ENVIRONMENTALLY FRIENDLY COMPLEXONES. THE THERMODYNAMIC CHARACTERISTICS OF THE FORMATION OF Al³⁺ ION COMPLEXES WITH ETHYLENEDIAMINEDISUCCINIC ACID IN AQUEOUS SOLUTIONS

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Abstract: Complex formation between Al³⁺ and ethylenediamine - N,N`-disuccinic acid (H_4L) was studied at 25°C against the background of 0.1, 0.5, 1.0 N solutions of KNO_3 by potentiometry and mathematical modeling. The extrapolation of concentration constants to zero ionic strength was used to calculate the thermodynamic constants of the formation of the AlL^-, $AlHL$ complexes using an equation with one individual parameter ($\log\beta^0 = 16.27 \pm 0.07$, 9.19 ± 0.2 respectively).

Keywords: aluminum, ethylenediaminedisuccinic acid, derivatives of ethylenediaminedisuccinic acid, complex formation, complexones, thermodynamic constants, concentration constants.

1. Introduction

Chelating derivatives of succinic acid - iminodisuccinic acid (IDS) ethylendiamindisuccinic acid (EDDS), have been created by the Department of Inorganic and Analytical Chemistry, Tver State University, are biologically active compounds and open up entirely new opportunities for process control in wildlife. The growing interest in coordination compounds of metals, having the biologically active properties, due to their high activity as the means against chlorosis of plants, as catalysts of metabolic reactions, as stabilizers of different degree of oxidation of metals, as the vehicle of physiologically important molecules, atoms and cations across membranes cells.

With increasing environmental problems is increasing interest in biologically active coordination compounds with new chelator-containing fragments of natural aminoacids. These include ethylenediamine - N,N`-disuccinic acid (H_4L, EDDS), which contains in its molecule of succinic residues and aspartic acids.
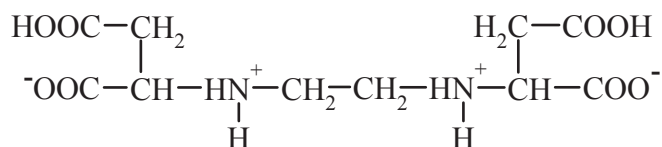
Earlier [1], data on the stability of medium EDDS complexes with aluminum were studied lgβ = 13,5. However, the paper does not mention the possible existence of protonated complexes. It is also not considered the effect of ionic strength on the complexation. To identify the concentration dependence of the stability constants, we carried out studies of EDDS - Al³⁺ - water at different ionic strength and calculated thermodynamic stability constants of aluminum etilendiamindisuccinates.

2. Experimental

To calculate the values lgβ the method of potentiometric titration at various ionic strengths in a KNO_3 medium at 298.2 K was used.

EDDS was synthesized by the interaction of ethylenediamine with maleic acid [2]. Working solutions (0.005 M) were prepared gravimetrically from dry complex one at the day of measurments. The concentration of solutions was controlled by potentiometric and complexonometric titration. of aluminum nitrate were prepared from weighed amounts of the salt of kh. ch. (chemically pure) grade, their concentration was determined by complexonometry [3]. Solutions of potassium nitrate were prepared gravimetrically from KNO_3 of kh. ch. grade. The salt was doubly recrystallized. Carbonate free 0.05 M solutions of NaOH were prepared from a 50% solution of NaOH by dissolving its necessary amount in preliminarily boiled water. The solutions were standardized by titration of preliminarily prepared sodium hydrophthalate. To broaden the working range of pH values, a standard solution of nitric acid prepared from concentrated HNO_3 and standardized against sodium tetraborate was used.

Potentiometric measurements were performed with an accuracy of ±0.05 pH units on an Akvalon pH-410 pH-meter-millivoltmeter using an ESLK - 01.7 combined pH electrode. The system was calibrated against standard buffer solutions with pH values of 1.68 and 9.18. Titration was performed in a temperature controlled cell at 298.2 K. The ionic strength value was changed by adding the necessary amount of potassium nitrate. The number of parallel measurements was no less than 4.

The experimental data were processed using the AUTOEQUIL universal computer program [4]. Its algorithm allows significant complex forms to be determined from a general sample of admissible forms and the corresponding formation constants to be calculated under the conditions of an automatic search for the model correctly describing pH-metric data.
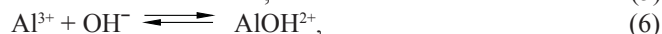
3. Results and discussion

The ratio between the concentrations of Al^{3+} and H_4L in the solutions studied was 1 : 1. The titration curves of the $c_{Al} : c_{EDDS} = 1 : 1$ systems (Fig. 1, curve 2) were different from the titration curve of pure H_4L acid (Fig. 1, curve 1) already at the initial pH values; that is, along with the step dissociation of H_4L, complex formation processes occurred in the system studied. We also titrated the $c_{Al} : c_{EDDS} = 1 : 2$ system. The character of the curves coincided; that is, the conclusion could be drawn that the system contained no biligand complexes. All the subsequent measurements were therefore performed only at a $c_{Al} : c_{EDDS} = 1 : 1$ ratio.
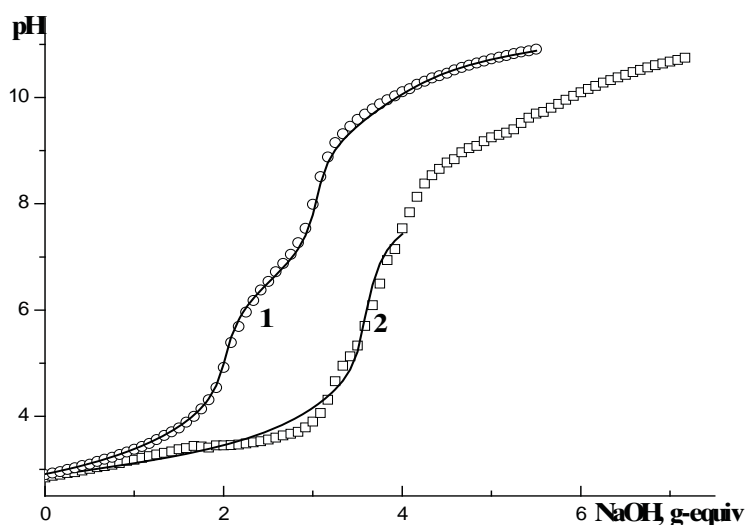
Fig. 1. Potentiometric titration curves of (1) H_4L (0,0010 mol/l) and (2) $Al^{3+} : H_4L = 1 : 1$. Titrant 0,0510 M NaOH (T = 298.2 K, ionic strength 0,5 (KNO_3)). Open circles are measurement results, lines correspond to calculations.

The resulting titration curves can be divided into two areas. In an acidic medium and the pH was observed the formation of protonated and medium-sized complexes. In the alkaline pH region is clearly flow processes to form various hydroxocomplexes, but to get the model adequately describes this region of the titration curve was not possible. Therefore, the calculation was carried out at pH less than 7.

Were used H^+, L^{4-}, Al^{3+} as basis particles in the calculations. The following equilibria were taken into account:

$$H_2O \rightleftharpoons H^+ + OH^-, \tag{1}$$
$$H_4L \rightleftharpoons H^+ + H_3L^-, \tag{2}$$
$$H_3L^- \rightleftharpoons H^+ + H_2L^{2-}, \tag{3}$$
$$H_2L^{2-} \rightleftharpoons H^+ + HL^{3-}, \tag{4}$$
$$HL^{3-} \rightleftharpoons H^+ + L^{4-}, \tag{5}$$
$$Al^{3+} + OH^- \rightleftharpoons AlOH^{2+}, \tag{6}$$
$$AlOH^{2+} + OH^- \rightleftharpoons Al(OH)_2^+, \tag{7}$$
$$Al(OH)_2^+ + OH^- \rightleftharpoons Al(OH)_3, \tag{8}$$
$$Al(OH)_3 + OH^- \rightleftharpoons Al(OH)_4^-. \tag{9}$$

We used the constants of the dissociation of H4L and aluminum hydrolysis obtained at various solution ionic strengths under the conditions indentical to those used in studies of aluminum interaction with EDDS. The values obtained closely agreed with each other and the literature data [5-8]. The results of this study are presented in the table.

The determination of aluminum hydrolysis constants showed that the concentration of $AlOH^{2+}$ formed in reaction (6) under the experimental conditions was negligibly low. Therefore, when calculating the stability constants of complexes of this equilibrium is not taken into account.

The values found for reactions of lgβ etilendiamindisuktsinatov aluminum at 298.2 K and I = 0,1; 0,5; 1,0 (KNO$_3$) are presented in the Table.

Logarithms of stability constants lgβ at 298.2 K

Particle	I			
	0	0.1	0.5	1,0
AlOH^{2+} + OH$^-$ ⇌ Al(OH)$_2^+$	9.0* [5]	9.13 ± 0.10	8.99 ± 0.20	8.93 ± 0.10
Al(OH)$_2^+$ + OH$^-$ ⇌ Al(OH)$_3$	8.5* [5]	7.94 ± 0.10	7.37 ± 0.10	7.36 ± 0.10
Al(OH)$_3$ + OH$^-$ ⇌ Al(OH)$_4^-$	4.6* [5]	4.63 ± 0.10	4.58 ± 0.20	4.58 ± 0.20
L^{4-} + H$^+$ ⇌ HL^{3-}	10.73 ± 0.16 11,12 [6]	10.02 ± 0.02 9,82 [7]	9,65 ± 0.02	10,03 ± 0.03 10.10 [6]
HL^{3-} + H$^+$ ⇌ H$_2$L^{2-}	7.23 ± 0.07 7,52 [6]	6,70 ± 0.02 6,83 [7]	6,57 ± 0.03	6,89 ± 0.04 6.65 [6]
H$_2$L^{2-} + H$^+$ ⇌ H$_3$L$^-$	4.01 ± 0.09 4.28 [6]	3.68 ± 0.03 3.86 [7]	3.57 ± 0.03	3,88 ± 0.05 3.81 [6]
H$_3$L$^-$ + H$^+$ ⇌ H$_4$L	2.68 ± 0.2 3.45 [6]	2.68 ± 0.05 2,40 [7]	2.50 ± 0.09	3.03 ± 0.07 3.28 [6]
Al^{3+} + HL^{3-} ⇌ AlHL	9.19 ± 0.2	7.29 ± 0.2	7.38 ± 0.07	7.41 ± 0.2
Al^{3+} + L^{4-} ⇌ AlL$^-$	16.27 ± 0.07	13,86 ± 0.1 13,52 [1]	13.15 ± 0.06	13,39 ± 0.1

* Values recalculated from hydrolysis constants

According to the survey were diagrams of the distribution of various forms of complex Al^{3+} with H$_4$L (Fig. 2).
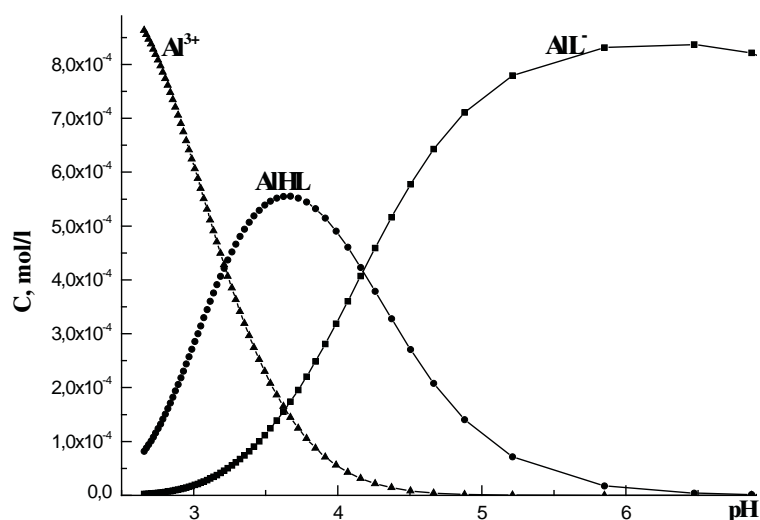

Fig. 2. The concentration diagram of complex forms of Al^{3+} with H$_4$L distribution

Concentration equilibrium constants depend on experimental conditions. Of considerable interest are thermodynamic constants β$_0$, which are more objective characteristics of ionic equilibria and are independent of the nature and concentration of solvents. They were calculated by the extrapolation of the data obtained (fig.3) at fixed ionic strength values to zero ionic strength using the equation with one individual parameter [9]:

$$\lg \beta_c - \frac{\Delta Z^2 A_\gamma I^{1/2}}{1 + 1.16 I^{1/2}} = \lg \beta_0 + bI$$

where β$_c$ and β$_0$ are the concentration and thermodynamic stability constants, respectively; ΔZ^2 is the

difference of the squares of charges of reaction products; A_{γ} is the limiting Debye law constant (0.5108 [10] at 298.2 K), I is the ionic strength of the solution, and b is the empirical coefficient.
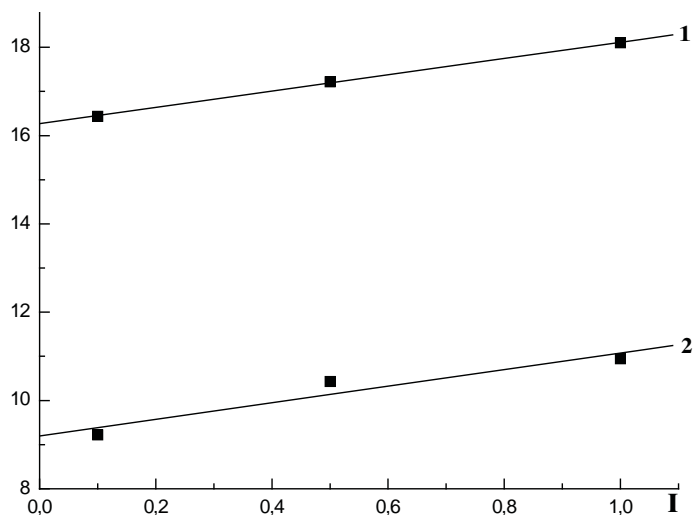
Fig. 3. Graphical determination of the thermodynamic stability constants of complexes at 298.2 K: *1 – AlL, 2 – AlHL*.

The resulting thermodynamic stability constants (Table) can be used for reliable interpretation of the results of calorimetric studies of complex formation involving ethylenediaminedisuccinic acid.

4. References

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