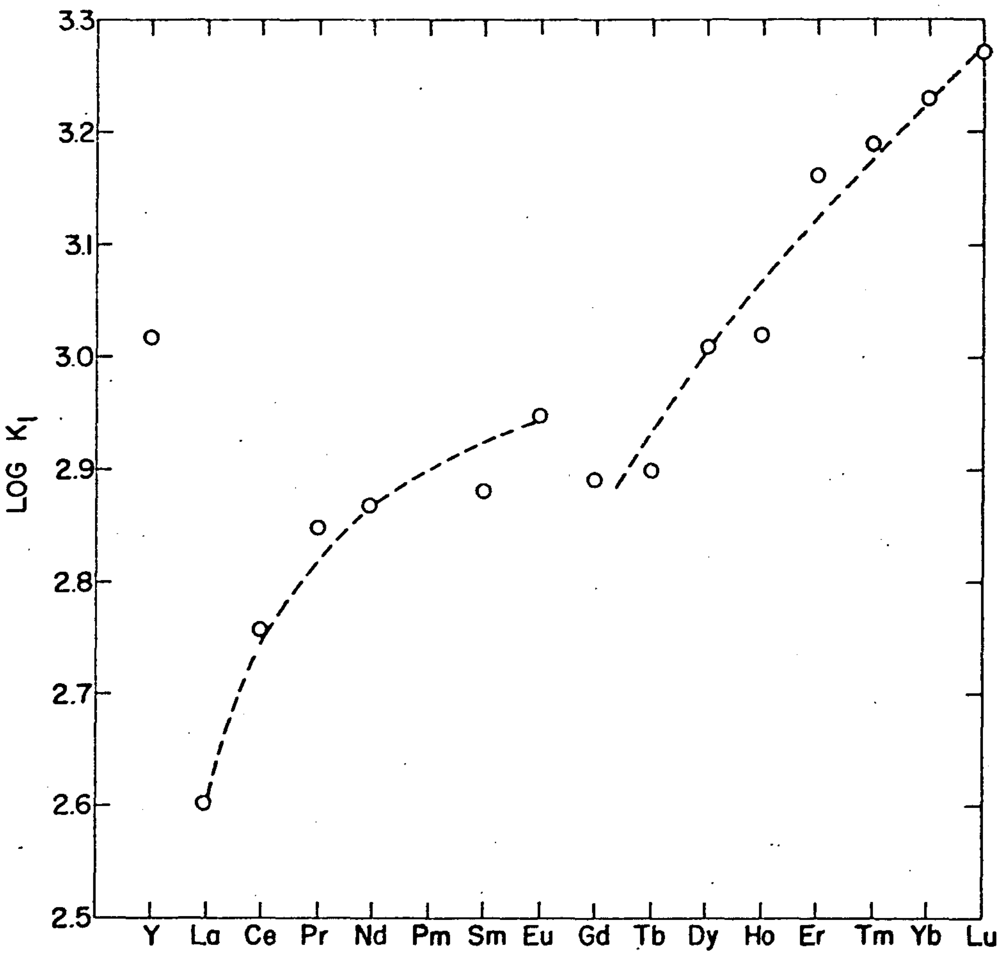

LOG K$_1$
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
Y
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

Figure 4. First stability constants of the rare-earth lactates


3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
LOG K1
Y
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

An abnormally low value has been observed for gadolinium in every series of stability constants that has been determined. This "gadolinium break" has been the subject of some discussions of rare-earth stability constants (7). Since gadolinium has a half-filled 4f-electron shell it would not be stabilized by the ligand field. Thus, it has been suggested that correlations of stability constants of rare-earth complexes should consider ligand-field stabilization (61,62).

The relationship of the yttrium stability constants to the rare-earth constants seems to vary markedly with the ligand. Sonesson found the yttrium acetate constants to be lower than any of the rare-earth acetate constants. The yttrium glycolate constants are among the light-rare-earth glycolate constants, and the yttrium lactate constants fall between the values for holmium and dysprosium lactates. The ionic radius of the yttrium ion is between the ionic radii of the holmium and dysprosium ions. In most stability constant series yttrium falls somewhat below the position predicted from ionic radii. This also may be due to the lack of ligand-field stabilization, since yttrium has no 4f electrons.

Powell and Farrell have made a complete study of the solubilities of the rare-earth glycolates (63). They found that the rare-earth glycolates precipitated from aqueous solution in two different forms. The heavy rare-earths and yttrium separated as dihydrated glycolates, while the light rare-earths separated as anhydrous glycolates. The transition from anhydrous to dihydrated glycolates occurred between europium and gadolinium just as the break in the stability constants occurred between europium and gadolinium. The molal solubility of yttrium glycolate dihydrate was between the solubilities of dysprosium and holmium in agreement with ionic radii, but not in agreement with stability constant trends.

A complete study of other ligands of this type should help elucidate the chemistry of the rare earths. The anomaly at gadolinium for nearly all measurements of rare earth properties should be studied further as should the inconsistent behavior of yttrium. Stability constants are a measure of the free energy of the complex, and are also related to the enthalpy and entropy as shown:

$$-RT\ln K = \Delta F = \Delta H - T\Delta S \quad .$$

It would be valuable to know if these strange phenomena are a result of differences in enthalpy, entropy, or both. Studies of this type could be done either calorimetrically or by obtaining stability constant data at other temperatures. Such studies might indicate whether any ligand-field stabilization effects are present in these complexes.

RARE-EARTH STABILITY CONSTANTS

Methods of Determining Strong Stability Constants

Some of the methods described in the first section of this thesis are applicable to determination of the stronger rare-earth chelates with aminopolyacetic acids. Others, however, either are not applicable or must be modified if they are to be used.

In particular, the methods using hydrogen-ion measurements must be modified. Schwarzenbach and associates (64,65) were able to determine the stability constants of the alkaline-earth EDTA complexes by a straight titration, but the stronger rare-earth EDTA complexes required some modification of the method. Schwarzenbach and Freitag (66) accordingly developed a procedure which proved to be successful for very stable chelates. They allowed two chelating agents to compete for a heavy metal ion. A second metal was then introduced which formed a very stable complex with one of the chelating agents and no complex with the other. Wheelwright, Spedding and Schwarzenbach (67) used copper and β, β', β''-triaminotriethylamine (tren) with this method to determine the rare-earth EDTA and HEDTA stability constants. The reaction was

$$\mathrm{CuCh^{-2} + H_3tren^{+3} + M^{+3} \rightleftarrows MCh^{-} + Cu(tren)^{+2} + 3H^{+}} \quad .$$

The hydrogen ion was partially neutralized with standard base and the excess measured with a pH meter. Wheelwright et al. were able to calculate the stability constants with the use of material balance equations, the equilibrium equation, and several independently measured constants.

The extinctiometric technique is somewhat simpler for aminopolycarboxylate complexes, due to the lesser number of species; but generally is not applicable, due either to a lack of change in absorbance on chelation or to the measurable species not occurring within the proper concentration range. The technique is severely limited by aqueous solutions which prevent the use of infrared absorption. Kolthoff and Auerbach (68), however, determined the iron (III) complex with EDTA by a spectrophotometric technique. In order to prevent 100% formation of the iron chelate, they conducted their measurements in 0.6 to 1-molar perchloric acid. A spectrophotometer was used to determine the concentration of iron chelate present and a pH determination was needed to calculate the concentration of chelate anion.

The remaining three methods discussed here have been applied with greatest success to very strong chelates. The first of these, the mercury electrode, was adapted for determining chelate stability constants by Reilley and Schmid (69). The potential of this electrode is determined by the concentration of mercuric ion in solution and, therefore, is a measure of the concentration of that ion. If the mercuric ion is allowed to compete with another metal ion for a chelate, the stability constant of that metal chelate may be determined from the concentration of mercuric ion and the mercuric-chelate stability constant. The method is limited by the fact that present calculations neglect the presence of non-chelated mercurous ions. If the ratio of the mercury-chelate stability constant to the other metal-chelate constant is less than a thousand, mercurous ions can not be neglected. There is, furthermore, a limitation upon the pH range of the determinations. Schwarzenbach and Anderegg (70) combined the mercury electrode with hydrogen-ion determinations to obtain not only metal-chelate stability constants, but also the formation constants of protonated and hydroxy substituted species.

There are two polarographic methods for measuring chelate stability constants. The first method can be applied only if the electrode reaction is thermodynamically reversible. Then, the polarographic half-wave potential of the dropping mercury electrode depends upon the stability of the chelated metal ion. The stability constant of the metal chelate is determined from the difference between the half-wave potential of the chelated metal ion and the half-wave potential of the non-chelated metal ion. This method has been reviewed very completely by Lingane (71).

The other polarographic technique is the one used to obtain data for this dissertation. It depends upon the change in the reduction potential of a metal ion when it is chelated. If the reduction potential is changed by as much as 0.2 volt, the polarographic waves will not overlap, and the individual diffusion currents may be measured. A complexing agent which will change the reduction potential of a metal ion by 0.2 volt generally forms such a stable chelate that virtually all of the metal ion in solution will be chelated. Therefore, the general technique is to allow two metal ions to compete for a chelating agent. One of the metal ions must have an easily read polarographic wave and its chelate stability constant must be known in order to evaluate the stability constant of the other metal chelate. The necessary equations are developed in the experimental part of this work. Schwarzenbach et al. (72) have used this method to measure a large number of metal-chelate stability constants.

Experimental

Derivation of equations

When a reference-metal ion (M^{+2}) competes with a rare-earth-metal ion (R^{+3}) for a chelating agent (Ch^{-4}) the following equilibrium exists:

$$MCh^{-2} + R^{+3} \rightleftharpoons RCh^{-} + M^{+2} \quad .$$

The equilibrium constant for this reaction is

$$K_{eq} = \frac{[M^{+2}][RCh^{-}]}{[MCh^{-2}][R^{+3}]} .$$

The stability constants for the rare-earth metal and reference-metal chelates are defined as

$$K_{RCh} = \frac{[RCh^{-}]}{[R^{+3}][Ch^{-4}]} \quad \text{and} \quad K_{MCh} = \frac{[MCh^{-2}]}{[M^{+2}][Ch^{-4}]} .$$

Now the equilibrium constant for the reaction may be written as

$$K_{eq} = \frac{K_{RCh}}{K_{MCh}} = \frac{[M^{+2}][RCh^{-}]}{[R^{+3}][MCh^{-2}]} .$$

If the solution contains equimolar quantities each of the two cations and the chelating agent, the following expressions apply at equilibrium:

$$[RCh^{-}] = [M^{+2}] \quad \text{and} \quad [MCh^{-2}] = [R^{+3}] = C_M-[M^{+2}]$$

where C_M is the initial concentration of the reference metal. Therefore, the equilibrium constant is

$$K_{eq} = \frac{K_{RCh}}{K_{MCh}} = \frac{[M^{+2}]^2}{(C_M-[M^{+2}])^2} .$$

Solving for the rare-earth stability constant and converting the reference-metal-ion concentrations to percentages of the total reference metal gives

$$K_{RCh} = K_{MCh}\frac{(\%M^{+2})^2}{(100-\%M^{+2})^2}$$

or

$$\log K_{RCh} = \log K_{MCh} + 2\log\frac{\%M^{+2}}{100-\%M^{+2}} \quad .$$

Thus, if the stability constant of the reference-metal chelate is known and the percentage of the total reference-metal ion that is not chelated is determined, the stability constant of the rare-earth chelate may be determined.

Actually, the protonated species of the complexant as well as protonated species of the reference-metal chelate and the rare-earth chelate should be included in the above equations. Hiller (8) considered all such species and derived the complete material balance equation for the total chelate present. He was then able to show that in the case of EDTA all terms except those relating to the RCH^- and MCh^{-2} species are negligible at a pH of 4.5

In order to prevent extensive hydrolysis of the rare-earth-metal ions in solution, the pH of the solution should be kept somewhat below the neutral equivalence point of the rare-earth salt used; but, in order to minimize the formation of the previously mentioned protonated species, the pH should not be too low. For these reasons, a sodium acetate-acetic acid buffer was used in this work to maintain a pH of about 4.65. Therefore, complex species formed by the association of the metals with acetate must also be considered. Hiller derived an equation for the equilibrium constant taking into account these species. For the sake of brevity, this straight-forward derivation will not be included here but only the resulting equation is reproduced.

$$\log K_{RCh} = \log K_{MCh} + 2 \log \frac{\% M^{+2}}{100-\% M^{+2}} + \log \frac{F(Ac)}{f(Ac)}$$

In this equation

$$F(Ac) = 1+K_1[Ac^-]+K_1K_2[Ac^-]^2+K_1K_2K_3[Ac^-]^3+\ldots$$

$$f(Ac) = 1+K_1'[Ac]+K_1'K_2'[Ac^-]^2+K_1'K_2'K_3'[Ac]^3+\ldots$$

where K_n and K_n' are the respective successive formation constants of the rare-earth and reference-metal acetate complexes.

Since the first and second acetate formation constants are now available at 0.1 ionic strength (48), a correction for acetate complexing is included in this work.

Materials and equipment

Rare-earth nitrate solutions The rare-earth nitrate stock solutions used in this work were prepared by the same technique described earlier for rare-earth perchlorates. One-hundredth-molar solutions were prepared from these stock solutions.

DCTA solution DCTA was obtained from Geigy Industrial Chemicals, a division of Geigy Chemical Corporation, Ardsley, New York. A one-hundredth-molar stock solution was prepared of the tetra-potassium salt of the chelating agent.

Acetate buffer A 0.10M sodium acetate-0.10M acetic acid buffer was prepared from standardized acetic acid and sodium hydroxide solutions.

Potassium nitrate A one-molar solution for adjusting the ionic strength was prepared from reagent grade potassium nitrate.

Cadmium and zinc nitrate Stock solutions of cadmium and zinc nitrates were prepared from reagent grade salts and standardized by titration with EDTA. One-hundredth-molar solutions were prepared from the stock solutions.

Polarograph A Sargent model XXI polarograph obtained from Sargent and Company, Chicago, Illinois, was used in this research. The polarographic cell was fashioned from a 100-milliliter beaker. A saturated calomel electrode was connected to the cell with a potassium nitrate-agar bridge, and the cell was immersed in a constant temperature bath at $20.0\pm0.02^{\circ}$ C.

Procedure

Samples were prepared by combining:

1. Ten milliliters of 0.0100M reference-metal nitrate (the reference metals used were zinc, cadmium and europium),
2. Ten milliliters of 0.0100M rare-earth nitrate,
3. Ten milliliters of 0.0100M tetra-potassium DCTA,
4. Ten milliliters of the 0.1000M sodium acetate-0.1000M acetic acid buffer, and
5. Enough potassium nitrate to adjust the ionic strength to 0.1 (allowances were made for the potassium nitrate formed in the reaction of the potassium DCTA with the rare-earth nitrate, and the change in ionic strength due to the different contributions of the divalent and trivalent metal chelates at equilibrium).

The mixtures were placed in one-hundred-milliliter volumetric flasks and diluted to the mark with distilled and deionized water.

Solutions of the reference-metal nitrates were prepared in the same manner without the chelating agent or the rare-earth nitrate. These were used for polarographic standards in the measurements. Also, solutions were prepared of the completely complexed reference metal by omiting the rare-earth nitrate.

The three reference metals used in this work gave distinctive reduction waves on the polarograph, and the reduction potentials of their DCTA chelates are so far removed from the reduction potentials of the free ions that there was no interference between the polarographic waves. Since the diffusion current is proportional to the concentration of the species producing the polarographic wave, the percentage of unchelated reference-metal ion was calculated from the ratio of the diffusion currents of the sample runs to those of the standard solutions. The actual measurement of the diffusion currents was done by the method described by Hiller (8).

The process of making a polarogram involved placing the sample in the cell in the constant temperature bath. Then, argon, which had been previously passed through a 0.1M potassium nitrate solution, was passed through the sample to remove the dissolved oxygen; and the polarogram was run. Before a series of polarograms and after every fifth polarogram, a sample of the appropriate standard was run.

The equations for the reduction waves used in this research and the observed half-wave potentials versus the calomel electrode were:

$2e^- + Cd^{+2}$ Cd, $E_{\frac{1}{2}}$ -0.59 volt
$2e^- + Zn^{+2}$ Zn, $E_{\frac{1}{2}}$ -1.03 volts
$e^- + Eu^{+2}$ Eu^{-2}, $E_{\frac{1}{2}}$ -0.68 volt.

With these potentials in mind, the voltage limits used in the polarograms were for cadmium -0.30 to -1.30, for zinc -0.50 to -1.50, and for europium -0.40 to -1.40.

All of the polarographic data are presented in Tables 10, 11, and 12; and the stability constants are plotted against the atomic number in Figures 5 and 6.

Table 10. Rare-earth DCTA stability constants at 20° C versus cadmium, $\mu = 0.10$ (KNO_3)

Rare-earth	% Free cadmium	log K_{MCh}	log K_{MCh}(corrected)
La	2.4	16.00	16.18 ± 0.55
Ce	5.2	16.71	16.96 ± 0.43
Pr	7.7	17.01	17.37 ± 0.28
Nd	9.9	17.31	17.66 ± 0.21
Sm	22.2	18.14	18.55 ± 0.10
Eu[a]			
Gd	35.3	18.70	19.02 ± 0.07
Tb	52.7	19.32	19.58 ± 0.07
Dy	65.4	19.78	20.02 ± 0.08
Ho	71.9	20.05	20.27 ± 0.08
Er	80.1	20.44	20.66 ± 0.12
Tm	83.5	20.64	20.87 ± 0.13
Yb	89.5	21.09	21.33 ± 0.20
Lu	90.0	21.14	21.39 ± 0.22
Y	60.6	19.60	19.81 ± 0.08

[a] The europium-DCTA constant could not be measured against cadmium because their respective reduction potentials are so close together that their polarograms interfere with each other.

Since all of the polarographic data on rare-earth stability constants in the literature were obtained with an acetate buffer, but the acetate complexing of the various metal ions

Table 11. Rare-earth DCTA stability constants at 20° C versus zinc, μ = 0.10 (KNO_3)

Rare-earth	% Free zinc	log K_{MCh}	log K_{MCh}(corrected)
La	5.7	16.23	16.41 ± 0.39
Ce	10.3	16.79	17.04 ± 0.21
Pr	14.5	17.13	17.43 ± 0.15
Nd	18.8	17.40	17.75 ± 0.12
Sm	34.3	18.10	18.51 ± 0.07
Gd	49.5	18.65	18.97 ± 0.05
	% Free europium		
Eu	53.6	18.57	18.99 ± 0.08
Eu	53.1	18.56	18.98 ± 0.08

was ignored; the logarithms of the stability constants are reported in the tables both with the acetate correction [log K_{MCh}(corrected)] and without the acetate correction (log K_{MCh}).

The values for the stability constants of the reference metals were obtained as follows:

Cadmium DCTA: Schwarzenbach _et al_. (72) reported a value of 19.23 for log K_{CdCh} from mercury electrode studies.

Zinc DCTA: Schwarzenbach _et al_. (72) reported a value of 18.67 for log K_{ZnCh} from a polarographic study using cadmium as the reference metal. Correcting this value for complexing due to acetate, as reported by

Table 12. Rare-earth DCTA stability constants at 20° C versus europium, μ = 0.10 (KNO_3)

Rare-earth	% Free europium	$\Delta\log K_{MCh}$	$\Delta\log K_{MCh}$(corrected)
La	6.9	-2.26	-2.50 ± 0.31
Ce	14.0	-1.58	-1.75 ± 0.15
Pr	17.6	-1.34	-1.46 ± 0.13
Nd	22.0	-1.10	-1.17 ± 0.10
Sm	39.3	-0.38	-0.38 ± 0.08
Eu			
Gd	54.7	0.16	0.06 ± 0.07
Tb	72.7	0.85	0.69 ± 0.09
Dy	81.8	1.31	1.13 ± 0.12
Ho	83.6	1.42	1.22 ± 0.13
Er	90.9	2.00	1.80 ± 0.24
Tm	92.4	2.16	1.97 ± 0.30
Yb	95.0	2.56	2.38 ± 0.47
Lu	96.2	2.81	2.63 ± 0.66
Y	76.8	1.04	0.83 ± 0.10

Kolat and Powell (48), adjusted the figure to 18.59.

Europium DCTA: The europium-DCTA stability constant was determined in this work from the polarogram of europium in a europium-zinc sample and the value of 18.99 for log K_{EuCh} was calculated from the zinc-DCTA stability constant.

Discussion

For several years investigators of the properties of rare-earth chelates have referred to the values of the DCTA chelate stability constants reported by Schwarzenbach *et al.*

Figure 5. Rare-earth DCTA stability constants based on cadmium DCTA

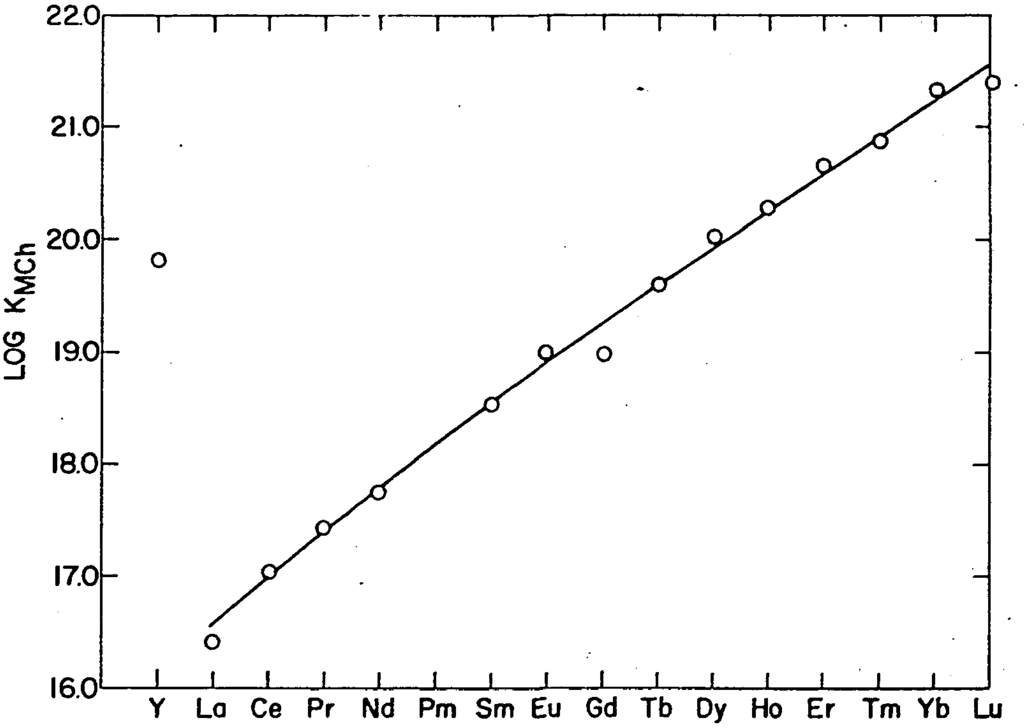
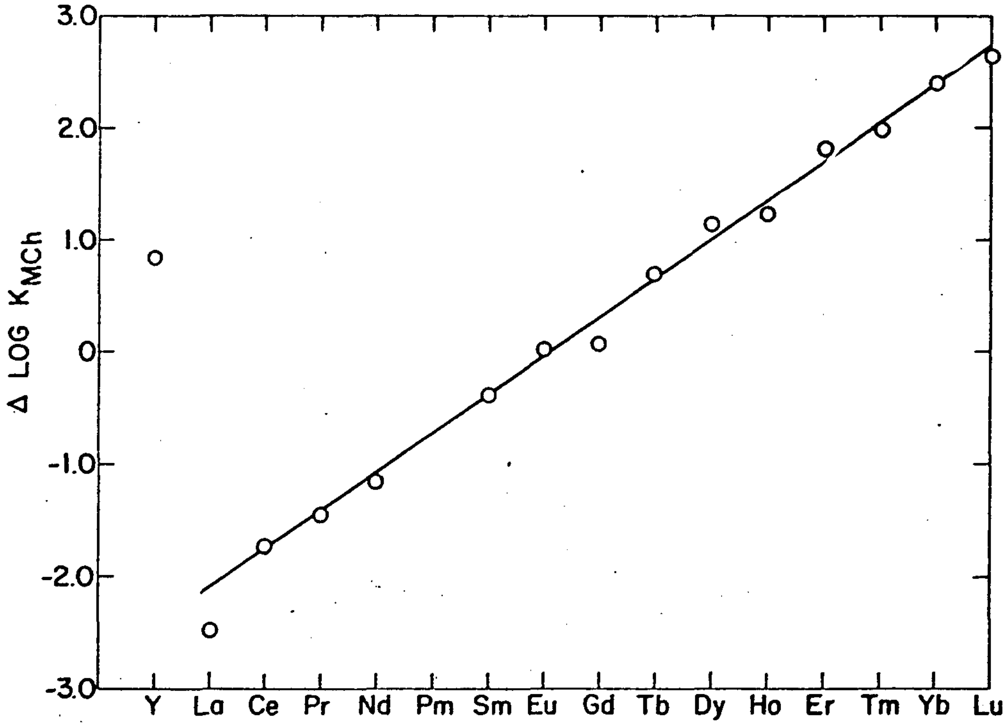

22.0
21.0
20.0
19.0
18.0
17.0
16.0
LOG K_{MCh}
Y
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

Figure 6. Rare-earth DCTA stability constants based on europium DCTA


Δ LOG K$_{MCh}$
3.0
2.0
1.0
0
-1.0
-2.0
-3.0
Y
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

(72). Their constants, Table 13, like those in this thesis show a general similarity with the EDTA stability constants.

Table 13. Stability constants of the rare-earth EDTA and DCTA chelates reported by Schwarzenbach, Gut, and Anderegg at 20° C and 0.10 ionic strength (not corrected for acetate complexing)

Rare-earth	EDTA log K_{MCh}	DCTA log K_{MCh}
La	15.50	16.26
Ce	15.98	16.76
Pr	16.40	17.31
Nd	16.61	17.68
Sm	17.14	18.38
Eu	17.35	18.62
Gd	17.37	18.77
Tb	17.93	19.50
Dy	18.30	19.69
Ho	18.74	
Er	18.85	20.68
Tm	19.32	20.96
Yb	19.51	21.12
Lu	19.83	21.51
Y	18.09	19.15

The DCTA chelates are stronger than the EDTA constants, and the graphs of the stability constants against atomic number of the rare earths have the same shape. The one noticeable difference is that the value of the yttrium-DCTA constant in their data lies between the values of the gadolinium and terbium constants; whereas, the value of the yttrium EDTA constant falls between the values of the terbium and dysprosium constants. There have been a great number of ion-exchange-elution studies of the rare earths and yttrium with EDTA which verify the relationship of the yttrium constant to the rare-earth constants, but there has not been a complete elution study of metal ions with DCTA. Due to the similarity of the two chelates and the trend of the stability constants of their rare-earth chelates, it was believed that the relationship of the yttrium-DCTA constant to the rare-earth constants given by Schwarzenbach, Gut and Anderegg might be in error. Indeed, when the complete series of rare-earth DCTA constants was run against both cadmium and europium in this work, the yttrium constant fell between the terbium and dysprosium constants in value.

The major source of errors in this work was the determination of the free metal ion with the polarograph. In general, the maximum error in any polarographic measurement of the concentration of a metal ion is ± 2 per cent. Calculating the maximum change in the stability constants due to a change of ± 2 in the percentages of free reference-metal ion gave the margins of error reported in the tables. The constants were run against both cadmium and zinc because the margin of error was less for the light-rare-earth stability constants with zinc, and less for the heavy-rare-earth stability constants with cadmium. The determinations made with europium as the reference metal should give good relative values of the stability constants. The values determined for these runs were reported as the difference in the logarithm of the stability constant from the logarithm of the stability constant of europium DCTA; and, if the europium DCTA stability constant could be determined by an independent method, these values would give an independent measurement of the series of rare-earth DCTA stability constants.

Unfortunately, all of the DCTA stability constants reported here depend upon the cadmium constant which Schwarzenbach determined with the mercury electrode. It would be worthwhile for future work to try to determine the zinc and europium constants independently and obtain another check on the absolute magnitude of all of the constants.

In the rare-earth DCTA stability constant sequence, the usual "gadolinium break" is noted. This break is more pronounced when acetate complexing is considered, due to stronger acetate complexing with europium than with gadolinium. The consideration of acetate complexes lowers the gadolinium constant with respect to europium by 0.10 log unit. The "gadolinium break" in the rare-earth EDTA constants was attributed to a change in coordination (67), and the same reasoning could apply to the rare-earth DCTA chelates. The "gadolinium break" has also been attributed to ligand-field stabilization (61,62).

From its rare-earth stability constants, the feasibility of using DCTA as an eluting agent in the separation of the rare-earths can be predicted. The separation factor for the separation of adjacent rare earths is the ratio of the stability constants of the rare earths. The ratio of the lutetium constant to the lanthanum constant is nearly ten times as large for DCTA as for EDTA, indicating a general increase in separation factor across the series. Due to the "gadolinium break", it appears that europium and gadolinium may be difficult to separate, and their elution order might even be reversed. In spite of the increased separation factors, DCTA would have the disadvantage of being kinetically slow in its aqueous exchange due to the stronger complexes. This factor would tend to make the height equivalent to a theoretical plate for the ion-exchange columns much larger and give a poorer separation. Also, the higher cost of DCTA tends to discourage its use for processes in which EDTA is adequate.

In the future, it would seem valuable for ion-exchange-elution studies to be conducted with DCTA to establish elution orders, for comparison with the stability constants. The position of yttrium in the rare-earth elution sequence is of particular interest. Furthermore, the high stability constants and the related slow exchange rates may make DCTA a valuable reagent in studies of ion-exchange kinetics.

SUMMARY

The first three successive formation or stability constants of the rare-earth complexes with glycolic and lactic acids were measured by a potentiometric technique. These constants were compared with the stability constants of the rare-earth acetates, and it was postulated that the glycolate and lactate ions were reacting as bidentate ligands. The variations of the stability constants with atomic number of the rare-earth central ion were observed and the "gadolinium break" noted.

The stability constants of the rare-earth chelates with 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid were determined by polarographic comparison with cadmium, zinc, and europium complexes. These constants were compared with those of the rare-earth chelates of ethylenediamine N,N,N',N'-tetraacetic acid, and the trends in both series were discussed. A comparison of the two chelating agents as eluants for the ion-exchange separation of rare-earths was made.

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APPENDIX

EXPERIMENTAL DATA FROM MEASUREMENT OF RARE-EARTH GLYCOLATE AND LACTATE STABILITY CONSTANTS

Lanthanum Glycolate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Gly^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Gly^-]$
1	3.14	0.594	0.180	303
2	3.83	1.148	0.309	269
4	4.18	2.331	0.522	224
6	4.18	3.632	0.697	192
8	4.07	5.074	0.833	164
10	4.00	6.528	0.968	148
12	3.91	8.076	1.079	134
14	3.81	9.723	1.165	120
16	3.72	11.43	1.236	108
20	3.56	15.01	1.337	89.1
24	3.48	18.49	1.465	79.2
28	3.39	22.19	1.536	69.2
32	3.30	26.10	1.557	59.6
38	3.21	31.93	1.599	50.1

$[Gly^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-4}$
0.3	1.107	357	6.7	
1.0	1.366	366	8.3	
2.0	1.762	381	11.0	
3.0	2.195	398	14.3	
4.0	2.666	417	15.5	
6.0	3.720	453	16.3	
8.0	4.941	493	17.3	
10.0	6.348	535	18.0	
12.0	7.928	577	18.5	8.3
15.0	10.63	642	19.1	10.7
18.0	13.72	707	19.5	11.1
22.0	18.50	795	20.0	11.4
26.0	23.96	883	20.3	10.8
30.0	29.97	966	20.4	9.7
34.0	36.52	1045	20.3	

Cerium Glycolate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Gly^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Gly^-]$
1	4.13	0.499	0.191	383
2	4.84	0.948	0.351	370
4	4.95	2.019	0.592	293
6	4.76	3.254	0.783	241
8	4.57	4.591	0.948	206
10	4.40	6.015	1.092	182
12	4.23	7.554	1.206	160
14	4.05	9.245	1.280	138
16	3.94	10.891	1.368	126
20	3.72	14.476	1.469	101.5
24	3.56	18.195	1.537	84.5
28	3.48	21.746	1.651	75.9
32	3.38	25.616	1.681	65.6
38	3.27	31.478	1.714	54.5

$[Gly^-] \times 10^{-3}$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-5}$
0.3	1.150	500		
1.0	1.522	522	27	
2.0	2.108	554	29.5	
3.0	2.765	588	31.0	
4.0	3.498	625	32.5	
6.0	5.241	707	35.3	
8.0	7.317	790	36.9	2.4
10.0	9.739	874	37.9	2.9
12.0	12.49	958	38.6	3.0
15.0	17.16	1077	38.8	2.5
18.0	22.62	1201	39.2	2.3
22.0	31.06	1412	41.7	3.0
26.0	40.95	1537	40.1	
30.0	51.59	1686	39.7	
34.0	63.87	1849	39.8	

Praseodymium Glycolate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Gly^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Gly^-]$
1	3.72	0.459	0.228	497
2	4.57	0.918	0.385	419
4	4.95	1.925	0.643	334
6	4.84	3.100	0.846	273
8	4.69	4.368	1.025	235
10	4.43	5.868	1.144	195
12	4.30	7.319	1.278	175
14	4.16	8.882	1.384	156
16	4.00	10.608	1.448	137
20	3.81	14.006	1.594	113.8
24	3.64	17.662	1.678	95.0
28	3.50	21.488	1.716	79.9
32	3.39	25.404	1.734	68.3
38	3.30	31.049	1.820	58.6

$[Gly^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-5}$
0.3	1.184	613	43	
1.0	1.647	647	47	
2.0	2.381	691	46	
3.0	3.216	739	46.3	
4.0	4.172	793	48.3	
6.0	6.439	907	51.2	
8.0	9.215	1027	53.4	6.8
10.0	12.52	1152	55.2	7.2
12.0	16.37	1281	56.8	7.3
15.0	23.18	1479	58.6	7.1
18.0	31.25	1681	60.1	6.7
22.0	43.93	1951	61.4	
26.0	58.53	2213	62.0	
30.0	74.96	2465	62.2	
34.0	93.88	2732	62.7	

Neodymium Glycolate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Gly^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Gly^-]$
1	4.03	0.403	0.250	620
2	4.91	0.836	0.414	495
4	5.30	1.781	0.687	386
6	5.19	2.873	0.912	317
8	4.88	4.187	1.075	257
10	4.69	5.528	1.235	223
12	4.47	7.030	1.354	193
14	4.34	8.502	1.483	174
16	4.13	10.266	1.537	150
20	3.91	13.641	1.688	124
24	3.75	17.136	1.810	105.6
28	3.58	21.002	1.839	87.6
32	3.47	24.812	1.884	75.9
38	3.33	30.767	1.892	61.5

$[Gly^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	X_3
0.3	1.247	823	143	
1.0	1.826	826	46	
2.0	2.759	880	50	
3.0	3.872	957	59	
4.0	5.174	1044	66	
6.0	8.353	1266	74	
8.0	12.35	1419	80	
10.0	17.25	1625	85	1.3
12.0	23.06	1838	88	1.3
15.0	33.58	2172	93	1.4
18.0	46.19	2511	96	1.3
22.0	66.47	2976	100	1.3
26.0	91.39	3477	104	1.2
30.0	118.7	3923	105	
34.0	147.5	4309	104	

Samarium Glycolate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Gly^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Gly^-]$
1	4.13	0.387	0.257	664
2	5.32	0.751	0.445	593
4	5.75	1.620	0.739	453
6	5.57	2.658	0.975	367
8	5.27	3.857	1.168	303
10	4.95	5.223	1.318	252
12	4.76	6.585	1.473	224
14	4.54	8.116	1.585	195
16	4.37	9.687	1.688	174
20	4.09	13.029	1.845	141.6
24	3.85	16.684	1.925	115.4
28	3.66	20.537	1.957	95.3
32	3.55	24.246	2.027	83.60
38	3.41	30.039	2.076	69.1

$[Gly^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.252	840		
1.0	1.905	905	85	
2.0	3.040	1020	100	
3.0	4.440	1147	109	
4.0	6.133	1283	116	
6.0	10.42	1570	125	3.7
8.0	16.05	1881	133	3.8
10.0	23.18	2218	140	3.7
12.0	32.00	2583	147	3.7
15.0	48.49	3166	156	3.5
18.0	68.53	3752	163	
22.0	101.1	4550	170	
26.0	141.5	5404	176	
30.0	190.5	6317	183	
34.0	247.6	7253	189	

Europium Glycolate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Gly^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Gly^-]$
1	4.23	0.371	0.263	709
2	5.32	0.751	0.445	593
4	5.81	1.601	0.745	465
6	5.66	2.611	0.989	379
8	5.36	3.788	1.187	313
10	5.07	5.093	1.354	266
12	4.86	6.444	1.511	234
14	4.57	8.061	1.599	198
16	4.37	9.687	1.688	174
20	4.13	12.899	1.879	146
24	3.87	16.596	1.948	117
28	3.72	20.201	2.043	101.1
32	3.56	24.177	2.045	84.6
38	3.39	30.219	2.030	67.2

$[Gly^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.266	887	90	
1.0	1.965	965	105	
2.0	3.169	1085	113	
3.0	4.661	1220	120	
4.0	6.470	1368	127	
6.0	11.10	1683	137	3.2
8.0	17.15	2019	145	3.4
10.0	24.73	2373	151	3.3
12.0	34.03	2753	158	3.3
15.0	51.79	3386	168	3.3
18.0	74.61	4089	179	3.4
22.0	112.7	5077	192	3.4
26.0	158.8	6069	200	3.2
30.0	212.9	7063	207	
34.0	277.1	8121	214	

Gadolinium Glycolate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Gly^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Gly^-]$
1	3.81	0.442	0.235	532
2	4.76	0.871	0.401	460
4	5.24	1.804	0.680	377
6	5.15	2.897	0.905	312
8	4.84	4.224	1.065	252
10	4.69	5.528	1.235	223
12	4.47	7.030	1.354	193
14	4.26	8.667	1.440	166
16	4.13	10.266	1.537	150
20	3.91	13.641	1.688	124
24	3.72	17.276	1.774	102.7
28	3.55	21.182	1.743	84.6
32	3.44	25.030	1.829	73.1
38	3.33	30.767	1.892	61.5

$[Gly^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.192	640		
1.0	1.686	686		
2.0	2.514	757	69	
3.0	3.507	836	72	
4.0	4.673	918	75	
6.0	7.524	1087	78	1.00
8.0	11.07	1259	80	1.00
10.0	15.37	1437	82	1.00
12.0	20.77	1648	86	1.17
15.0	30.28	1952	89	1.13
18.0	41.82	2268	92	1.11
22.0	60.17	2690	94	1.00
26.0	81.63	3102	95	0.88
30.0	106.4	3513	96	
34.0	133.4	3909	97	

Terbium Glycolate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Gly^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Gly^-]$
1	3.87	0.431	0.239	555
2	4.84	0.852	0.408	479
4	5.24	1.804	0.680	377
6	5.27	2.825	0.926	328
8	4.95	4.124	1.093	265
10	4.72	5.491	1.245	227
12	4.51	6.965	1.372	197
14	4.42	8.343	1.525	183
16	4.23	10.016	1.602	160
20	4.00	13.328	1.768	133
24	3.78	16.998	1.845	108.5
28	3.61	20.825	1.884	90.5
32	3.50	24.597	1.938	78.8
38	3.39	30.218	2.030	67.2

$[Gly^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.199	663		
1.0	1.716	716	56	
2.0	2.572	786	63	
3.0	3.605	868	69	
4.0	4.815	954	74	
6.0	7.777	1130	78	
8.0	11.50	1313	82	
10.0	16.15	1515	86	
12.0	21.84	1737	90	
15.0	32.42	2095	96	1.00
18.0	45.32	2462	100	1.05
22.0	66.01	2955	104	1.05
26.0	91.17	3468	108	1.04
30.0	121.8	4027	112	1.03
34.0	157.8	4612	116	1.03

Dysprosium Glycolate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Gly^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Gly^-]$
1	4.14	0.385	0.257	668
2	5.15	0.784	0.433	552
4	5.62	1.664	0.725	436
6	5.50	2.695	0.964	358
8	5.24	3.881	1.161	299
10	4.99	5.179	1.330	257
12	4.76	6.585	1.473	224
14	4.52	8.153	1.575	193
16	4.38	9.664	1.694	175
20	4.09	13.029	1.845	142
24	3.91	16.424	1.992	121
28	3.71	20.256	2.029	100.2
32	3.61	23.839	2.131	89.4
38	3.47	29.515	2.208	74.8

$[Gly^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.254	847		
1.0	1.890	890		
2.0	2.971	986	73.0	
3.0	4.305	1102	87.3	
4.0	5.919	1230	97.5	
6.0	10.04	1507	111.2	
8.0	15.42	1803	120.4	3.4
10.0	22.21	2121	128.1	3.5
12.0	30.61	2468	135.7	3.5
15.0	46.49	3032	146.2	3.5
18.0	66.70	3650	156.1	3.5
22.0	101.0	4545	168.4	3.4
26.0	144.5	5519	180.0	
30.0	197.3	6543	190.1	
34.0	259.3	7597	198.7	

Holmium Glycolate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Gly^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Gly^-]$
1	4.34	0.355	0.270	761
2	5.36	0.743	0.448	603
4	5.81	1.601	0.745	465
6	5.57	2.658	0.975	367
8	5.36	3.788	1.187	313
10	5.04	5.125	1.345	262
12	4.80	6.528	1.488	228
14	4.57	8.061	1.599	198
16	4.40	9.619	1.705	177
20	4.07	13.094	1.828	140
24	3.91	16.424	1.992	121
28	3.75	20.037	2.085	104.1
32	3.66	23.509	2.214	94.2
38	3.48	29.429	2.230	75.8

$[Gly^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.307	1023		
1.0	2.076	1076		
2.0	3.344	1172	96	
3.0	4.890	1297	106	
4.0	6.761	1440	115	
6.0	11.56	1760	130	3.3
8.0	17.91	2114	142	4.0
10.0	25.61	2461	148	3.8
12.0	35.16	2847	156	3.8
15.0	53.03	3469	166	3.7
18.0	75.92	4162	177	3.7
22.0	115.3	5195	192	3.7
26.0	166.3	6358	207	3.7
30.0	231.0	7667	223	3.8
34.0	309.2	9065	238	3.8

Erbium Glycolate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Gly^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Gly^-]$
1	4.47	0.337	0.278	825
2	5.73	0.677	0.474	700
4	6.18	1.489	0.782	525
6	6.04	2.430	1.044	430
8	5.71	3.539	1.258	355
10	5.36	4.803	1.433	298
12	5.01	6.243	1.565	251
14	4.80	7.661	1.705	223
16	4.57	9.251	1.802	195
20	4.26	12.498	1.982	159
24	4.00	16.048	2.088	130
28	3.91	19.206	2.296	120
32	3.75	22.939	2.356	102.7
38	3.61	28.360	2.498	88.1

$[Gly^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.313	1043	110	
1.0	2.136	1136	126	
2.0	3.636	1318	154	
3.0	5.558	1519	170	
4.0	7.966	1742	183	
6.0	14.25	2208	200	
8.0	22.72	2715	213	7.3
10.0	33.73	3273	226	7.1
12.0	47.65	3888	240	7.1
15.0	74.79	4919	261	7.1
18.0	110.7	6094	282	7.1
22.0	173.3	7832	310	7.0
26.0	257.9	9881	341	7.2
30.0	366.5	12183	372	7.2
34.0	501.9	14732	404	

Thulium Glycolate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Gly^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Gly^-]$
1	4.69	0.308	0.290	942
2	5.98	0.638	0.490	768
4	6.64	1.367	0.824	603
6	6.38	2.286	1.088	476
8	5.98	3.367	1.308	388
10	5.57	4.611	1.487	322
12	5.24	5.957	1.642	276
14	4.95	7.421	1.769	238
16	4.72	8.948	1.881	210
20	4.37	12.177	2.065	170
24	4.09	15.689	2.180	139
28	3.91	19.206	2.296	120
32	3.78	22.754	2.406	105.7
38	3.61	28.360	2.498	88.1

$[Gly^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.363	1210	250	
1.0	2.338	1338	203	
2.0	4.167	1584	225	
3.0	6.555	1852	239	
4.0	9.551	2138	251	9.5
6.0	17.61	2768	272	9.8
8.0	28.83	3469	314	10.1
10.0	43.79	4279	314	10.1
12.0	62.72	5143	334	10.1
15.0	100.2	6613	365	10.1
18.0	149.2	8233	394	10.1
22.0	235.2	10645	432	10.0
26.0	350.9	13458	474	10.0
30.0	500.4	16647	517	10.1
34.0	692.5	20338	565	10.4

Ytterbium Glycolate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Gly^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Gly^-]$
1	4.93	0.280	0.303	1082
2	6.30	0.591	0.510	863
4	6.79	1.330	0.837	629
6	6.51	2.277	1.094	480
8	6.11	3.334	1.319	396
10	5.60	4.585	1.494	326
12	5.27	5.922	1.651	279
14	4.99	7.359	1.785	243
16	4.74	8.909	1.891	212
20	4.40	12.092	2.087	178
24	4.11	15.611	2.200	141
28	3.92	19.157	2.309	121
32	3.76	22.877	2.375	103.8
38	3.61	28.360	2.500	88.2

$[Gly^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.423	1410	200	
1.0	2.589	1589	239	
2.0	4.696	1848	249	
3.0	7.423	2141	264	
4.0	10.89	2473	281	
6.0	20.30	3217	311	12.7
8.0	33.46	4058	339	13.0
10.0	51.02	5002	365	13.0
12.0	73.72	6060	393	13.2
15.0	118.3	7820	431	13.1
18.0	177.5	9806	470	13.1
22.0	281.6	12755	518	12.9
26.0	420.3	16127	568	12.8
30.0	599.5	19950	620	12.8
34.0	829.5	24368	677	13.0

Lutetium Glycolate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Gly^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Gly^-]$
1	4.97	0.275	0.306	1113
2	6.59	0.553	0.527	953
4	7.15	1.250	0.866	693
6	6.85	2.110	1.144	542
8	6.32	3.171	1.365	430
10	5.87	4.362	1.556	357
12	5.47	5.695	1.713	301
14	5.13	7.151	1.841	257
16	4.88	8.646	1.961	227
20	4.51	11.790	2.165	184
24	4.20	15.271	2.287	150
28	3.98	18.864	2.384	126
32	3.81	22.573	2.452	108.6
38	3.66	27.968	2.600	93.0

$[Gly^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.433	1443		
1.0	2.718	1718	318	18
2.0	5.177	2089	345	
3.0	8.483	2494	365	
4.0	12.71	2928	382	
6.0	24.46	3910	418	20
8.0	41.26	5033	454	19
10.0	64.15	6315	492	19
12.0	94.41	7784	532	19
15.0	155.2	10280	592	19
18.0	236.5	13083	649	19
22.0	382.4	17336	724	19
26.0	581.1	22312	804	19

Yttrium Glycolate

C_A x 10^3	[H^+] x 10^4	[Gly^-] x 10^3	$\bar{n}$	$\bar{n}$/[Gly^-]
1	3.72	0.452	0.230	509
2	4.65	0.885	0.395	446
4	5.12	1.826	0.672	368
6	4.99	2.954	0.886	300
8	4.80	4.199	1.070	255
10	4.57	5.596	1.215	217
12	4.43	6.992	1.363	195
14	4.26	8.540	1.472	172
16	4.09	10.216	1.548	152
20	3.87	13.582	1.701	125
24	3.70	17.116	1.814	106.0
28	3.52	21.050	1.826	86.7
32	3.41	24.882	1.865	75.0
38	3.29	30.686	1.911	62.3

[Gly^-] x 10^3	X_j	X_1	X_2 x 10^{-3}	X_3 x 10^{-5}
0.3	1.184	613		
1.0	1.664	664	54	
2.0	2.467	734	62	
3.0	3.420	807	66	
4.0	4.511	878	67	
6.0	7.168	1028	70	
8.0	10.54	1193	73	
10.0	14.67	1367	76	
12.0	19.61	1551	78	
15.0	28.56	1837	82	4.7
18.0	39.38	2132	85	5.6
22.0	56.71	2532	87	5.5
26.0	77.55	2944	90	5.8
30.0	102.0	3367	92	5.7
34.0	129.9	3791	94	5.6

Lanthanum Lactate

C_A x 10^3	$[H^+]$ x 10^4	$[Lac^-]$ x 10^3	$\bar{n}$	$\bar{n}/[Lac^-]$
1	2.96	0.561	0.184	328
2	3.61	1.071	0.323	302
4	3.85	2.216	0.542	245
6	3.85	3.442	0.736	214
8	3.75	4.799	0.894	186
10	3.62	6.283	1.020	162
12	3.52	7.809	1.136	145
14	3.47	9.286	1.265	136
16	3.39	10.903	1.359	125
20	3.23	14.377	1.414	98.4
24	3.13	17.860	1.613	90.3
28				
32	2.96	25.278	1.755	69.4
38	2.87	31.011	1.819	58.7

$[Lac^-]$ x 10^3	X_j	X_1	X_2 x 10^{-3}	X_3 x 10^{-5}
0.3	1.122	407		
1.0	1.415	415	15.0	
2.0	1.869	435	17.5	
3.0	2.371	457	14.0	
4.0	2.929	482	20.5	
6.0	4.217	536	22.7	
8.0	5.795	599	24.9	3.6
10.0	7.619	662	26.2	4.2
12.0	9.768	731	27.6	4.7
15.0	13.60	840	29.3	4.9
18.0	18.15	953	30.7	4.8
22.0	25.39	1109	32.2	4.6
26.0	33.89	1265	33.3	4.4
30.0	43.83	1461	35.4	4.5
34.0	55.04	1589	35.0	

Cerium Lactate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Lac^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Lac^-]$
1	4.13	0.433	0.208	480
2	4.61	0.875	0.363	415
4	4.69	1.862	0.625	336
6	4.54	2.971	0.850	286
8	4.25	4.301	1.015	236
10	4.11	5.604	1.190	212
12	3.91	7.110	1.312	185
14	3.78	8.611	1.436	167
16	3.61	10.335	1.503	145
20	3.42	13.682	1.665	122
24	3.26	17.261	1.769	102.5
28	3.16	20.802	1.885	90.6
32	3.06	24.575	1.940	78.9
38	2.95	30.300	2.008	66.3

$[Lac^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-5}$
0.3	1.175	583	43.3	
1.0	1.605	605	35.0	
2.0	2.302	651	40.5	
3.0	3.124	708	46.0	
4.0	4.074	769	50.0	
6.0	6.375	896	54.3	
8.0	9.276	1035	58.1	
10.0	12.78	1178	60.8	
12.0	16.93	1328	63.2	8.5
15.0	24.46	1564	66.3	8.9
18.0	33.64	1813	69.1	8.9
22.0	48.67	2167	72.6	8.9
26.0	67.22	2547	76.0	8.8
30.0	89.54	2951	79.4	8.8
34.0	115.6	3371	82.4	8.6

Praseodymium Lactate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Lac^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Lac^-]$
1	3.64	0.407	0.239	587
2	4.43	0.819	0.406	496
4	4.76	1.725	0.688	399
6	4.57	2.826	0.908	321
8	4.37	4.032	1.101	273
10	4.23	5.275	1.287	244
12	4.00	6.757	1.411	209
14	3.78	8.397	1.495	178
16	3.65	9.981	1.596	160
20	3.47	13.196	1.788	135
24	3.23	17.080	1.811	106
28	3.16	20.413	1.976	96.8
32	3.01	24.538	1.941	78.1
38	2.91	30.193	2.025	67.1

$[Lac^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.217	723	60.0	
1.0	1.772	772	67.0	
2.0	2.695	848	71.5	
3.0	3.786	929	74.7	
4.0	5.062	1016	77.8	
6.0	8.282	1214	84.8	
8.0	12.44	1430	90.6	1.3
10.0	17.47	1647	94.2	1.4
12.0	23.35	1863	96.5	1.4
15.0	33.93	2195	99.3	1.3
18.0	46.98	2554	102.7	1.3
22.0	68.94	3088	108.3	1.3
26.0	95.94	3652	113.3	1.3
30.0	127.6	4220	117.2	1.2
34.0	173.0	4765	119.4	

Neodymium Lactate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Lac^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Lac^-]$
1	3.72	0.393	0.245	623
2	4.65	0.769	0.424	551
4	4.95	1.650	0.711	431
6	4.74	2.716	0.940	346
8	4.51	3.900	1.138	292
10	4.26	5.236	1.298	248
12	4.03	6.705	1.425	213
14	3.85	8.240	1.536	186
16	3.72	9.789	1.646	168
20	3.50	13.081	1.817	139
24	3.28	16.816	1.878	112
28	3.16	20.413	1.976	96.8
32	3.01	24.538	1.941	79.1
38	2.96	29.679	2.154	72.6

$[Lac^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.227	757		
1.0	1.833	833	93.0	
2.0	2.873	937	98.5	2.8
3.0	4.124	1041	100	2.3
4.0	5.611	1153	103	2.5
6.0	9.305	1384	107	2.3
8.0	14.10	1638	112	2.4
10.0	20.15	1915	118	2.5
12.0	27.51	2209	122	2.4
15.0	41.28	2685	130	2.5
18.0	58.43	3191	136	2.4
22.0	86.98	3908	144	2.3
26.0	122.4	4669	151	2.2
30.0	165.3	5477	158	
34.0	215.1	6297	163	

Samarium Lactate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Lac^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Lac^-]$
1	3.78	0.383	0.249	650
2	4.80	0.738	0.436	591
4	5.19	1.563	0.739	473
6	4.95	2.591	0.976	377
8	4.65	3.776	1.172	310
10	4.47	4.980	1.367	274
12	4.16	6.488	1.482	228
14	3.87	8.196	1.548	189
16	3.75	9.708	1.667	172
20	3.50	13.081	1.817	139
24	3.28	16.816	1.878	112
28	3.13	20.610	1.926	93.4
32	3.01	24.538	1.941	79.1
38	2.89	30.404	1.971	64.8

$[Lac^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.230	767		
1.0	1.876	876		
2.0	3.035	1018	129	3.0
3.0	4.449	1150	130	2.3
4.0	6.145	1286	132	2.3
6.0	10.49	1582	137	2.3
8.0	16.08	1885	141	2.3
10.0	23.01	2201	144	2.1
12.0	31.51	2543	149	2.2
15.0	47.50	3100	156	2.2
18.0	67.41	3689	163	2.2
22.0	99.15	4461	168	
26.0	136.3	5204	171	
30.0	178.9	5930	172	
34.0	228.3	6685	174	

Europium Lactate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Lac^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Lac^-]$
1	3.94	0.358	0.259	723
2	4.99	0.701	0.450	642
4	5.24	1.546	0.746	483
6	5.15	2.482	1.008	406
8	4.76	3.683	1.198	325
10	4.47	4.980	1.367	274
12	4.23	6.377	1.512	237
14	4.00	7.922	1.620	204
16	3.81	9.552	1.707	179
20	3.55	12.894	1.865	145
24	3.33	16.560	1.943	117
28	3.18	20.283	2.009	99.0
32	3.04	24.293	2.003	82.5
38	2.96	29.679	2.154	72.6

$[Lac^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.275	917		
1.0	2.026	1026		
2.0	3.329	1165	138	
3.0	4.974	1325	145	
4.0	6.970	1493	151	
6.0	12.10	1850	160	
8.0	18.95	2244	169	2.4
10.0	27.56	2656	177	2.7
12.0	37.93	3098	184	2.8
15.0	57.07	3738	190	2.7
18.0	81.10	4450	198	2.7
22.0	121.8	5491	209	2.7
26.0	172.3	6588	219	2.7
30.0	232.3	7710	227	2.6
34.0	300.5	8809	233	

Gadolinium Lactate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Lac^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Lac^-]$
1	3.85	0.372	0.253	680
2	4.69	0.761	0.427	561
4	5.07	1.605	0.726	452
6	4.88	2.632	0.964	366
8	4.54	3.873	1.145	296
10	4.30	5.186	1.311	253
12	4.09	6.603	1.452	220
14	3.85	8.240	1.536	186
16	3.64	10.009	1.589	159
20	3.57	13.196	1.788	135
24	3.26	16.920	1.852	109
28	3.13	20.610	1.926	93.4
32	2.96	24.956	1.835	73.5
38	2.89	30.404	1.971	64.8

$[Lac^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.246	820		
1.0	1.885	885		
2.0	3.005	1003	112	
3.0	4.374	1125	115	1.7
4.0	5.996	1249	117	1.8
6.0	10.03	1505	121	1.8
8.0	15.26	1783	124	1.8
10.0	21.62	2062	128	1.8
12.0	29.34	2362	132	1.8
15.0	43.48	2832	137	1.8
18.0	60.57	3309	141	1.7
22.0	87.85	3948	144	
26.0	120.7	4604	147	
30.0	159.3	5277	150	
34.0	203.5	5956	152	

Terbium Lactate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Lac^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Lac^-]$
1	3.78	0.383	0.249	650
2	4.95	0.708	0.447	631
4	5.41	1.490	0.763	512
6	5.12	2.497	1.004	402
8	4.80	3.650	1.208	331
10	4.57	4.865	1.398	287
12	4.23	6.377	1.512	237
14	4.00	7.922	1.620	204
16	3.81	9.552	1.707	179
20	3.52	13.006	1.837	141
24	3.28	16.816	1.878	112
28	3.16	20.413	1.976	96.8
32	3.03	24.374	1.982	81.3
38	2.91	30.193	2.025	67.0

$[Lac^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.250	833		
1.0	1.941	941		
2.0	3.233	1117	164	
3.0	4.839	1280	163	
4.0	6.798	1450	165	
6.0	11.91	1818	171	
8.0	18.62	2203	177	2.1
10.0	27.18	2618	183	2.3
12.0	37.61	3051	188	2.3
15.0	56.76	3717	195	2.3
18.0	80.70	4428	202	2.3
22.0	120.1	5414	210	2.3
26.0	167.8	6415	216	
30.0	224.3	7443	222	
34.0	287.6	8429	225	

Dysprosium Lactate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Lac^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Lac^-]$
1	4.23	0.318	0.276	868
2	5.41	0.628	0.478	761
4	5.71	1.399	0.793	567
6	5.57	2.277	1.070	470
8	5.07	3.444	1.266	368
10	4.72	4.703	1.442	307
12	4.37	6.165	1.568	254
14	4.09	7.743	1.667	215
16	3.91	9.302	1.772	190
20	3.61	12.676	1.921	152
24	3.41	16.166	2.044	126
28	3.21	20.091	2.058	102.4
32	3.10	23.819	2.123	89.4
38	2.94	29.883	2.103	70.4

$[Lac^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.326	1087		
1.0	2.266	1266		
2.0	3.970	1485	233	4.0
3.0	6.204	1735	238	4.3
4.0	8.976	1994	244	4.7
6.0	16.22	2537	253	4.7
8.0	25.83	3104	261	4.5
10.0	38.10	3710	269	4.4
12.0	53.58	4882	280	4.6
15.0	82.78	5519	300	5.0
18.0	119.7	6594	310	4.7
22.0	181.2	8191	326	4.6
26.0	257.5	9865	340	
30.0	347.6	11553	351	
34.0	449.8	13200	358	

Holmium Lactate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Lac^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Lac^-]$
1	4.26	0.314	0.278	885
2	5.50	0.614	0.484	788
4	6.04	1.310	0.824	629
6	5.85	2.157	1.107	513
8	5.27	3.304	1.306	395
10	4.84	4.581	1.476	322
12	4.51	5.967	1.621	272
14	4.26	7.424	1.751	236
16	4.00	9.087	1.828	201
20	3.70	12.362	2.002	162
24	3.44	16.023	2.080	130
28	3.23	19.965	2.090	104.7
32	3.13	23.588	2.181	92.5
38	2.96	29.679	2.154	72.6

$[Lac^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.329	1097		
1.0	2.295	1295	245	
2.0	4.192	1596	273	
3.0	6.694	1898	283	7.0
4.0	9.812	2203	288	6.5
6.0	18.16	2860	302	6.7
8.0	29.62	3578	316	6.8
10.0	44.51	4351	330	6.8
12.0	63.26	5188	345	6.9
15.0	99.25	6550	367	7.0
18.0	144.8	7989	386	6.4
22.0	220.6	9982	406	6.5
26.0	314.8	12069	424	
30.0	429.0	14267	441	
34.0	562.5	16515	455	

Erbium Lactate

C_A x 10^3	$[H^+]$ x 10^4	$[Lac^-]$ x 10^3	$\bar{n}$	$\bar{n}/[Lac^-]$
1	4.61	0.272	0.297	1092
2	5.98	0.546	0.513	940
4	6.43	1.216	0.857	705
6	6.23	2.011	1.153	573
8	5.62	3.084	1.370	444
10	5.19	4.256	1.566	368
12	4.84	5.544	1.735	313
14	4.47	7.065	1.846	261
16	4.23	8.580	1.961	229
20	3.93	11.625	2.192	189
24	3.58	15.387	2.243	146
28	3.33	19.359	2.244	116
32	3.21	22.994	2.332	101.4
38	3.05	28.797	2.377	82.5

$[Lac^-]$ x 10^3	X_j	X_1	X_2 x 10^{-3}	X_3 x 10^{-6}
0.3	1.467	1557	323	
1.0	2.784	1784	324	
2.0	5.353	2177	359	
3.0	8.883	2628	389	
4.0	13.47	3118	415	
6.0	26.37	4228	461	
8.0	44.76	5470	501	
10.0	70.02	6902	544	
12.0	103.7	8558	592	14.3
15.0	170.7	11313	657	15.8
18.0	258.0	14278	712	16.2
22.0	407.9	18495	774	16.1
26.0	604.5	23250	838	16.1
30.0	852.2	28373	897	15.2
34.0	1157	34000	957	15.8

Thulium Lactate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Lac^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Lac^-]$
1	4.80	0.252	0.307	1218
2	6.28	0.509	0.530	1041
4	6.96	1.106	0.898	812
6	6.68	1.860	1.202	646
8	6.04	2.853	1.438	504
10	5.50	4.003	1.637	409
12	5.07	5.282	1.806	342
14	4.72	6.678	1.949	292
16	4.37	8.298	2.035	245
20	3.91	11.685	2.177	186
24	3.62	15.215	2.287	150
28	3.39	19.012	2.332	123
32	3.23	22.851	2.368	104
38	3.03	28.988	2.329	80.3

$[Lac^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.489	1630		
1.0	2.959	1959	409	
2.0	6.075	2538	494	
3.0	10.51	3170	540	
4.0	16.85	3963	603	
6.0	33.65	5442	649	
8.0	59.10	7263	714	25.5
10.0	93.94	9294	774	26.4
12.0	139.4	11533	832	26.8
15.0	229.2	15213	911	26.7
18.0	347.4	19244	983	26.3
22.0	554.1	25141	1072	
26.0	820.8	31531	1153	
30.0	1153	38400	1228	
34.0	1553	45647	1297	

Ytterbium Lactate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Lac^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Lac^-]$
1	5.07	0.227	0.320	1410
2	6.64	0.469	0.549	1171
4	7.36	1.033	0.926	896
6	7.13	1.728	1.246	721
8	6.32	2.716	1.479	545
10	5.73	3.833	1.685	440
12	5.24	5.103	1.855	364
14	4.84	6.507	1.994	306
16	4.43	8.182	2.065	252
20	4.00	11.417	2.256	197
24	3.70	14.881	2.372	159
28	3.41	18.899	2.361	125
32	3.28	22.499	2.457	109
38	3.11	28.236	2.519	89.2

$[Lac^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.559	1863	543	
1.0	3.301	2301	601	
2.0	7.129	3065	683	
3.0	12.74	3913	738	
4.0	20.83	4958	815	39
6.0	42.68	6847	875	36
8.0	75.92	9365	958	37
10.0	121.4	12040	1034	37
12.0	181.5	15042	1112	38
15.0	305.4	20290	1239	39
18.0	472.4	26189	1361	39
22.0	763.4	34655	1498	38
26.0	1147	44077	1630	37
30.0	1641	54667	1766	37

Lutetium Lactate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Lac^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Lac^-]$
1	5.24	0.212	0.328	1547
2	7.08	0.425	0.571	1344
4	7.78	0.965	0.953	988
6	7.28	1.687	1.260	747
8	6.64	2.574	1.523	592
10	5.98	3.663	1.734	473
12	5.41	4.935	1.902	385
14	4.88	6.451	2.009	311
16	4.47	8.107	2.085	257
20	4.06	11.245	2.290	204
24	3.72	14.799	2.393	162

$[Lac^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-6}$	$X_3 \times 10^{-6}$
0.3	1.612	2040	0.550	
1.0	3.685	2685	0.810	50
2.0	8.220	3610	0.868	54
3.0	15.08	4693	0.939	60
4.0	24.64	5910	1.009	62
6.0	53.02	8670	1.133	62
8.0	95.08	11760	1.236	60
10.0	153.9	15390	1.352	59
12.0	233.6	19383	1.459	58
15.0	395.6	26310	1.629	58

Yttrium Lactate

$C_A \times 10^3$	$[H^+] \times 10^4$	$[Lac^-] \times 10^3$	$\bar{n}$	$\bar{n}/[Lac^-]$
1	4.26	0.318	0.277	871
2	5.43	0.633	0.478	755
4	5.89	1.367	0.806	590
6	5.75	2.227	1.087	488
8	5.32	3.313	1.305	394
10	4.95	4.532	1.491	329
12	4.65	5.854	1.653	282
14	4.40	7.273	1.782	246
16	4.13	8.907	1.877	211
20	3.78	12.251	2.032	166
24	3.55	15.719	2.159	137
28	3.40	19.199	2.285	119
32	3.26	22.930	2.349	102.4
38	3.12	28.508	2.451	86.0

$[Lac^-] \times 10^3$	X_j	X_1	$X_2 \times 10^{-3}$	$X_3 \times 10^{-6}$
0.3	1.330	1100	200	
1.0	2.255	1255	215	
2.0	4.012	1506	233	
3.0	6.339	1780	247	
4.0	9.287	2072	258	
6.0	17.33	2722	280	9.2
8.0	28.59	3449	301	9.5
10.0	43.39	4239	320	9.5
12.0	62.10	5092	338	9.4
15.0	98.66	6511	365	9.3
18.0	147.0	8111	393	9.3
22.0	233.0	10545	432	9.4
26.0	350.0	13423	476	9.7
30.0	495.7	16490	515	9.7
34.0	677.4	19894	555	9.7