The Difference of the Complex Formation of the Samarium (3+) Ion with the L-malic Acid as Compared to the Neodymium (3+) Ion

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Abstract
The complex formation of the neodymium Nd\(^{3+}\) ion and the samarium Sm\(^{3+}\) ion with L-malic acid (H\(_3\)Mal) in the aqueous solutions was studied by pH-metric titration in pH region 2.80 to 10.00 and constant ionic strength 0.1 M KCl at 25°C. The ratios of the concentrations of the rare-earth elements (Ln) and the L-malic acid were 1:0.5, 1:1 and 1:2. The number of experimental points of each curve of pH-metric titration was 160-190 at 5-6 independent titrations. Inasmuch as the literature data give mainly the dissociation constants for the racemic DL-malic acid, acid-base equilibria of L-malic acid at ionic strength of 0.1 M KCl were also previously studied in pH 3.1-11.0 range. The number of experimental points for the each titration curve of L-malic acid was 70-100 at 8 independent titrations. The dissociation constants of L-malic acid were calculated.

The compositions and the stability constants of the rare-earth element complexes with L-malic acid were calculated by SuperQuad program for complex equilibria. It was shown, that in addition to 1:1 and 1:2 complexes with differently deprotonated L-malic acid, the hydroxocomplexes and protonated complexes of the rare-earth elements are also formed. The difference of the complex formation of the Sm\(^{3+}\) ion with L-malic acid as compared to the Nd\(^{3+}\) ion was discussed.

Introduction
The malic acid is believed to be one of the best selective reagents for the industrial separation of the rare-earth elements and the transuranium elements [1] by the ion-exchange chromatography method [2].

The complex formation of the Nd\(^{3+}\) ion and the Sm\(^{3+}\) ion with the malic acid was studied by potentiometric methods [3-11] and spectroscopy method [12]. At low pH values the LnH\(_2\)Mal\(^{2+}\), LnHM\(_2\)Al\(^{+}\) and Ln(HM)\(_2\)\(^{-}\) complex only were found [5]. Patnaik et al. [7] reported that in the Ln–H\(_2\)Mal system the complexes of 1:1 and 1:2 compositions are formed at pH < 7, whereas at pH > 7 the formation of polynuclear complexes with the coordination of the oxy-group of the malic acid is observed. Yatsimirsky et al. [4] assumed the existence of Ln\(_2\)(HM)\(_2\)\(^{3+}\), Ln(Mal)\(_2\)\(^{5}\) and LnMal\(^{5}\) complexes in the aqueous solutions. The isolation of [Ln(H\(_2\)Mal)(HM)\(_2\)]\(^{3+}\) and Ln\(_2\)(HM)\(_2\)\(^{5}\) complexes in the solid state was also reported by Patnaik et al. [7]. It should be noted that the complex formation with the racemic DL-malic acid was studied in most cases.

Thus, the complex formation of the Sm\(^{3+}\) ion and the Nd\(^{3+}\) ion with the malic acid in the aqueous solutions at low pH values is rather well studied, though the data on the composition and the stability constants of the complexes with malic acid formed in this pH range are contradictory (Table 1) and are not critically estimated. Table 1 data show the considerable dispersion of stability constant values. So there is the difference in 1.0–1.2 lgK unit for 1:1 complexes and more than 2.5 lgK unit for 1:2 complexes. It should be noted that the most part of presented stability constant values (Table 1) are critically selected IUPAC SC-Database data [14].

In the case of even the simplest malate complexes LnHM\(_2\)\(^{+}\) and Ln(HM)\(_2\)\(^{3+}\) the considerable differences of stability constant values take place. The cause of that is a priori models of complex formation without statistic model assessment. For example, the results of the investigation [5] are significant in this sense. There are some inevitable contradictions in it though the authors used the method of math-
Complexing of Sm$^{3+}$ and Nd$^{3+}$ with L-malic Acid

For example at the concentration ratio $C(\text{Ln(NO}_3)_3):C(\text{H}_3\text{Mal}) = 1:1$ authors do not even take into account the formation of $\text{Ln(HMal)}_2^-$ complexes whereas the modeling of equilibrium composition in the $\text{Ln(NO}_3)_3$,$\text{H}_3\text{Mal}$ system with malate stability constants of Sm$^{3+}$ and Nd$^{3+}$, dissociation constants of malic acid of present article and $pK_w$ value shows that the fraction of the accumulation of $\text{Ln(HMal)}_2^-$ complexes is up to 8%. At the other concentration ratios $C(\text{Ln(NO}_3)_3):C(\text{H}_3\text{Mal})$ the stability constants values are also contradictory. The uncoordinated scheme of equilibrium of complex formation appears to be used by authors [5].

Up to now, the stoichiometry and the stability constants of the complexes of the Nd$^{3+}$ ion and the Sm$^{3+}$ ion with the malic acid formed at pH $\geq 7$ have not been definitely determined.

In this work the results of a study of the complex formation of the complexes of the Nd$^{3+}$ ion and Sm$^{3+}$ ion with the L-malic acid by pH-metric titration and mathematical modeling of complex equilibrium in solutions [15] are presented.

### Experimental

Chemically pure L-malic acid, chemically pure NdCl$_3$, SmCl$_3$, chemically pure carbonate-free KOH, chemically pure KCl, and high-purity grade HCl were used. The Ln$^{3+}$ content was determined by complexometric titration with EDTA, and xylene orange as the indicator [16]. A CO$_2$ free solution of 0.0275 M KOH solution was used as a titrant. The concentration of the titrant was determined by potentiometric titration with 0.1 M HCl solution. The L-malic acid were prepared by the weighting means and then the concentration was precisely by pH-metric titration method from equivalent points. Taking into account the low complex ability of the metals of the cerium subgroup of rare-earth elements with chloride ions [17], KCl was used as a background electrolyte.

The L-malic acid concentration employed was $10^{-3}$ mol×dm$^{-3}$. Solutions containing rare-earth ions and L-malic acid were titrated in metal:ligand ratios 1:0.5, 1:1 and 1:2.

PH-metric titration was carried out in an isolated thermostatically controlled (25±0.1)$^\circ$C 40-ml cell at a variable volume and constant ionic strength (0.1 M KCl). The measurements were carried out on a Beckman digital pH-meter, Model 4500, using a glass-electrode combination Volta-pH-3002 (Saint-Petersburg, Saint-Petersburg State University). The estimated accuracy of titration system was ±0.2 mV and ±0.005 cm$^3$ for e.m.f. and titrant volume readings, respectively. The certain amount of titrant was added and the equilibrium potential values were measured while the e.m.f. was stable within 0.2 mV for 3 min. During the titration in titration cell, pure nitrogen was bubbled in order to avoid O$_2$ and CO$_2$ inside, and the solutions were magnetically stirred.

The electrode was calibrated by a titration of strong acid with strong base as a source of solutions with known hydrogen ion concentration [18-19]. GLEE computer program for glass electrode calibration [20] was used.

The initial volume of the solutions titrated was 25.00 ml. All solutions were prepared in deionized water (8 MΩ).

### Table 1

| Reference | Background | T, °C | NdH$_3$Mal$^{2-}$ | NdHMal$^-$ | Nd(HMal)$_2^-$ | SmH$_3$Mal$^{2-}$ | SmHMal$^-$ | Sm(HMal)$_2^-$ |
|-----------|------------|-------|------------------|-------------|----------------|-----------------|-------------|----------------|
| [3]       | 0.2 M KCl  | 25    | -                | 4.45        | 8.23           | -               | 4.42        | 8.29           |
| [5]       | 0.1 M KNO$_3$ | 20    | 2.09             | 4.59        | 7.20           | 2.23           | 4.76        | 7.82           |
| [6]       | 0.2 M NaClO$_4$ | 25    | -                | 4.45        | -              | -              | 4.50        | -              |
| [9]       | 0.1 M NaClO$_4$ | 25    | -                | 4.77        | 7.94           | -              | 4.89        | 8.16           |
| [10]      | 0.1 M KCl   | 20    | -                | 4.65        | 7.17           | -              | -           | -              |
| [11]      | 0.1 M KCl   | 30    | -                | 5.12        | 8.76           | -              | 5.42        | 10.00          |
| [12]      | 0.2 M NaClO$_4$ | 25    | -                | 5.66        | 11.02          | -              | -           | -              |
| [13]      | 0.1 M NaClO$_4$ | 25    | -                | 4.77        | 7.94           | -              | 4.90        | 8.20           |
Results and Discussion

The pH-metric titration data (Fig. 1) were used for the calculations of the formation functions $Z_{ii+}$ [21], the protonation constants of ligand $K_{\alpha i}$ and the stability constants of the malate complex species $K$. The pH-metric titration data were treated by the calculation procedure described in work [15], taking into account the recommendations given in works [21-22]. The complex formation parameters were calculated using the SuperQuad program [23].

So as the literature data give mainly the dissociation constants for the racemic DL-malic acid, acid-base equilibria of L-malic acid at ionic strength of 0.1 M KCl were previously studied in pH 3.1-11.0 range. The number of experimental points for each titration curve of L-malic acid (Fig. 1) was 70 - 100 at 8 independent titrations. The calculated dissociation constants of L-malic acid given in Table 2 can be compared with the literature data displayed in the same table. It is not amazing that there is a difference between dissociation constants of L-malic acid we have calculated and the literature data, because in various works the form of the L-malic acid under study is not specified. Besides, the $pK_{\alpha}$ value used for the calculation of the protonation constants was not indicated. The obtained dissociation constants of L-malic acid were used in further calculations of the stability constants of the complexes.

It should be noted that there are significantly different literature data on the dissociation constant $pK_{\alpha3}$ of the L-malic acid hydroxyl group. In the investigation [26] 11.55 (0.1 M KNO₃, 293 K) value was used whereas Khalil et al. [27] used $pK_{\alpha3}$ value 15.46 (0.5 M NaNO₃, 298 K). These $pK_{\alpha3}$ values significantly differ from the one 14.3 [28] used in series of works described in monograph [15]. Therefore we carried out the additional experimental series of pH – titration up to pH 12.5–12.6. Our calculated $pK_{\alpha3}$ value was $12.34 \pm 0.15$.

Since the formation of the $\alpha$-hydroxy-carboxylate chelate cycle is proved at the complex formation of the rare-earth elements with the L-malic acid at neutral region of pH [15], this may be an evidence in support of the lesser $pK_{\alpha3}$ value in comparison with the $pK_w$ value. The $pK_w$ value 13.78 was used [29].

The results of the titration of the rare-earth element – L-malic acid systems at 1:0.5, 1:1 and 1:2 molar ratios and ionic strength of 0.1 M KCl are given in Fig. 1. The ligand concentration was varied so as to determine complex species with different ligand and metal ion content.

The number of experimental points of the each curve of pH-metric titration (Figure 1) was 160-190 at concentration ratio C(LnCl₃):C(H₃Mal) =1:0.5, 1:1 and 1:2 for 5-6 independent titrations in the pH range 2.8-10.0. At pH $> 8.5$ the formation of a precipitate was observed.

The initial model for each system was as in the works [15,30]. Salnikov et al. have investigated the complex formation of DL-malic acid with heavy rare-earth metal by pH-metric titration and proton spin-lattice relaxation methods. We have investigated the possible formation of the species ML, ML₂ and ML₃, the protonated and the hydrolysed species. The protonated species MH₂L and M(H₂L)₂ were introduced in our model because these species were observed that the titration curves had initial values of pH higher than expected. Assuming that hydrolysis begins with the loss of protons from water molecules coordinated to the complex and that it is followed by dimerization and subsequent polymerization, then it is obvious that this process involves a complex equilibrium [21]. On the other hand, it was of interest to evaluate

![Fig. 1. The pH-metric titration data: A – H₃Mal, B – NdCl₃-H₃Mal (1:0.5), C – NdCl₃-H₃Mal (1:1), D – NdCl₃-H₃Mal (1:2).](image_url)
the pH range where hydrolysis process initiated. Thus, using only the part of the titration curves (1:0.5 and 1:1 metal:ligans ratios) where it was began the hydrolysis, it was possible to set up a model with the simplest hydrolysed species: MLOH, ML(OH)₂, M₂L₂(OH) and MOH, M₂(OH)₂, M(OH)₃, and M(OH)₄.

The results of pH-metric titration were recounted by equation (1) in order to obtain the functional dependence of $Z_{Hi}$ vs. pH (Fig. 2). The $Z_{Hi}$ function is a formation function since it reflects the contribution of each complex species to the change of pH [21]. Thus

$$Z_{Hi} = \frac{10^{-\rho pH} (V_{H_{3}Mal} + V_{OH}) + C_{OH} \cdot V_{OH} - 10^{(pH-pKw)} (V_{H_{3}Mal} + V_{OH})}{C_{H_{3}Mal} \cdot (V_{H_{3}Mal} + V_{OH})}$$

where C(OH) is a concentration of titrant, C(H₃Mal) is a concentration of L-malic acid, V(OH) is a volume of titrant, V(H₃Mal) is an initial volume of acid.

Comparison of the results of pH-metric titration of free acid and in the presence of rare-earth elements shows that the complex formation starts at pH < 2.5. In the presence of the rare-earth elements the formation function $Z_{Hi}$ reaches the value of 1.5 at pH > 3.5, which points to the formation of complex species containing an $\alpha$-hydroxycarboxylate chelate ring according to the data of work [15]. Further abrupt increase of $Z_{Hi}$ to 2.5 at pH > 7.5 testifies to the formation of complexes with the probable compositions LnMal$^+$ and Ln₂(HMal)Mal. At concentration ratio C(LnCl₃):C(H₃Mal) = 1:0.5 the $Z_{Hi}$ value is > 4.0, which may be an evidence of the formation of hydroxocomplexes.

The pH-metric titration data were treated using the SuperQuad program, which is successfully used for the treatment of the pH-metric titration data [23]. The recommendations given in work [21] were used during the development of models of complex formation and their validation for adequacy.

The formation of complexes in the studied system was considered according to the general equilibrium:

$$pLn^{3+} + qH_{3}Mal = Ln_{q}H_{3p-r}Mal_{r}^{3p-r+} + rH^{+}$$

with equilibrium constant

$$K = \frac{[Ln_{q}H_{3p-r}Mal_{r}^{3p-r+}] \times [H^{+}]^{q}}{[Ln^{3+}]^{p} \times [H_{3}Mal]^{q}}$$

Calculated stability constants corresponding general equilibrium (2) were recounted to form presented in Table 3. Stability constant expressions presented in Table 3 do not include the acid-base equilibrium constants of ligand and water. It is possible to compare our data to the data of other authors (Table 1).

Table 3 shows that, in addition to protonated and deprotonated complexes of compositions 1:1 Ln(H₂Mal)$^{2+}$, Ln(HMal)$^{3+}$ and 1:2 Ln(H₂Mal)$^{3+}$, Ln(HMal)$^{5+}$ and hydroxocomplexes LnMalOH$^{-}$ and Ln(Mal)$₂$OH$^{4-}$ are also formed.

It should be noted that there is a significant amount of hydroxocomplexes of the rare-earth elements along with hydroxomalates. Calculated stability constants of hydroxocomplexes are satisfactorily agreed with data [31-33]. Binuclear complexes with various stoichiometry to a considerable amounts are not detected by us. Calculated stability constants of L-malate complexes are satisfactorily agreed with data [3,5,6,8,9-13]. In works [10-11] calculated stability constants of mononial complexes were probably overestimated because of the neglect of protonated complexes. And it is possible to explain the understated stability constants of dimalate complexes [3,5,6,8,9,12,13] by use both of the uncoordinated scheme of equilibrium and the neglect of protonated complexes and hydroxocomplexes.
The formed complexes of the Sm$^{3+}$ ion with L-malic acid are more stable as compared to that of the Nd$^{3+}$ ion. This fact can be explained by strengthening of the spin-orbital coupling and a decrease of the ionic radii in this series of rare-earth elements [1,34-35].

The distribution of complex species formed in the L-malic acid-SmCl$_3$ system and the L-malic acid-NdCl$_3$ system depending on pH is given in Fig. 3 a,b and Fig. 4 a,b. Hyperquad simulation and speciation (HySS) program was used [36]. The presented distribution diagrams testify to the formation of a significant amount of hydroxomalate and protonated complex species, which were ignored in previous works [3-7].

A great variety of complexes of the Nd$^{3+}$ and Sm$^{3+}$ ions with L-malic acid as compared to gadolinium should be noted. Complex formation of gadolinium with DL-malic acid was studied in detail in work [30] by pH-metric and proton magnetic relaxation methods. This fact appears to be explained by a greater coordination number and radii of the aqua ion of the cerium subgroup of rare-earth element ions (coordin-
Complexing of Sm\textsuperscript{3+} and Nd\textsuperscript{3+} with L-malic Acid

Conclusions

Thus the investigation we have carried out shows that not only 1:1 and 1:2 complexes are formed in the L-malic acid and the rare-earth elements of cerium subgroup (Nd, Sm) systems under study as described in literature, but also protonated and hydroxocomplexes, which should be taken into account when described equilibria with the participation of L-malic acid and ions of Sm\textsuperscript{3+} and Nd\textsuperscript{3+}.

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Fig. 4a. Distribution of complex species in the SmCl\textsubscript{3}-L-malic acid system (1:2) depending on pH.

Fig. 4b. Distribution of complex species in the NdCl\textsubscript{3}-L-malic acid system (1:2) depending on pH.

A difference of the coordination ability of the Sm\textsuperscript{3+} ion from that of Nd\textsuperscript{3+} ion can be explained by the above reasons, because for the Sm\textsuperscript{3+} aqua ion in aqueous solutions an intermediate coordination number 8.50±0.04 was established by the X-ray and neutron diffraction methods, and luminescent spectrophotometry as well [37-40]. This coordination number shows the equilibrium between eight or nine coordination aqua ions. Consequently, the existence of two coordination polyhedron Sm(H\textsubscript{2}O)\textsubscript{9}\textsuperscript{3+} and Sm(H\textsubscript{2}O)\textsubscript{8}\textsuperscript{3+} is the cause of a greater variety of the composition of complexes of the Sm\textsuperscript{3+} ion as compared to the aqua ion with the constant coordination number.
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