

# STABILITIES OF TARTRATE COMPLEXES OF RARE-EARTH ELEMENTS AND YTTRIUM IN WATER AND IN AQUEOUS ETHANOL SOLUTIONS

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The stability constants of complex compounds in mixtures of water and an organic solvent must depend on the change in the dielectric constant  $D$  of the medium and on the character of the solvation of each of the participants in the reaction. Over a considerable range of compositions of mixtures in which the oversolvation of ions is absent we may expect that the dielectric constant of the solvent will have a determining effect on the stability of complexes of the "electrostatic type."

The stabilities of tartrate complexes of rare-earth elements (REE) in water at ionic strengths of 0.1 and 0.2 have been studied previously [1, 2]. In the present work we have investigated the stabilities of tartrate complexes of REE and yttrium of composition  $\text{LnTar}^+$  in water and alcohol-water mixtures containing 25, 40, and 50 vol. % of azeotropic ethanol (which correspond, according to pycnometric determinations, to 19.8, 30.0, and 40.3 wt. % of ethanol respectively) and the relation of  $\log \beta_1$  ( $\beta_1 = [\text{LnTar}]/[\text{Ln}][\text{Tar}]$ ) to the reciprocal of the dielectric constant of the solvent. The determinations were made at 25°, and the ionic strength  $I$  was 0.05.

## EXPERIMENTAL

The complex formation of REE and yttrium ions with tartrate ions was studied by pH-potentiometric titration of  $\sim 0.05$  M solutions of the metal perchlorates with an  $\sim 0.005$  M solution of D-tartaric acid ( $\text{H}_2\text{Tar}$ ) in the appropriate solvent. In work with 40 and 50 vol. % solutions of alcohol the concentrations of the reactants were lowered to prevent the formation of precipitates. To avoid the hydrolysis of the REE and yttrium perchlorates a definite acidity was established in the solutions ( $1 \cdot 10^{-3}$ – $5 \cdot 10^{-4}$  M). The concentrations of metal ions were determined by gravimetric and EDTA-titration methods, while the concentrations of  $\text{H}_2\text{Tar}$  were determined by pH-potentiometric titration with  $\text{CO}_2$ -free NaOH solution. The ionic strength of the solutions was maintained constant at 0.05 with the aid of NaCl and  $\text{NaClO}_4$ .

Measurements of  $p[\text{H}] = -\log [\text{H}]$  were made with the use of an LPU-01 pH meter as a null indicator in a cell without transference:

glass electrode	solution under investigation [Cl] = 0.01 g-ion/liter	AgCl   Ag
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The glass electrode was calibrated by means of HCl solutions of known concentration in the appropriate solvent with  $I = 0.05$  and  $[\text{Cl}] = 0.01$  g-ion/liter. The silver chloride electrode was prepared by the thermal method [3]. Equilibrium at the electrodes was established in the course of 7–10 min. The solutions were agitated by the passage of nitrogen saturated with solvent vapor.

For the calculation of stability constants we used material-balance equations, in which the metal ion and ligand were denoted by  $M$  and  $A$  respectively:

$$c_M = [M] + [MA], \quad c_A = [A] + [MA], \quad c_H = [A] + h.$$

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TABLE 1. Values of  $\log \beta_1$  for DyTar<sup>+</sup> at I = 0.05 and 25°

H <sub>2</sub> O			25 vol. % C <sub>2</sub> H <sub>5</sub> OH			40 vol. % C <sub>2</sub> H <sub>5</sub> OH		
$c_M = 6.20, c_H^0 = 0, *$ $v_M = 5 \text{ ml}, c_A = 5.00$			$c_M = 5.06, c_H^0 = 1.00,$ $v_M = 5 \text{ ml}, c_A = 5.00$			$c_M = 2.54, c_H^0 = 1.00,$ $v_M = 10 \text{ ml}, c_A = 1.96$		
$v_A, \text{ml}$	p [H]	$\lg \beta_1$	$v_A, \text{ml}$	p [H]	$\lg \beta_1$	$v_A, \text{ml}$	p [H]	$\lg \beta_1$
3	2.735	4.08	3	2.650	4.66	2	2.915	4.80
5	2.688	4.10	5	2.624	4.77	3	2.896	4.82
6	2.679	4.09	6	2.624	4.78	4	2.872	4.93
7	2.671	4.10	7	2.636	4.73	5	2.859	4.98
9	2.661	4.12	9	2.644	4.72	6	2.847	5.04
10	2.661	4.11	10	2.647	4.73	7	2.838	5.08
11	2.659	4.12	11	2.650	4.74	8	2.830	5.14
13	2.661	4.10	13	2.656	4.77	9	2.826	5.16

\*Free acidity in Dy(ClO<sub>4</sub>)<sub>3</sub> solution. All concentrations are given in mmole/liter.

TABLE 2. Values of  $\log \beta_1$  and  $\log \beta_1^0$  for 25° and I = 0.05 and O Respectively

Element	H <sub>2</sub> O		25 vol. %		40 vol. %		50 vol. %	
	$\lg \beta_1$	$\lg \beta_1^0$	$\lg \beta_1$	$\lg \beta_1^0$	$\lg \beta_1$	$\lg \beta_1^0$	$\lg \beta_1$	$\lg \beta_1^0$
La	3.74±0.07	4.77	4.39±0.05	5.66	—	—	5.22±0.04	6.90
Pr	4.08±0.09	5.11	4.67±0.08	5.94	—	—	5.47±0.10	7.15
Nd	4.20±0.03	5.23	4.76±0.06	6.03	—	—	5.53±0.19	7.21
Sm	4.27±0.02	5.30	4.83±0.10	6.10	5.15±0.18	6.57	5.65±0.10	7.33
Eu	4.33±0.09	5.36	4.80±0.04	6.07	5.03±0.07	6.45	—	—
Gd	4.15±0.01	5.18	4.70±0.01	5.97	5.06±0.12	6.48	—	—
Tb	4.06±0.05	5.09	4.70±0.01	5.97	—	—	5.57±0.17	7.25
Dy	4.13±0.01	5.16	4.73±0.04	6.00	5.00±0.14	6.42	—	—
Ho	4.14±0.01	5.17	4.76±0.03	6.03	5.04±0.07	6.46	—	—
Er	4.14±0.10	5.17	4.79±0.03	6.06	—	—	5.46±0.07	7.14
Tm	4.18±0.11	5.21	4.85±0.11	6.12	5.09±0.11	6.51	—	—
Yb	4.26±0.10	5.29	4.91±0.06	6.18	5.22±0.10	6.64	5.74±0.07	7.42
Lu	4.32±0.06	5.35	4.97±0.05	6.24	5.40±0.10	6.82	—	—
Y	4.03±0.04	5.06	4.68±0.08	5.95	5.12±0.10	6.54	5.52±0.10	7.20

Here h is the equilibrium hydrogen ion concentration [H];  $f = 1 + \Sigma B_i h^i$ ;  $\varphi = \Sigma B_i h^i$ , and the protonation constant of the tartrate ion  $B_1 = [H_1A]/[A]h^1$  was determined by us:  $\log B_1 = 4.159$ ,  $\log B_2 = 7.085$  for water;  $\log B_1 = 4.324$ ,  $\log B_2 = 7.541$  for a 25% solution of C<sub>2</sub>H<sub>5</sub>OH;  $\log B_1 = 4.361$ ,  $\log B_2 = 7.752$  for a 40% solution of C<sub>2</sub>H<sub>5</sub>OH;  $\log B_1 = 4.735$ ,  $\log B_2 = 8.184$  for a 50% solution of C<sub>2</sub>H<sub>5</sub>OH. The value of D for water was taken to be 78.3 [4], while the values of D for the water-ethanol mixtures, equal to 67.1, 61.0, and 55.1 respectively, were found by the interpolation of data in the literature [5, 6].

So as to be sure of the predominance in the system of the complex of composition MA, the molar ratios  $c_M:c_A$  were varied in the titration within narrow limits: from 5 to 0.5. Typical experimental data are given in Table 1.

The calculation of stability constants was conducted on an M-20 electronic computer. The results, with the average values for two or three titration curves, are given in Table 2; confidence intervals for values of  $\log \beta_1$  were estimated with the aid of the Student criterion for an accuracy of 95%.

## DISCUSSION OF RESULTS

Let the reactions between the substances A<sub>i</sub> with the charges z<sub>i</sub> be written in the form  $\Sigma \nu_i A_i = 0$  ( $\nu_i$  is the stoichiometric coefficient of the i-th participant of the reaction). Following N. A. Izmailov [7], by the symbols  $\gamma_{0i}$  and  $\gamma_i^*$  we denote the null and concentrational activity coefficients of the i-th substances. Then the equilibrium constants K and K', standardized on infinitely dilute solutions in water and the given solvent respectively, are related by the equation

$$\ln K' = \ln K - \Sigma \nu_i \ln \gamma_{0i}$$

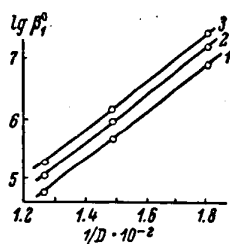


Fig. 1

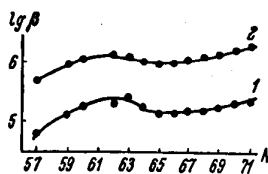


Fig. 2

Fig. 1. Relation of the stability constants of tartrate complexes of La (1), Y (2), and Yb (3) at  $I = 0$  to the dielectric constant of the solvent.

Fig. 2. Relation of the stability constants of tartrate complexes of REE at  $I = 0$  in water (1) and in 25 wt. % ethanol solution (2) to the atomic numbers of the elements  $N$ .

i.e., the dependence of the equilibrium constants on the medium is determined by the term  $\sum \nu_i \ln \gamma_{oi}$ . Since in the absence of oversaturation the values of  $\ln \gamma_{oi}$  for the ions in mixed solvents depend linearly on  $1/D$  [7], values of  $\ln K'$  must also depend linearly on  $1/D$ .

To reveal the relation of the stability constant of the tartrate complexes to  $D$ , the stability constants determined for  $I = 0.05$  were recalculated to  $I = 0$  with the aid of Davies's equation [8]:

$$\lg \gamma_i^0 = -A_D z_i^2 \left( \frac{\sqrt{I}}{1 + B_D \sqrt{I}} - 0.3I \right).$$

For  $A_D$  we used the theoretical values of the limiting slopes of Debye for the given solvents [7];  $B_D$ , following Davies, was taken as unity in water, but on transition to mixed solvents it was considered that it changes in proportion to  $(d_0/D)^{1/2}$ , in which  $d_0$  is the density of the solvent.

Table 2 gives values of  $\log \beta_1^0$  ( $I = 0$ ), while Fig. 1 shows the relation of values of  $\log \beta_1^0$  for some REE to  $1/D$ . For all REE and yttrium ions a linear relation is observed between  $\log \beta_1^0$  and  $1/d$ .

Our results on the stability of the tartrate complexes agree satisfactorily with data in the literature. When recalculated to  $I = 0$ , the values of  $\log \beta_1^0$  for La given in [1], [2], and [9] are 4.75, 4.35, and 4.59 respectively, while our value is 4.77.

The values of stability constants that we have obtained in water and mixed solvents rise from La to Eu; there follows a diffuse minimum in the region Gd - Er, and there is again a small rise to Lu (Fig. 2). A relation of this form between  $\log \beta_1$  and the atomic numbers of the REE is in accord with one of the types of relation described by K. B. Yatsimirskii et al. [10]. The "trough" in the region of Gd arises as a result of the absence of the effect of extrastabilization of its  $f^7$  shell by the field of the ligands.

## CONCLUSIONS

The logarithms of the thermodynamic stability constants of the complexes  $\text{LnTar}^+$  in water and water-alcohol mixtures containing up to 40.3 wt. % of ethanol depend linearly on the reciprocal of the dielectric constant of the solvent.

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