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Thermodynamic Properties of Rare Earth Complexes

I. Stability Constants for the Rare Earth Diglycolate Complexes

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The stability constants for the diglycolate complexes of the tervalent rare earths were determined in an aqueous perchlorate medium of the ionic strength $I = 1.00$ M and at a temperature of 20.0°C. Corresponding values of $\bar{n}$ and [A] were determined by a potentiometric standard method *viz.* the determination of the concentration hydrogen-ion by means of the quinhydrone electrode. From the $\bar{n}$-[A] data stability constants for three mononuclear complexes were determined. No evidence of the formation of polynuclear or acid complexes was found in the concentration range used.

During the last ten years a large number of investigations concerning the stability of various rare earth carboxylate complexes has been published.[1–21] The ligands investigated were in most cases various aminopolycarboxylates,[1–3] but also ligands such as acetate [4–7] and various α-hydroxy carboxylates [8–10] have been studied. Complexes with dicarboxylic acids (*e.g.* oxalate,[11–13] oxaloacetate,[14] malonate [15,16] and dipicolinate [17]) have also been investigated. The trends in the stability constants have been given various electrostatic and steric explanations.[1,22] If a more unambiguous interpretation of the data is wanted it is necessary to determine all the changes in the thermodynamic functions, free energy, enthalpy and entropy for the various reactions. The interpretation is also facilitated if less complicated ligands are studied. In order to get a better understanding of the factors of importance for the formation of rare earth complexes we have started a series of investigations of the thermodynamic properties of the acetate, glycolate, thioglycolate, diglycolate and dipicolinate complexes of these elements. The change in free energy for the various complex formation reactions was obtained from the stability constants and the corresponding enthalpy change from a direct calorimetric determination.

In this investigation we have determined what species are formed in the rare earth-diglycolate solutions and also the stability constants for the various equilibria. The constants refer to a medium of the ionic strength $I = 1.00$ M (using sodium perchlorate as neutral salt) and a temperature of 20.0°C. The

measurements were made by a potentiometric standard method *viz.* the determination of the concentration free ligand by means of $[H^+]$-measurements. From the experimental values of $\bar{n}$ and [A] the stability constants β_j were computed by the method of Leden and Fronæus[23] and finally refined using the least square procedure "Letagrop Vrid" developed by Sillén and Ingri.[24]

CALCULATION OF STABILITY CONSTANTS FROM POTENTIOMETRIC DATA

Notation:

C_M,C_A = total concentrations of metal ion and ligand.
C_H = total concentration of hydrogen and dissociable hydrogen ions.

$$C_H = 2[H_2A] + [HA^-] + [H^+]$$

[A],$[H^+]$ = the concentration of free ligand and hydrogen ion.
β_j = the stability constant of the j:th mononuclear complex.
K_j = the j:th stepwise stability constant

$$\beta_j = \Pi K_j$$

δ_j = the stability constant of the j:th proton complex where

$$\delta_j = \frac{H_jA}{[H^+]^j[A]}$$

Corresponding values of $\bar{n}$ and [A] are obtained from the following equations:

$$\bar{n} = \frac{C_A - [A](1 + \delta_1 \cdot [H^+] + \delta_2 \cdot [H^+]^2)}{C_M} \quad (1)$$

$$[A] = \frac{C_H - [H^+]}{\delta_1[H^+] + 2\delta_2[H^+]^2} \quad (2)$$

Graphical evaluation of the integral:

$$\ln X([A]_j) = \int_0^{[A]_j} \frac{\bar{n}}{[A]}\, d[A] \quad (3)$$

leads to sets of corresponding values of X and [A] from which the stability constants β_j are determined. The stability constants δ_j can be determined in the same way. For further details the reader is referred to Ref.[23] In order to save numerical work and to get a satisfactory statistical treatment of the data [29] we refined all stability constants by using a Ferranti-Mercury Computer and the least-square program "Letagrop Vrid".[24] The reader is referred to the appendix for details about the programs we used. The total concentration ligand was chosen as the error-carrying variable. The weight of each value of C_{Ai} was equal to unity. The "best" set of constants β_j was the set that minimized the error-square sum U where:

$$U = \sum_i (C_{Ai} - C_{Ai\ calc})^2$$

$C_{Ai\ calc}$ is the value of the total ligand concentration computed from the values of $(C_M)_i$, $[H^+]_i$, β_j and δ_j.

EXPERIMENTAL

Chemicals used. Stock solutions of the various rare earth perchlorates were prepared and analysed as described before.[25] The purity of the various rare earths (Lindsay Chemical Co.) was > 99.9 %. The concentration of free perchloric acid in the rare earth stock solutions was determined potentiometrically. The various diglycolate buffer solutions were prepared by partial neutralization of the acid with sodium hydroxide. The equivalent weight of diglycolic acid (Fluka, Eastman Kodak, p.a.) was determined by a titration with sodium hydroxide. A value of 67.0 (calc. 67.0) was obtained. Sodium perchlorate was prepared from perchloric acid (Bakers' analysed) and sodium carbonate (Merck p.a.).

Procedure. The emf E of galvanic cells of the following composition was measured:

Au	10 mM $HClO_4$ I = 1.00 M Quinhydrone	1 M $NaClO_4$	C_M C_{H_2A} C_{Na_2A} I = 1.00 M Quinhydrone	Au

where C_{Na_2A} and C_{H_2A} are the total concentrations of Na_2A and H_2A. The solution in the right half-cell was prepared by adding known amounts of a buffer solution T to 3.00 ml of a solution S. The small volumes of T were added from an Agla micrometer syringe with an error of 0.5 % at most. The solutions S and T had the following composition:

$$\text{S} \begin{cases} [M^{3+}] = C_M \\ [H^+] = C_{HClO_4} \\ I = 1.00 \text{ M} \end{cases} \qquad \text{T} \begin{cases} C_M \\ C_{Na_2A} \\ C_{H_2A} = k \cdot C_{Na_2A} \\ I = 1.00 \text{ M} \end{cases}$$

The solutions were mixed by passing nitrogen through the right half-cell. All titrations were performed by using at least two different values of C_M. For each values of C_M two or three different buffer solutions were used. All titrations were repeated at least twice and the reproducibility of the emf was usually within 0.1 mV. Titrations were also made at $C_M = 0$ in order to determine the formation constants δ_j.

RESULTS

The $[H^+]-[A]$ system. The stability constants δ_j were determined using 8 different buffer solutions with the ratio Na_2A/H_2A varying from 0 to 4. All the buffer solutions had the same total concentration (C_A = 50 mM). The following constants were obtained:

$$\delta_1 = (5.51 \pm 0.07) \times 10^3$$
$$\delta_2 = (3.44 \pm 0.02) \times 10^6$$

In order to check if the values of δ_j varied with the total concentration buffer we measured the hydrogen-ion concentration of two different buffer solutions as a function of the total concentration C_A. In the first buffer (C_{H_2A}/C_{Na_2A} = 1:0) C_A was varied in the range 0—80 mM and in the second buffer (C_{H_2A}/C_{Na_2A} = 2:1 in the range 0—150 mM. The $[H^+]$-values measured agreed within ± 2 % with the $[H^+]$-values computed from the above constants. The $[H^+]$-values obtained by the quinhydrone electrode were checked by repeating the above titrations using a glass electrode. The results for the 2:1 buffer are given in Table 1. The agreement between the two titrations was within 0.1 mV. There is a small systematic change in value of $[H^+]-[H^+]_{calc}$ (Table 1). The differ-

Table 1. The potentials E (quinhydrone) and E (glasselectrode) as function of C_A. $[H^+] \approx 1.1$ mM.

C_A (mM)	$-E$ (mV) Quinhydrone	$-E$ (mV) Glasselectrode	$[H^+]-[H^+]_{calc} \times 10^2$ (mM)
4.84	64.1	64.0	2.0
11.54	58.9	58.8	2.3
21.43	56.6	56.7	2.3
30.00	55.7	55.7	2.6
50.0	55.0	54.9	1.5
75.0	54.8	54.9	0.0
100.0	54.8	54.8	−1.2
125.0	54.8	54.8	−1.9
150.0	54.8	54.8	−2.4

ence is smaller than the uncertainty in $[H^+]_{calc}$ caused by the errors in δ_j and we did not make any attempt to correct for this difference by a corresponding change in the δ_j-values.

The stability constants δ_j were determined in a medium with $C_M = 0$ and we have assumed that their value remained unchanged even when $C_M \neq 0$. This assumption was checked by using the least-square procedure. The stability constants δ_j are two additional constants and can be determined simultaneously with the β_j-values in our program (see the appendix). As an example we tried to determine δ_1 and δ_2 from a neodymium titration. In the first attempt δ_2 was kept constant equal to 3.44×10^6, δ_1 and β_j were varied until the minimum of the error-square sum was found. The following constants were obtained:

$$\beta_1 = (2.82 \pm 0.04) \times 10^5$$
$$\beta_2 = (3.19 \pm 0.05) \times 10^9$$
$$\beta_3 = (1.51 \pm 0.09) \times 10^{12}$$
$$\delta_1 = (5.46 \pm 0.10) \times 10^3$$

The value of δ_1 agrees well with the value determined in solutions with $C_M = 0$. In the second attempt all the five constants were varied. The following δ_j-values were obtained:

$$\delta_1 = (6.2 \pm 0.7) \times 10^3$$
$$\delta_2 = (3.8 \pm 0.3) \times 10^6$$

The standard deviations of the constants are very big but the δ_j-values agree even in this case (within the above error limits) with the constants previously determined. The reason for the low accuracy of the last set of values is that $[H^+]$ does not change sufficiently for an accurate determination of two acid constants.

In the following we will use values of $\delta_1 = (5.51 \pm 0.07) \times 10^3$ and $\delta_2 = (3.44 \pm 0.02) \times 10^6$ and conclude that the variations of δ_j-values with C_M or C_A are within the limits given.

Table 2. Values of [A] and $\bar{n}/[A]$ for the praseodymium diglycolate system calculated from the corresponding values C_A and E.

$C_M = 20.96$ (mM) $C_{H_2A}/C_{Na_2A} = 2.667$					$C_M = 20.96$ (mM) $C_{H_2A}/C_{Na_2A} = 1.667$				
$C_A \times 10^3$ (M)	E (mV)	[A] $\times 10^6$ (M)	$\bar{n}/[A] \times 10^{-3}$ (M^{-1})	$(C_A - C_{A\,calc}) \times 10^3$(M)	$C_A \times 10^3$ (M)	E (mV)	[A] $\times 10^6$ (M)	$\bar{n}/[A] \times 10^{-3}$ (M^{-1})	$(C_A - C_{A\,calc}) \times 10^3$(M)
11.96	6.4 + 0.2	4.01	111.2	0.85	11.54	2.6 + 0.1	4.18	108.4	0.96
15.80	10.0 + 0.4	5.09	106.5	0.24	15.19	6.2 + 0.2	5.46	102.0	0.38
20.79	12.7 + 0.5	6.76	95.4	−0.18	23.08	9.5 + 0.3	9.27	79.1	−0.09
25.67	14.0 + 0.5	8.85	81.8	−0.19	27.27	9.9 + 0.3	12.05	67.1	−0.08
37.34	14.9 + 0.6	14.81	59.2	−0.30	37.61	9.3 + 0.3	21.15	45.8	−0.11
51.49	14.1 + 0.6	24.89	41.1	−0.35	53.42	6.3 + 0.2	44.34	26.5	−0.06
63.63	12.7 + 0.5	37.04	30.6	−0.30	66.23	3.1 + 0.1	75.69	17.5	0.11
82.14	10.0 + 0.4	63.38	20.3	−0.21	90.70	− 3.3	181.5	8.82	0.11
102.7	6.7 + 0.2	108.3	13.3	−0.02	120.0	−11.5	461.3	4.07	0.04
142.9	0.0	266.0	6.48	0.02	150.0	−18.8	1006	2.09	−0.34
					180.0	−24.5	1851	1.24	−0.59
					230.8	−31.7	3996	0.63	−0.75

Table 3. Values of [A] and $\bar{n}/[A]$ for the praseodymium diglycolate system calculated from the corresponding values of C_A and E.

$C_M = 10.48$ (mM) $C_{H_2A}/C_{Na_2A} = 1.667$					$C_M = 10.48$ (mM) $C_{H_2A}/C_{Na_2A} = 1:0$				
$C_A \times 10^3$ (M)	E (mV)	[A] $\times 10^6$ (M)	$\bar{n}/[A]$ $\times 10^{-3}$ (M^{-1})	$(C_A - C_{A\,calc}) \times 10^3$ (M)	$C_A \times 10^3$ (M)	E (mV)	[A] $\times 10^6$ (M)	$\bar{n}/[A]$ $\times 10^{-3}$ (M^{-1})	$(C_A - C_{A\,calc}) \times 10^3$ (M)
4.37	−17.1	3.10	123.2	0.38	2.94	−14.7	1.59	162.8	0.01
7.59	− 8.0	6.08	97.7	0.11	4.37	− 6.3	2.04	178.5	−0.52
9.38	− 5.6	8.15	84.4	0.04	5.77	− 1.7	3.17	138.3	−0.17
13.64	− 3.3	14.74	58.3	0.03	7.60	2.3 + 0.1	4.39	116.8	−0.01
15.67	− 3.1	18 72	49.4	0.04	9.38	5.3 + 0.2	5.21	111.1	−0.19
23.24	− 4.4	39.19	28.8	0.06	11.54	7.8 + 0.2	6.36	100.0	−0.18
30.00	− 6.6	66.52	19.3	0.05	13.64	9.7 + 0.3	7.24	94.7	−0.31
33.12	− 7.8	83.20	16.3	0.07	17.65	12.1 + 0.4	9.10	82.5	−0.29
45.35	−13.0	182.6	8.71	0.18	21.43	13.8 + 0.5	10.58	75.7	−0.35
60.00	−19.2	399.7	4.57	0.13	25.00	15.1 + 0.6	11.82	71.1	−0.44
90.00	−29.4	1294	1.68	−0.09	31.58	16.9 + 0.7	14.03	63.7	−0.50
115.4	−35.0	2500	0.94	−0.10	37.50	18.1 + 0.8	15.85	58.8	−0.53

Table 4. The functions X, X_1, and X_2 for the praseodymium diglycolate system.

[A] × 10^6 (M)	X	$X_1 \times 10^{-5}$ (M^{-1})	$X_2 \times 10^{-8}$ (M^{-2})
2.00	1.393	1.97	
6.00	2.231	2.05	
10.00	3.151	2.15	
15.00	4.384	2.26	
20.00	5.673	2.34	
30.00	8.506	2.50	
50.00	15.19	2.84	
70.00	23.15	3.16	
100.0	37.61	3.66	16.60
300.0	216.8	7.19	17.30
500.0	560.5	11.19	18.38
900.0	1771	19.67	19.63
1500	5308	35.38	22.25
2500	16770	67.08	26.03
4000	52660	131.7	32.41

The $[M^{3+}]$—$[A]$ *systems.* The emf E of the cells used had to be corrected for the liquid junction potential. This was done as described by Ahrland and Rosengren [26] (on the assumption that the liquid junction potential only depends on $[H^+]$). The correction is tabulated in Tables 2 and 3 after corresponding values of the emf. The experimental data for the various titrations are given in Figs. 1, 2, and 3 as plots of $\bar{n}$ versus log [A]. Tables 2, 3, and 4 give details of the experimental data and calculations for one of the systems (the praseodymium system) investigated. From the graphs it is obvious that for a given value of [A], $\bar{n}$ varies neither with C_M nor with the buffer used. The concentration of polynuclear and acid complexes, $M_xH_yA_z$, $x > 1$, $y > 0$, is thus negligible (if they are formed at all) in the concentration range

Table 5. Determination of $\bar{n}$ for high $[A]$-values for the dysprosium diglycolate system.

$C_M = 8.84$ (mM)
$C_{H_2A}/C_{Na_2A} = 0.344$

$C_A \times 10^3$ (M)	$-E$ (mV)	[A] × 10^3 (M)	$\bar{n}$
37.88	51.7	0.978	2.75
45.80	65.2	2.80	2.91
52.70	73.6	5.27	2.97
60.60	80.0	8.65	3.00
75.75	87.3	15.88	3.02
90.90	91.4	23.41	3.05
106.1	94.1	31.34	3.03
116.5	95.6	37.08	2.99

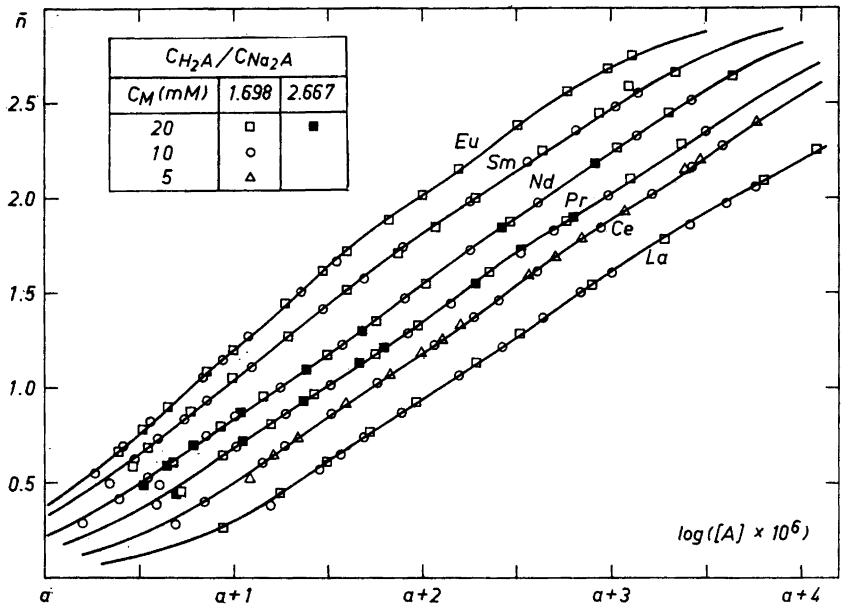

Fig. 1. $\bar{n}$ = f (log [A] · 10^6) for the $La^{3+}-Eu^{3+}$ diglycolate systems. The values of a are for the various systems beginning with La^{3+}: 0.3, −0.2, −0.1, 0, + 0.1 and + 0.2.

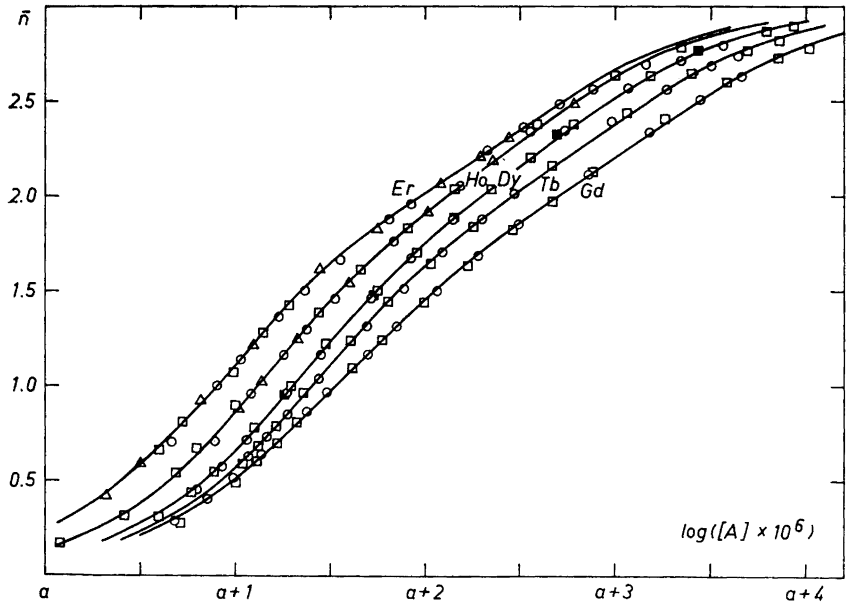

Fig. 2. $\bar{n}$ = f (log [A] · 10^6) for the $Gd^{3+}-Er^{3+}$ diglycolate systems. The values of a are for the various systems beginning with Gd^{3+}: −0.5, −0.4, − 0.3, − 0.1 and + 0.1.

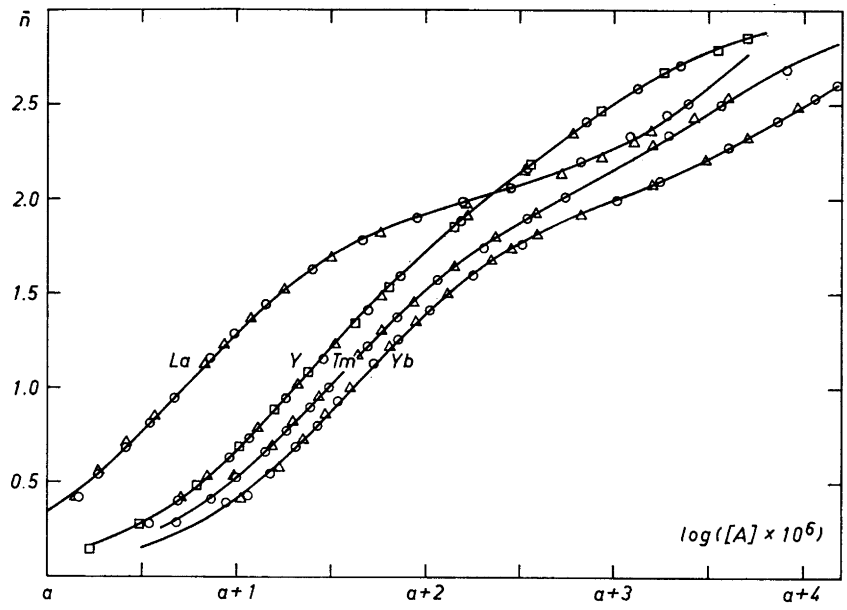

Fig. 3. $\bar{n}$ = f (log [A] · 10^6) for the Tm^{3+}, Yb^{3+}, Lu^{3+} and Y^{3+} diglycolate systems. The values of a are respectively: −0.6, −0.8, 0 and −0.2.

used here. The highest $\bar{n}$-value obtained is three (Table 5), only three complexes are thus formed. Most titrations were interrupted before $\bar{n} = 3$ was reached (for the first elements at $\bar{n} \approx 2.3$ and for the later ones at $\bar{n} \approx 2.7$). In no case did we find evidence of the formation of complexes with more than three ligands.

It was not possible to determine [A] with any accuracy for low values of $\bar{n}$ because $C_H - [H^+] \ll C_H$. This is because β_1 is approximately two powers of ten bigger than δ_1 and δ_2/δ_1. The lack of accurate values of $\bar{n}/[A]$ for low values of [A] leads to difficulty in the graphical evaluation of the expression (3). To overcome this difficulty the first part of the $\bar{n}/[A]$ *versus* [A] curve was computed from a value of β_1 calculated from the simultaneous equations of Block and Mc Intyre [27] (using accurate $\bar{n}$—[A] values). An alternative way is to evaluate the integral

$$\ln \frac{X([A]_j)}{X([A]_i)} = \int_{[A]_i}^{[A]_j} \frac{\bar{n}}{[A]} \, d[A]$$

where the lower integration limit is chosen in a region where accurate $\bar{n}$—[A] values can be determined. For further details see Ref.[28] Both methods involved much numerical work and were only used for a few complex systems. The computer refined final constants with their corresponding standard deviations are given in Table 6. The fulldrawn curves in Figs. 1, 2, and 3 were computed

Table 6. The stability constants β_j with their corresponding standard deviations for the rare earth diglycolate systems.

Central ion	$\beta_1 \times 10^{-5}$ (M^{-1})	$\beta_2 \times 10^{-9}$ (M^{-2})	$\beta_3 \times 10^{-11}$ (M^{-3})
La	0.85 ± 0.01	0.258 ± 0.004	0.176 ± 0.005
Ce	1.44 ± 0.03	0.828 ± 0.018	1.69 ± 0.09
Pr	2.16 ± 0.05	1.68 ± 0.040	4.22 ± 0.2
Nd	2.82 ± 0.04	3.19 ± 0.040	14.6 ± 0.3
Sm	3.54 ± 0.09	7.83 ± 0.18	62.3 ± 2
Eu	3.35 ± 0.10	11.0 ± 0.40	160 ± 5
Gd	2.53 ± 0.06	8.50 ± 0.16	109 ± 3
Tb	2.11 ± 0.06	9.51 ± 0.16	179 ± 5
Dy	2.05 ± 0.04	9.60 ± 0.14	231 ± 6
Ho	1.90 ± 0.07	8.95 ± 0.25	202 ± 9
Er	2.20 ± 0.05	10.5 ± 0.30	170 ± 6
Tm	3.11 ± 0.05	16.7 ± 0.20	194 ± 4
Yb	3.56 ± 0.09	23.1 ± 0.40	148 ± 4
Lu	4.34 ± 0.11	35.4 ± 0.60	144 ± 5
Y	1.75 ± 0.05	5.80 ± 0.20	108 ± 5

using these constants. In Tables 2 and 3 we have tabulated the error in C_A, $(C_A - C_{A\,calc})$ using the final set of constants. If systematic errors were absent we would expect $(C_{Ai} - C_{Ai\,calc})$ to be normal distributed. This was not the case here, however, the systematic error is small.

DISCUSSION

Most of the discussion will be postponed until all the experimental material in this series has been presented. However, we wish to point out some similarities between the stability constants of the diglycolate and the dipicolinate complexes. The variations of the K_j-values through the lanthanide series are very similar for both the systems even though the dipicolinate complexes are much more stable than the corresponding diglycolate complexes. The stability constant for the first yttrium complex has for both the diglycolate and the dipicolinate systems a value between the corresponding values for the cerium and the praseodymium complexes. Part II of this series is a determination of the changes in free enery, enthalpy and entropy for the various reactions in the rare-earth diglycolate and dipicolinate systems.

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APPENDIX

Computer calculation of stability constants using the "Letagrop" method.[29] The following computer programs have been written by Sillén and Ingri. The calculations were made using a Ferranti-Mercury Computer. All programs were written in the Ferranti-Mercury autocode. The set of stability constants was determined from a set of S titrations where all titrations were used simultaneously. Each titration was characterized by four constants B_1; B_2; J and E_7. B_1 denotes the ratio

$$B_1 = \frac{2[H_2A] + [HA^-] + [A]}{C_A}$$

B_2 the acid excess in the metal perchlorate solutions, J the number of experimental points in each titration and E_7 denotes the total concentration of metal ion, C_M: These constants with the corresponding experimental values of C_A and $[H^+]$ were punched on the data tape. In order to treat the data the chapter 0 had to be rewritten as follows:

Chapter 0; Variables 1; Title; Satsvis 1; $H = \psi\log$ (10); $I = 0$; Jump 17, $T = 8$; Jump 1;
2) Read (S); Print (S) 2,0; $A_{13} = S + 0.1$; Newline; $Q = 0$; $I = 0$;
30) $I = I + 1$; $F_I = Q + 1 + 0.1$; Print (F_I) 2,0; Read (J); F (I + 20) $= Q + J + 0.1$; Print ($Q + J$) 2,0; Print (J) 2,0; Jump 31;
32) $K = 1$ (1) J; $O = Q + K$; Read (U_0); Read (Z_0); Repeat; $Q = Q + J$; Jump 30, $S > I$; $D_{13} = Q + 0{,}1$; Across 1/4;
3) $X = 0$; $F_0 = 0$; $K = P$; Jump 16;
6) $V = D$; $G = 2$; $E_0 = EB$; Jump 7;
8) $D_0 = \psi\text{mod}\ (B_0 - B)$; Jump 10, $E_0 > D_0$; Jump 9, $B > B_0$; $G = 0.5$; $D = GD$; $V = V - D$; Jump 7;
9) $D = GD$; $V = V + D$; Jump 7;
14) $W = Z_0 - Z_K$; Jump 11, $T = 0$;
12) $X = X + G_0WW$; $F_0 = F_0 + G_0$; $K = K + 1$; Jump 13, $K > Q$; Jump 5, $F > 5$; Jump 19, $K > S$; Jump 5;
15) Across 1/1;
18) Jump 13, $T = 3$; Jump 25, $F > 5$; $Q = \psi\text{intpt}\ (D_{13})$; $O = 0$;
19) $O = O + 1$; $S = \psi\text{intpt}\ (F_{(O+20)})$; $E_{(N+1)} = F_{(O+40)}$; Jump 25;
20) Jump 23, $F > 5$; $R = 1$; $G_1 = N + 1$; Read (H_1); ψ_7 (361) H_1, 1; $F = 10$; $O = 0$;
21) 21) $O = O + 1$; $S = \psi\text{intpt}\ (A_{13})$; Jump 24, $O > S$; $P = \psi\text{intpt}\ (F_0)$; $Q = \psi\text{intpt}\ (F_{(O+20)})$; $E_{(N+1)} = F_{(O+40)}$; ψ_7 (301) $E_{(N+1)}$, 1; Newline; $T = 1$; Jump 3;
23) $F_{(O+40)} = E_{(N+1)}$; Jump 21;
24) $F = 0$; Across 2/4; → ;

The special program (SP) was as follows — when necessary we have given a chemical translation:

1) Title;
Me 3 + Diglyk;
1) Newline; Jump 2;
16) $I = 1$ (1) 6; Print (E_I) 0,3; Jump 4, $I \neq 3$; Newline;
4) Repeat: Jump 18;
25) $B_1 = F_{(O+60)}$; $B_2 = F_{(O+80)}$;
5) $U = U_K$; $Y = B_1ZK + B_2 - U$; ($Y = C_H - [H^+]$)
$C_1 = E_5U$; ($E_5 = \delta_1$; $E_6 = \delta_2$; $U = [H^+]$)
$C_2 = E_6UU$; $W = C_1 + 2C_2$;
$A = Y/W$; $\left(A = [A] = \frac{C_H - [H^+]}{\delta_1 \cdot [H^+] + 2\delta_2[H^+]^2}\right)$
7) $C_3 = E_1A$; $C_4 = E_2AA$; ($E_1 = \beta_1$; $E_2 = \beta_2$; $E_3 = \beta_3$)
$C_5 = E_3AAA$;
10) $C_6 = 1 + C_3 + C_4 + C_5$; ($C_6 = X = 1 + \Sigma\ \beta_n[A]^n$)
$C_7 = E_4\ E_7/C_6$; ($E_4 = 1$, $C_7 = [M^{3+}]$)

$C_8 = 1 + C_1 + C_2$; $C_9 = C_3 + 2C_4 + 3C_5$; $Z_0 = AC_8 + C_7C_9$;
($Z_0 = C_A$); $G_0 = 1$; $A \sim R$; Jump 14;
11) Newline; Print (K) 2,0; Print (U_K) 0,3; Print (Z_K) 0,4; Print (100 000 W) 2,0;
Print (C_9/C_8) 1,3; Jump 12;
13) Print (X) 0,5; Newline; Jump 15, $T = 1$;
17) Across 2/4;
31) Read (W); Print (W) 0,3; $F_{(I+40)} = W$; Read (W); Print (W) 0,3;
$F_{(I+60)} = W$; Read (W), Print (W) 0,3; $F_{(I+80)} = W$; Newline; Jump 32;
φexp; Close; → ;

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