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> PHYSICAL CHEMISTRY OF SOLUTIONS =

# Formation Constants and Composition of Ga<sup>3+</sup> and In<sup>3+</sup> Complexes with Iminodisuccinic Acid in Aqueous Solutions According to Potentiometric Data

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**Abstract**—The complexation of  $Ga^{3+}$  and  $In^{3+}$  with iminodisuccinic acid (H<sub>4</sub>L) at 25°C in 0.1, 0.4, 0.6, and 0.8 M KNO<sub>3</sub> supporting solutions was studied by potentiometry and mathematical modeling. The thermodynamic constants of formation of neutral, protonated, and hydroxo complexes were calculated by extrapolating the concentration constants to the zero ionic strength using an equation with one individual parameter.

*Keywords:* gallium, indium, iminodisuccinic acid, iminodisuccinates, complexation, complexons, thermodynamic constants, concentration constants.

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### **INTRODUCTION**

Complexons have become a part of our everyday life; they are used in agriculture, medicine, cosmetic and construction industries, analytical laboratories, household chemical goods, etc. Ethylenediaminetetraacetic acid (EDTA) is a widely used complexon, whose release in the global ocean has become dangerous. Therefore, synthesis of ecologically safe analogs of traditional complexons capable of biodegradation and thus not apt to accumulation in the environment and studies of their properties have recently become an area of active interest. Iminodisuccinic acid H<sub>4</sub>L (IDSA) occupies a special place among ecologically safe complexons. It is a member of the homologous series of complexons which are the derivatives of carboxylic acids. Two succinic acid residues in IDSA are bonded via the amine nitrogen atom:



(IDSA)

The complexon is of interest for researchers because of its increased biological activity and ecological safety of its complexes. In living nature, metal iminodisuccinates can decompose into fragments involving metal ions in assimilable form and amino acids that form the basis of the complexon, for example, aspartic acid [1]. Data on the stability of IDSA complexes with alkaline earth, rare-earth, and 3*d* metals are available, while complexation with strong complexing agents such as Subgroup IIIA elements remains understudied. Previously [2], we studied processes in the Al<sup>3+</sup>– IDSA–water system. Neutral, protonated, and hydroxo complexes of IDSA with Al<sup>3+</sup> formed in the system. The same paper presented the calculated thermodynamic and concentration stability constants of the complexes. The goal of this work was a potentiometric study of  $M^{3+}$ –IDSA–water systems, where  $M^{3+}$  is Ga<sup>3+</sup> or In<sup>3+</sup>.

# **EXPERIMENTAL**

The experimental procedure was similar to the one described in [2]. Iminodisuccinic acid was synthesized by adding an aspartic acid molecule to the maleic acid molecule while heating the mixture in an alkaline medium. The working solutions (0.005 M) were prepared from a dry complexon sample on the day of experiment. The concentration of the complexon solutions was checked chelatometrically or pH-potentiometrically. The former method involved titration of copper nitrate of known concentration with a complexon solution in the presence on an ammonia buffer and a murexide indicator [3]. The latter procedure involved pH-potentiometric titration of a complexon solution and determination of the amount of alkali spent on titration of one equivalent of complexon. When the potentiometric curve showed a jump, a small excess of copper nitrate was added during titration and hydrogen displaced by copper was titrated.

The equivalent amount of alkali spent on titration of released hydrogen was determined from the difference between the jumps on the potentiometric curve. The criterion of the correctness of calculations was the coincidence of data obtained by the two methods.

The solutions of  $Ga(NO_3)_3$  (0.0224 M) and  $In(NO_3)_3$  (0.0181 M) were prepared by dissolving the corresponding metals in twice distilled HNO<sub>3</sub>. The exact concentration of metal solutions was determined chelatometrically [4]. A carbonate-free 0.05 M NaOH solution was prepared from a 50% NaOH solution by dissolving the required amount in preliminarily boiled water followed by standardization by titrating the pre-liminarily prepared potassium hydrogene phthalate [5]. To expand the working range of pH, we used a standard solution of nitric acid prepared from concentrated HNO<sub>3</sub> and standardized relative to sodium tetraborate. To maintain the ionic strength, we used KNO<sub>3</sub> of "ch.d.a." (analytical) or "kh.ch." ("chemically pure") grade, which was twice recrystallized from water.

Potentiometric measurements to an accuracy of  $\pm 0.05$  pH units were performed using an Akvilon pH-410 pH-meter-millivoltmeter and a combined Akvilon ESLK-01.7 pH-electrode. The system was calibrated against the standard buffer solutions. Titration was performed in a thermostatted cell at 298.2 K. The ionic strength was varied by adding the required quantity of potassium nitrate. Each system was titrated at last four times.

The formation constants of the complexes were determined using the systems containing equivalent amounts of the metal ion and IDSA (0.001 M) in the presence of the calculated amount of the KNO<sub>3</sub> standard solution (1 M). An exact amount of HNO<sub>3</sub> was added to the solution to expand the titration range of the system in the acid region. The volume of each sample for analysis was 50 mL. The formation constants of the complexes were calculated from the experimental equilibrium concentration of one of the components using the AUTOEQUIL program designed for studying equilibria with arbitrary numbers of reactions in solution [6]. While modeling, we took into account not only the possibility of neutral monoligand complexes (ML<sup>-</sup>) forming in solution, but also the equilibria corresponding to the formation of protonated complexes (MHL) and hydroxo complexes (MOHL<sup>2-</sup>) and the formation of metal ion hydroxo complexes  $(M(OH)_{n}^{3-n}).$ 

# **RESULTS AND DISCUSSION**

The titration curves of the solutions containing  $M^{3+}$  and complexon (Fig. 1) lie in the region of lower pH values than the titration curves of the solutions containing the complexon alone. Consequently, complexations with displacement of hydrogen ions from the complexon occur in M-L-H<sub>2</sub>O systems.



**Fig. 1.** Potentiometric titration curves of the solutions of (1) IDSA, (2) IDSA and Ga<sup>3+</sup>, (3) IDSA and In<sup>3+</sup>;  $c_{\rm L} = c_{\rm M} = 0.001$  M; I = 0.1; T = 298 K; dots: experiment; lines: calculation.

The titration curves can be divided into two regions. The protonated and neutral complexes dominate in the acid and neutral regions. Hydroxo complexes are formed in the alkaline region.

The following processes were taken into account in calculations:

-water dissociation

$$H_2O \rightleftharpoons H^+ + OH^-,$$

-dissociation of the complexon H<sub>4</sub>L

$$\begin{split} H_4L \rightleftharpoons H^+ + H_3L^-, \\ H_3L^- \rightleftharpoons H^+ + H_2L^{2-}, \\ H_2L^{2-} \rightleftharpoons H^+ + HL^{3-}, \\ HL^{3-} \rightleftharpoons H^+ + L^{4-}, \end{split}$$

-metal hydrolysis

$$M^{3+} + OH^{-} \rightleftharpoons MOH^{2+},$$
  
 $M(OH)_{n}^{3-n} + OH^{-} \rightleftharpoons M(OH)_{n+1}^{3-(n+1)}$ 

where n = 1-3 for Ga<sup>3+</sup> and 1-2 for In<sup>3+</sup> [7].

The formation constants were calculated for all complex forms with allowance for the above processes at different ionic strengths (table). For  $M^{3+}-H_4L-H_2O$  aqueous solutions, the mathematical model was calculated using the algorithm for automated retrieval of the most probable complex forms from the set of possible forms given by the expanded component matrix of stoichiometric coefficients in the H<sup>+</sup>, L<sup>4-</sup>, and M<sup>3+</sup> basis set. The calculations used the dissociation constants of IDSA obtained in our previous experiments under the same conditions [2]. The indium hydrolysis constants obtained in our previous

#### TOLKACHEVA, NIKOL'SKII

I = 0.8	I = 0.6	I = 0.4	I = 0.1	I = 0	b
$15.58\pm0.06$	$15.81\pm0.08$	$15.60\pm0.05$	$16.67\pm0.06$	$19.03\pm0.15$	1.25
$3.36\pm0.07$	$3.35\pm0.10$	$3.31\pm0.06$	$3.32\pm0.10$	$3.55\pm0.07$	0.40
$8.86\pm0.05$	$8.82\pm0.07$	$8.81\pm0.04$	$8.70\pm0.05$	$9.15\pm0.06$	0.77
$15.27\pm0.07$	$15.32\pm0.08$	$15.43\pm0.05$	$16.32\pm0.04$	$18.77\pm0.04$	1.27
$3.80\pm0.09$	$3.74\pm0.09$	$3.71\pm0.06$	$3.72\pm0.06$	$3.91\pm0.06$	0.34
$2.33\pm0.2$	$2.31\pm0.2$	$2.25\pm0.1$	$2.20\pm0.2$	$2.19\pm0.2$	0.17
$8.32\pm0.08$	$8.24\pm0.08$	$8.07\pm0.05$	$7.91\pm0.04$	$8.05\pm0.04$	0.83
	$I = 0.8$ $15.58 \pm 0.06$ $3.36 \pm 0.07$ $8.86 \pm 0.05$ $15.27 \pm 0.07$ $3.80 \pm 0.09$ $2.33 \pm 0.2$ $8.32 \pm 0.08$	$I = 0.8$ $I = 0.6$ $15.58 \pm 0.06$ $15.81 \pm 0.08$ $3.36 \pm 0.07$ $3.35 \pm 0.10$ $8.86 \pm 0.05$ $8.82 \pm 0.07$ $15.27 \pm 0.07$ $15.32 \pm 0.08$ $3.80 \pm 0.09$ $3.74 \pm 0.09$ $2.33 \pm 0.2$ $2.31 \pm 0.2$ $8.32 \pm 0.08$ $8.24 \pm 0.08$	$I = 0.8$ $I = 0.6$ $I = 0.4$ $15.58 \pm 0.06$ $15.81 \pm 0.08$ $15.60 \pm 0.05$ $3.36 \pm 0.07$ $3.35 \pm 0.10$ $3.31 \pm 0.06$ $8.86 \pm 0.05$ $8.82 \pm 0.07$ $8.81 \pm 0.04$ $15.27 \pm 0.07$ $15.32 \pm 0.08$ $15.43 \pm 0.05$ $3.80 \pm 0.09$ $3.74 \pm 0.09$ $3.71 \pm 0.06$ $2.33 \pm 0.2$ $2.31 \pm 0.2$ $2.25 \pm 0.1$ $8.32 \pm 0.08$ $8.24 \pm 0.08$ $8.07 \pm 0.05$	$I = 0.8$ $I = 0.6$ $I = 0.4$ $I = 0.1$ $15.58 \pm 0.06$ $15.81 \pm 0.08$ $15.60 \pm 0.05$ $16.67 \pm 0.06$ $3.36 \pm 0.07$ $3.35 \pm 0.10$ $3.31 \pm 0.06$ $3.32 \pm 0.10$ $8.86 \pm 0.05$ $8.82 \pm 0.07$ $8.81 \pm 0.04$ $8.70 \pm 0.05$ $15.27 \pm 0.07$ $15.32 \pm 0.08$ $15.43 \pm 0.05$ $16.32 \pm 0.04$ $3.80 \pm 0.09$ $3.74 \pm 0.09$ $3.71 \pm 0.06$ $3.72 \pm 0.06$ $2.33 \pm 0.2$ $2.31 \pm 0.2$ $2.25 \pm 0.1$ $2.20 \pm 0.2$ $8.32 \pm 0.08$ $8.24 \pm 0.08$ $8.07 \pm 0.05$ $7.91 \pm 0.04$	$I = 0.8$ $I = 0.6$ $I = 0.4$ $I = 0.1$ $I = 0$ $15.58 \pm 0.06$ $15.81 \pm 0.08$ $15.60 \pm 0.05$ $16.67 \pm 0.06$ $19.03 \pm 0.15$ $3.36 \pm 0.07$ $3.35 \pm 0.10$ $3.31 \pm 0.06$ $3.32 \pm 0.10$ $3.55 \pm 0.07$ $8.86 \pm 0.05$ $8.82 \pm 0.07$ $8.81 \pm 0.04$ $8.70 \pm 0.05$ $9.15 \pm 0.06$ $15.27 \pm 0.07$ $15.32 \pm 0.08$ $15.43 \pm 0.05$ $16.32 \pm 0.04$ $18.77 \pm 0.04$ $3.80 \pm 0.09$ $3.74 \pm 0.09$ $3.71 \pm 0.06$ $3.72 \pm 0.06$ $3.91 \pm 0.06$ $2.33 \pm 0.2$ $2.31 \pm 0.2$ $2.25 \pm 0.1$ $2.20 \pm 0.2$ $2.19 \pm 0.2$ $8.32 \pm 0.08$ $8.24 \pm 0.08$ $8.07 \pm 0.05$ $7.91 \pm 0.04$ $8.05 \pm 0.04$

Logarithms of the complexation constants  $\log\beta$  in M–IDSA–H<sub>2</sub>O systems, M = Ga<sup>3+</sup> and In<sup>3+</sup> (KNO<sub>3</sub> medium, T = 298 K)

study and used for calculations and the corresponding calculation procedure are given in [8].

The gallium hydrolysis constants calculated by a similar procedure are in good agreement with the literature data [7].

At high pH, the increased degree of metal hydrolysis in complexonates leads to a complete decomposition of the complexes accompanied by the separation of a solid phase. Since the thermodynamic model was constructed only for homogeneous systems, the stability of the complexes could not be evaluated over the whole range of pH values because the system's homogeneity was broken. In this case, calculation was performed only at those pH values at which the solutions remained homogeneous. Thus opalescence, which suggests the formation of a solid in solution, was observed at pH > 9.5 for gallium(III) complexonate and at pH > 8.0 for indium(III) complexonate.



**Fig. 2.** Concentration diagram of the distribution of significant complex forms in the Ga<sup>3+</sup>–IDSA system;  $c_{\rm L} = c_{\rm M} = 0.001$  M; I = 0.1; T = 298 K; KNO<sub>3</sub> medium.

The thermodynamic constants of complexation were determined by the equation with one individual parameter:

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

where  $\beta_c$  and  $\beta_0$  are the concentration and thermodynamic stability constants, respectively;  $\Delta Z^2$  is the difference between the squared charges of the reaction products and the starting species;  $A_{\gamma}$  is the constant of the Debye limiting law, which is 0.5108 [10] at 298.2 K; *I* is the ionic strength of the solution; and *b* is the empirical coefficient. The results are presented in the table (*I* = 0). The obtained thermodynamic stability constants can be used for reliable interpretation of calorimetric data for complexations involving iminodisuccinic acid.

On the basis of these data we constructed the diagrams of the concentration distribution of various



**Fig. 3.** Concentration diagram of the distribution of significant complex forms in the In<sup>3+</sup>–IDSA system;  $c_{\rm L} = c_{\rm M} = 0.001$  M; I = 0.1; T = 298 K; KNO<sub>3</sub> medium.

complex forms formed by the metal ions with IDSA at different pH values. The diagrams are shown in Figs. 2 and 3. The pH range in which the neutral indium and gallium complexes of IDSA exist is shifted to the acid region and amounts to two pH units, which is considerably smaller than the same range for Group II cations. The discovered neutral indium and gallium complexes are highly stable.

A comparison of the stability of the neutral complexes of the metals under study with that of the neutral aluminum complex ( $\log \beta_0 = 16.48$  [2]) showed that the former was ~2.5 orders of magnitude higher. This suggests that the bond of Ga<sup>3+</sup> and In<sup>3+</sup> with the complexon atoms capable of polarization is more covalent than the chemical bond of Al<sup>3+</sup> with the same atoms of IDSA. This behavior of gallium and indium is explained by the presence of a bulky 18-electron shell under their valence electron shell ( $ns^2np^1$ ); this shell imparts specific polarization properties to these metals, namely, easy deformability and aptitude toward additional polarization.

We can thus assume that the stability of the complexes increases with the covalent component of the  $M^{3+}$ -ligand bond. The approximately equal log $\beta$  values for Ga<sup>3+</sup> and In<sup>3+</sup> complexes with IDSA can be explained by the structural match between the central ions and the ligand. The most stable complexes are fluoride complexes for gallium with its relatively small ionic radius and chloride and bromide complexes for indium and thallium, which have large ionic radii. The gallium ion with its relatively small ionic radius is likely to form more stable complexes with the small IDSA ligand than the indium ion, whose ionic radius is larger. For EDTA with its large molecule and more mobile skeleton, this anomaly is not observed, the stability of neutral complexes steadily increasing from alumi-

num to indium:  $log\beta_{AlL}~(16.3)$  <  $log\beta_{GaL}~(20.3)$  <

 $\log \beta_{InL}$  (25.0) at I = 0.1 and 20°C [4].

Since IDSA remains a tetradentate (but never pentadentate) ligand in most of its complexes, we can assume that with Subgroup IIIA elements, this complexon is also tetradentate, forming two five-membered glycine rings and one six-membered alanine ring.

The protonated complexes are clear-cut acids. They are much less stable than neutral complexes, and the values change symbatically. The protonation of  $M^{3+}$  complexonates is probably accompanied by a decrease in ligand dentation by analogy with the  $Ga^{3+}$ -EDTA complex [11]. This study showed that the protonated acetate branch was not involved in complexation and its site in the octahedron around gallium(III) was occupied by the water molecule.

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