

STABILITY CONSTANTS OF RARE EARTHS COMPLEXES. I.

THERMODYNAMIC STABILITY CONSTANTS OF COMPLEXES OF EUROPIUM AND TERBIUM WITH α -HYDROXYISOBUTYRIC ACID

J. ALEXA

*Institute of Nuclear Research,
Czechoslovak Academy of Sciences, Prague-Řež*

Received July 22nd, 1970

In previous papers^{1,2} the data on concentration stability constants of rare earths complexes with α -hydroxyisobutyric acid in mixed media systems were published. For better elucidation of the influence of mixed media on complexation reaction it was desirable to determine the values of thermodynamic stability constants. The elaboration of a suitable method for this purpose was the aim of this paper. Because mixed media systems are rather complicated the derived method was first applied to the aqueous system.

For the determination of thermodynamic stability constants the common method, namely the determination of the dependence of concentration stability constants on the ionic strength and the extrapolation to the zero ionic strength, was applied. The concentration stability constants were determined with aid of the least-squares analysis of the distribution function of rare earth ions *i.e.* of the dependence of the distribution coefficient of rare earth ion on the molarity of the complexing anion in the system after equilibration with the cation exchange resin. The distribution coefficient is defined as the ratio of equilibrium concentrations of the studied rare

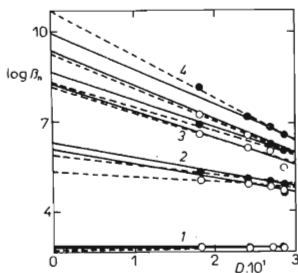


FIG. 1

Dependence of Experimental Values of Stability Constants of Europium and Terbium Complexes on D

○ Eu, ● Tb, - - - - original, — final
1—4 number of ligands in the complex.

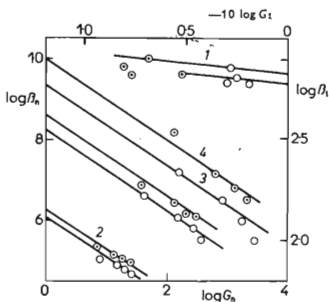


FIG. 2

Dependence of Experimental Values of Stability Constants of Europium and Terbium Complexes on $\log G$

○ Eu, ⊙ Tb, 1—4 number of ligands in the complex.

earth ion in the solid and liquid phases in the system, containing the cation exchange resin, the solution having the requested concentration of the complexing agent and of sodium perchlorate for adjusting of the ionic strength.

Four stepwise complexes are supposed to exist in the system rare earth ion- α -hydroxyisobutyric acid, namely MA^{2+} , MA_2^+ , MA_3 and MA_4^- . The range of existence of the first complex is lying about the concentration of $1 \cdot 10^{-3} - 1 \cdot 10^{-4} \text{ mol l}^{-1}$ of complexing anion. The distribution coefficient in such a system reaches the value of about $1 \cdot 10^5$ if the ionic strength is 0.1. For this reason the concentration of the central ion in the liquid phase after sorption is extremely low and the inaccuracy of its determination is therefore considerable. The accuracy of the determination of the stability constant of the first complex is therefore insufficient. For the same reason the systems with ionic strength not lower than 0.1 can be studied and the extrapolation of the nonlinear dependence of the stability constant on the ionic strength to the zero point is not exact. It was therefore necessary to find a way how to obtain more exact values of the stability constant of the first complex and how to linearise the dependence of stability constants on the ionic strength. If a way how to obtain a linear dependence of stability constants on some function of the ionic strength in the range used would be found, so much the more the linear course in the systems of lower ionic strengths could be supposed. Then a better validity of Debye-Hückel equation can be expected and the eventual empirical term would approach to zero.

Experimental conditions and methods of the determination of the distribution function in systems, containing the metallic ion studied, the cation exchange resin and the solution of complexing agent were published in the previous paper¹. The distribution functions obtained were analysed with help of the least squares method on the automatic computer.

RESULTS AND DISCUSSION

The concentration stability constants of complexes of europium and terbium with α -hydroxyisobutyric acid were determined in the systems the ionic strength of which was 0.1, 0.3, 0.5 and 0.7. For results see Table I. To obtain more accurate values of these constants and the values of thermodynamic constants following suppositions and operations were used.

The thermodynamic stability constant β_{n0} of complexes of a trivalent central ion M^{3+} and n molecules of a ligand A^- is defined as

$$\beta_{n0} = ([MA_n^{(3-n)+}]/[M^{3+}][A^-]^n) (\gamma_{3-n}/\gamma_3 \cdot \gamma_1^n) = \beta_n G_n, \quad (1)$$

where β_n is the concentration stability constant, γ_z the activity coefficient of the ion having the charge z and G_n the ratio of activity coefficients. G_n can be theoretically calculated with help of the Debye-Hückel formula

$$\log G_n = H_n AD, \quad (2)$$

where $H_n = (2z_c - n + 1)n$, $D = I^{1/2}/(1 + dBI^{1/2})$, z_c is the charge of the central ion, A and B are the Debye-Hückel constants and d the distance of closest approach.

For balancing of experimental results and for extrapolation to the zero ionic strength the plot of β_n versus D was used, because the linearity of this dependence according to Eq. (1) and (2) can be supposed. For the calculation of D the values $A = 0.5091$, $B = 0.3286$ and $d = 6.5 \text{ \AA}^3$ were used. For the plot see Fig. 1, dotted lines.

The ionic strength applied was relatively high. For this reason it can be supposed that Eq. (2) does not express the value of G accurately. It would be therefore desirable to find a correction term for each ion existing in the system. Unfortunately there are six different ions in the system

TABLE I

Experimental and Calculated Values of Stability Constants

For Eu: $M = 5.998$; $L = -5.720$; for Tb: $M = 6.020$; $L = -5.591$.

I	Experimental				Calculated			
	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
Eu								
0	—	—	—	—	2.78	6.11	8.10	9.40
0.1	2.78	5.04	6.60	7.19	2.80	5.20	6.61	7.19
0.3	2.81	4.93	6.07	6.53	2.81	4.91	6.08	6.47
0.5	2.86	4.86	5.82	5.99	2.81	4.77	5.84	6.15
0.7	2.79	4.70	5.55	5.53	2.81	4.69	5.67	5.95
Tb								
0	—	—	—	—	2.83	6.32	8.64	10.05
0.1	2.82	5.33	6.89	8.16	2.85	5.41	7.00	7.84
0.3	2.90	5.16	6.47	7.14	2.85	5.13	6.51	7.12
0.5	2.82	4.99	6.21	6.79	2.86	4.99	6.21	6.80
0.7	2.86	4.98	6.11	6.51	2.86	4.91	6.06	6.60

but only four complexes and therefore four equations of the (I) type are available. The derivation of the correction term of Eq. (2) was therefore found as only possible.

The correction term of Eq. (2) has to preserve the linearity of the function $\log G_n = f(D)$ and is therefore expected to be a function of D , too. The aim of following operations was to find this term with aid of successive approximation.

The first step was the application of Eq. (2) in the form

$$\log G_n = H_n AD - C_n. \quad (3)$$

The values of $\log G_n$ obtained as $\log \beta_{n0} - \log \beta_n$ balanced as the linear function of D were used for the calculation of C_n with aid of Eq. (3). It was found that C_n was not constant but that it was dependent on the number of ligands (n) in the complex and, as expected, on D . The dependence of C_n on D can be expressed by the equation

$$C_n = k_n D. \quad (4)$$

The plot of k_n versus z showed, that k_n is the linear function of the charge of the complex and can be expressed by the equation

$$k_n = (Mz + L) A, \quad (5)$$

where M and L are empirical constants.

With aid of values of k_n balanced according to Eq. (5) the corrected values of C_n and G_n were calculated. Corrected values of $\log \beta_{n0}$ and $\log \beta_n$ were then obtained with aid of the function $\log \beta_n = f(\log G)$ (Fig. 2). The corrected values of $\log \beta_{n0}$ can be plotted as the linear function

of the logarithm of the number of ligands in the complex. The values of thermodynamic constants were therefore corrected also in this way (Fig. 3) and then used for the correction of the plot of the dependence of $\log \beta_n$ versus D (Fig. 1, full lines). In such a way more accurate values of $\log \beta_n$ and $\log \beta_{n0}$ were obtained and the above mentioned operations were then repeated until the values of thermodynamic stability constants showed out the difference in the second decimal in last two operation sets.

For results see Table I. In the Table and in all figures besides Fig. 1 the values obtained in the last operation set are presented.

From the results it can be concluded that for the calculation of thermodynamic stability constants of complexes of rare earths with α -hydroxyisobutyric acid following equation can be used

$$\log \beta_{n0} = \log \beta_n + A\{(2z_c - n + 1)n - M \cdot z - L\} \cdot (I^{1/2}) / (1 + BDI^{1/2}). \quad (6)$$

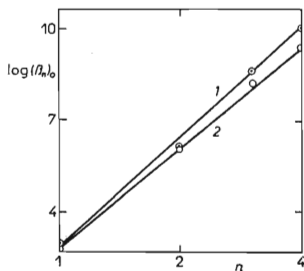


FIG. 3

Dependence of the Logarithm of Thermodynamic Stability Constants on the Logarithm of the Number of Ligands in the Complex

○ Eu, □ Tb, n number of ligands in the complex.

With respect to the lack of data the physical significance of the constants M and L cannot be elucidated. Nevertheless, since they are expressing in some way the nonideality of the system, it can be supposed, that they are in connection with the diameter of reacting ions, with their dipolmoments and from it following difference in the real and theoretical charge of complex ions and with the relative permittivity of the system.

The author wishes to express his thanks Dr E. Šimová, Institute of Nuclear Research, Czechoslovak Academy of Sciences, for the computation of stability constants on the automatic computer and Mrs M. Veselá for carrying out of complicated experiments and measurements.

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Translated by the author.