



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

Vladimir Yu. Buzko, Igor V. Sukhno*, Margarita B. Gavriluyk and Victor T. Panyushkin

Department of General and Inorganic Chemistry, Kuban State University,
Krasnodar 350040, Stavropolskaya Street 149, Russia

Abstract

The complex formation of the neodymium Nd^{3+} ion and the samarium Sm^{3+} ion with L-malic acid (H_3Mal) 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 $\text{LnH}_2\text{Mal}^{2+}$, LnHMal^+ and $\text{Ln}(\text{HMal})_2^-$ complexes only were found [5]. Patnaik *et al.* [7] reported that in the Ln- H_3Mal system the complexes of 1:1 and 1:2 compositions are formed at $\text{pH} < 7$, whereas at $\text{pH} > 7$ 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 $\text{Ln}_2(\text{HMal})_3^0$, $\text{Ln}(\text{Mal})_2^{3-}$ and LnMal^0 complexes in the aqueous solutions. The isolation of $[\text{Ln}(\text{H}_2\text{Mal})(\text{HMal})]^0$ and $\text{Ln}_2(\text{HMal})_3^0$ complexes in the solid state was also reported by Patnaik *et al.* [7]. It should be noted that the complex forma-

*corresponding author. E-mail: Sukhno@chem.kubsu.ru

tion 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 $\lg K$ unit for 1:1 complexes and more than 2.5 $\lg K$ 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 LnHMal^+ and $\text{Ln}(\text{HMal})_2^-$ 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-

Table 1
Logarithms of apparent stability constants of malate complexes of Sm³⁺ and Nd³⁺ ions

Reference	Background	T, °C	NdH ₂ Mal ²⁺	NdHMal ⁺	Nd(HMal) ₂ ⁻	SmH ₂ 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

emational modeling. For example at the concentration ratio C(Ln(NO₃)₃):C(H₃Mal) = 1:1 authors do not even take into account the formation of Ln(HMal)₂⁻ complexes whereas the modeling of equilibrium composition in the Ln(NO₃)₃-H₃Mal system with malate stability constants of Sm³⁺ and Nd³⁺, dissociation constants of malic acid of present article and *pK_w* value shows that the fraction of the accumulation of Ln(HMal)₂⁻ complexes is up to 8%. At the other concentration ratios C(Ln(NO₃)₃):C(H₃Mal) 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 Nd³⁺ ion and the Sm³⁺ ion with the malic acid formed at pH ≥ 7 have not been definitely determined.

In this work the results of a study of the complex formation of the complexes of the Nd³⁺ ion and Sm³⁺ 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 NdCl₃, SmCl₃, chemically pure carbonate-free KOH, chemically pure KCl, and high-purity grade HCl were used. The Ln³⁺ content was determined by complexometric titration with EDTA, and xylenol orange as the indicator [16]. A CO₂ 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 solutions of

the L-malic acid were prepared by the weighting means and then the concentration was précised 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)°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 cm³ for e.m.f. and titrant volume reading, 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 O₂ and CO₂ 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).

Results and Discussion

The pH-metric titration data (Fig. 1) were used for the calculations of the formation functions Z_{H^+} [21], the protonation constants of ligand K_{oi} 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].

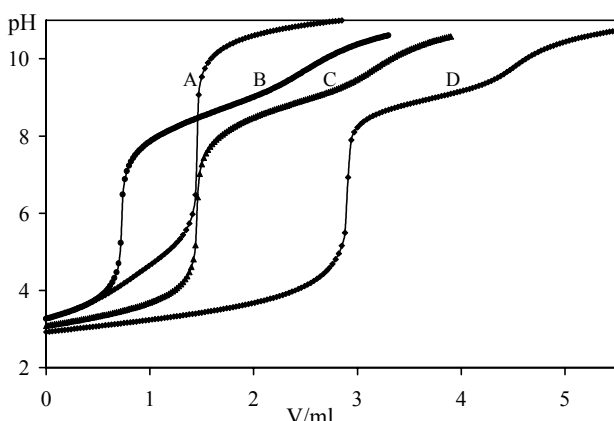


Fig. 1. The pH-metric titration data: A – H_3Mal , B – $NdCl_3-H_3Mal$ (1:0.5), C – $NdCl_3-H_3Mal$ (1:1), D – $NdCl_3-H_3Mal$ (1:2).

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 the 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_w 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 $pK_{\alpha 3}$ of the L-malic acid hydroxyl group. In the investigation [26] 11.55 (0.1 M KNO_3 , 293 K) value was used whereas Khalil *et al.* [27] used $pK_{\alpha 3}$ value 15.46 (0.5

Table 2

The apparent dissociation constants of malic acid at 25°C

$pK_{\alpha 1}$	3.24	$3.26 \pm 0.01^{(a)}$	3.26	3.22	3.26
$pK_{\alpha 2}$	4.68	$4.78 \pm 0.01^{(a)}$	4.68	4.72	4.71
Ionic strength	0.1 (KCl)	0.1 (KCl)	0.2 (KCl)	0.1 (KNO_3)	0.1 (KNO_3)
Reference	[24]		[3]	[25]	[5]

^(a) The apparent dissociation constants of L-malic acid were calculated in present work.

M $NaNO_3$, 298 K). These $pK_{\alpha 3}$ 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 $pK_{\alpha 3}$ value was 12.34 ± 0.15 .

Since the formation of the α -hydroxycarboxylate 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 $pK_{\alpha 3}$ 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 $C(LnCl_3):C(H_3Mal)=1:0.5, 1:1$ 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, ML_2 and ML_3 , the protonated and the hydrolysed species. The protonated species MH_2L and $M(H_2L)_2$ 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

the pH range where hydrolysis process initiated. Thus, using only the part of the titration curves (1:0.5 and 1:1 metal:ligands ratios) where it was began the hydrolysis, it was possible to set up a model with the simplest hydrolysed species: M(OH) , ML(OH)_2 , $\text{M}_2\text{L}_2(\text{OH})$ and MOH , $\text{M}_2(\text{OH})_2$, M(OH)_2 and M(OH)_3 .

The results of pH-metric titration were recounted

$$Z_{H^+} = \frac{10^{-pH} (V_{H_3Mal} + V_{OH}) + C_{OH} \cdot V_{OH} - 10^{(pH-pK_w)} (V_{H_3Mal} + V_{OH})}{C_{H_3Mal} \cdot (V_{H_3Mal} + V_{OH})} \quad (1)$$

where $C(\text{OH})$ is a concentration of titrant, $C(\text{H}_3\text{Mal})$ is a concentration of L-malic acid, $V(\text{OH})$ is a volume of titrant, $V(\text{H}_3\text{Mal})$ 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 $\text{pH} < 2.5$. In the presence of the rare-earth elements the formation function Z_{H^+} reaches the value of 1.5 at $\text{pH} > 3.5$, which points to the formation of complex species containing an α -hydroxycarboxylate chelate ring according to the data of work [15]. Further abrupt increase of Z_{H^+} to 2.5 at $\text{pH} > 7.5$ testifies to the formation of complexes with the probable compositions LnMal^0 and $\text{Ln}_2(\text{HMal})\text{Mal}$. At concentration ratio $C(\text{LnCl}_3):C(\text{H}_3\text{Mal}) = 1:0.5$ the Z_{H^+} 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.

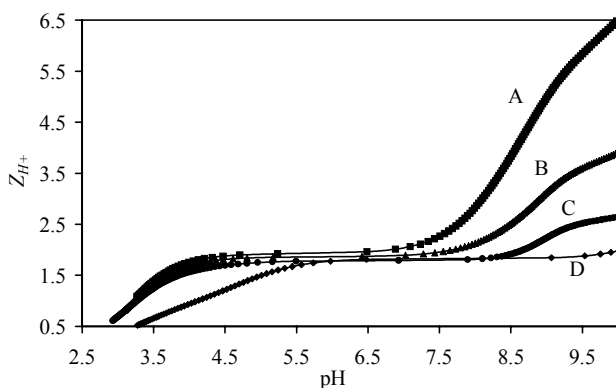
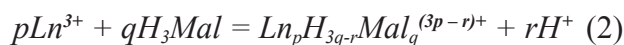


Fig. 2. Formation functions: A – $\text{NdCl}_3\text{-H}_3\text{Mal}$ (1:0.5), B – $\text{NdCl}_3\text{-H}_3\text{Mal}$ (1:1), C – $\text{NdCl}_3\text{-H}_3\text{Mal}$ (1:2), D – H_3Mal .

by equation (1) in order to obtain the functional dependence of Z_{H^+} vs. pH (Fig. 2). The Z_{H^+} are the average degrees of ligand titrate. The Z_{H^+} function is a formation function since it reflects the contribution of each complex species to the change of pH [21]. Thus $Z_{H^+} = \sum \alpha_i Z_{(H^+)_i}$, when α_i - equilibrium concentration of i - complex species

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



with equilibrium constant

$$K = \frac{[\text{Ln}_p\text{H}_{3q-r}\text{Mal}_q^{(3p-r)+}] \times [\text{H}^+]^r}{[\text{Ln}^{3+}]^p \times [\text{H}_3\text{Mal}]^q} \quad (3)$$

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 $\text{Ln}(\text{H}_2\text{Mal})^{2+}$, $\text{Ln}(\text{HMal})^+$ and 1:2 $\text{Ln}(\text{H}_2\text{Mal})_2^+$, $\text{Ln}(\text{HMal})_2^-$ and hydroxocomplexes LnMalOH^- and $\text{Ln}(\text{Mal})_2\text{OH}^{4-}$ 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 monomalate 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.

Table 3
The apparent stability constants of L-malate complexes of Sm³⁺ and Nd³⁺ ions (0.1 M KCl, 25±0.1°C)

Coefficients of equation (2)			Expression for K	lgK	
q	p	r		Nd ⁽³⁺⁾	Sm ⁽³⁺⁾
1	1	1	$[\text{LnH}_2\text{Mal}^{2+}][\text{Ln}^{3+}]^{-1}[\text{H}_2\text{Mal}^-]^{-1}$	2.40 ± 0.03	2.90 ± 0.04
1	1	2	$[\text{LnHMal}^+][\text{Ln}^{3+}]^{-1}[\text{HMal}^{2-}]^{-1}$	4.60 ± 0.02	4.95 ± 0.02
1	1	3	$[\text{LnMal}][\text{Ln}^{3+}]^{-1}[\text{Mal}^{3-}]^{-1}$	< 7.5 ^(a)	8.28 ± 0.15
1	1	4	$[\text{LnMal}(\text{OH})][\text{Ln}^{3+}]^{-1}[\text{Mal}^{3-}]^{-1}[\text{OH}^-]^{-1}$	13.24 ^(b) ± 0.05	13.78 ^(b) ± 0.05
2	1	2	$[\text{Ln}(\text{H}_2\text{Mal})_2^+][\text{Ln}^{3+}]^{-1}[\text{H}_2\text{Mal}^-]^{-2}$	5.10 ± 0.07	5.33 ± 0.06
2	1	4	$[\text{Ln}(\text{HMal})_2][\text{Ln}^{3+}]^{-1}[\text{HMal}^{2-}]^{-2}$	9.16 ± 0.03	9.62 ± 0.03
2	1	5	$[\text{Ln}(\text{HMal})\text{Mal}^{2-}][\text{Ln}^{3+}]^{-1}[\text{HMal}^{2-}]^{-1}[\text{Mal}^{3-}]^{-1}$	10.56 ^(c) ± 0.06	11.49 ^(c) ± 0.06
2	1	6	$[\text{Ln}(\text{Mal})_2^{3-}][\text{Ln}^{3+}]^{-1}[\text{Mal}^{3-}]^{-2}$	15.79 ± 0.06	-
2	1	7	$[\text{Ln}(\text{Mal})_2\text{OH}^4][\text{Ln}^{3+}]^{-1}[\text{Mal}^{3-}]^{-2}[\text{OH}^-]^{-1}$	-	20.67 ^(b) ± 0.10
0	1	1	$[\text{LnOH}^{2+}][\text{Ln}^{3+}]^{-1}[\text{OH}^-]^{-1}$	5.76 ± 0.03	5.88 ± 0.03
0	1	2	$[\text{Ln}(\text{OH})_2^+][\text{Ln}^{3+}]^{-1}[\text{OH}^-]^{-2}$	11.09 ± 0.05	11.24 ± 0.05
0	2	2	$[\text{Ln}_2(\text{OH})_2^{4+}][\text{Ln}^{3+}]^{-2}[\text{OH}^-]^{-2}$	13.39 ^(c) ± 0.09	13.68 ^(c) ± 0.08
0	1	3	$[\text{Ln}(\text{OH})_3][\text{Ln}^{3+}]^{-1}[\text{OH}^-]^{-3}$	15.24 ± 0.08	15.86 ± 0.07

^(a) a reliable value of stability constant is not calculated because the fraction of LnMal complex is no more 2%. The approximate limit value is given in the table.

^(b) the species form at pH > 8.5 in the sedimentation region.

^(c) the fraction of species is no more than 3%.

The formed complexes of the Sm³⁺ ion with L-malic acid are more stable as compared to that of the Nd³⁺ 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-SmCl₃ system and the L-malic acid-NdCl₃ 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 Nd³⁺ and Sm³⁺ 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 (coordi-

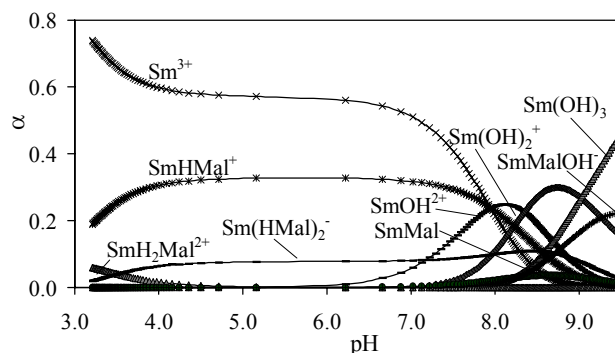


Fig. 3a. Distribution of complex species in the SmCl₃-L-malic acid system (1:0.5) depending on pH.

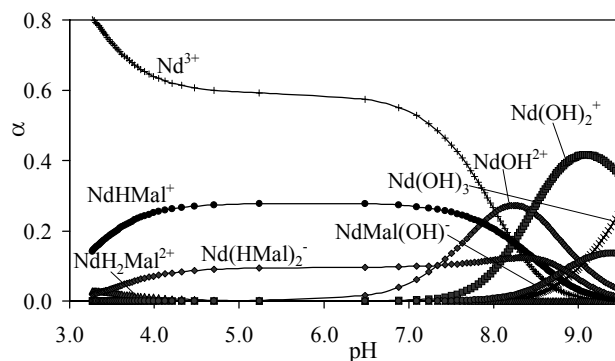


Fig. 3b. Distribution of complex species in the NdCl₃-L-malic acid system (1:0.5) depending on pH.

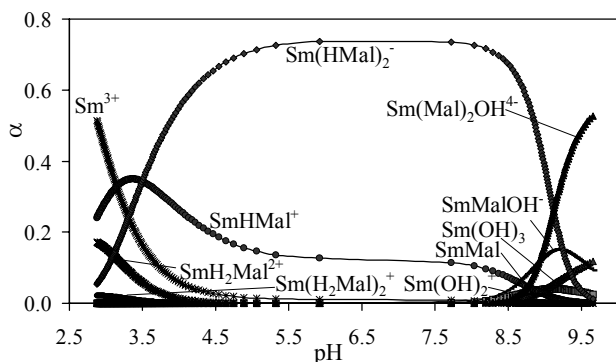


Fig. 4a. Distribution of complex species in the SmCl_3 -L-malic acid system (1:2) depending on pH.

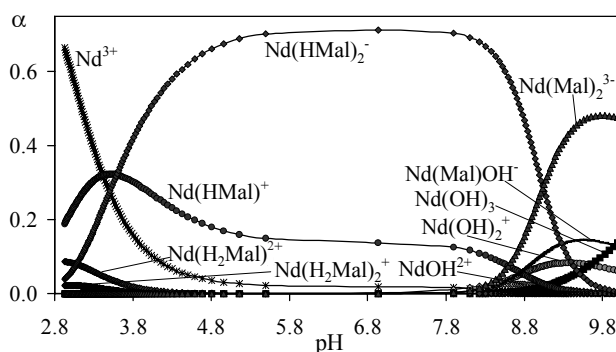


Fig. 4b. Distribution of complex species in the NdCl_3 -L-malic acid system (1:2) depending on pH.

nation number 9) compared with that of gadolinium (coordination number 8) [1,35,37-40], and consequently, by a greater variety of the composition of complexes of rare-earth elements with L-malic acid according to the less tension of the metalcomplex mode.

A difference of the coordination ability of the Sm^{3+} ion from that of Nd^{3+} ion can be explained by the above reasons, because for the Sm^{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 $\text{Sm}(\text{H}_2\text{O})_9^{3+}$ and $\text{Sm}(\text{H}_2\text{O})_8^{3+}$ is the cause of a greater variety of the composition of complexes of the Sm^{3+} ion as compared to the aqua ion with the constant coordination number.

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 ce-

rium 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^{3+} and Nd^{3+} .

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