ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 6, pp. 849–856. © Pleiades Publishing, Inc., 2006.
Original Russian Text © I.V. Sukhno, V.Yu. Buz'ko, V.T. Panyushkin, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 6, pp. 887–894.

Complex Formation in Rare-Earth Metal–Propionic Acid–Diamagnetic Salt Systems by ^{1}H NMR Spectroscopy

I. V. Sukhno, V. Yu. Buz'ko, and V. T. Panyushkin

Kuban State University, 149 ul. Stavropol'skaya, Krasnodar, 350040 Russia
e-mail: Sukhno@chem.kubsu.ru

Received February 25, 2005

Abstract—Complex formation of propionic acid with ions of rare-earth metals of the yttrium subgroup (D_2O, 5.0 M $NaNO_3$) in the absence and presence of diamagnetic Mg^{2+} cations was studied by ^{1}H NMR spectroscopy in combination with mathematic simulation of complicated equilibria. Stability constants for monopropionate complexes of rare-earth ions decrease when the rare-earth cation and Mg^{2+} are present in the system together.

DOI: 10.1134/S1070363206060028

Complex formation of rare-earth metals with monocarboxylic acids have been studied for many years. Recently the interest in lanthanide monocarboxylates has mounted in view of the fact that complexes of rare-earth metals with monocarboxylic acids play a dominant role in geochemical migrations and transformations of rare-earth metals [1–4].

It is assumed that the stoichiometry and types of propionate complexes of rare-earth metals in aqueous solutions are well-understood [5, 6]. At the same time, the stability constants of these complexes, determined by different authors for equal ionic strengths and compositions of background electrolyte, vary essentially. For example, in [7–13], different stability constants the same conditions are given. Several reasons can be responsible for this discrepancy.

First, complex formation models advanced a priory are not subsequently statistically substantiated. For example, Debert et al. [14, 15], in spite of the high accuracy of pH-metry and attempts to make the most account for interparticle interactions, neglected the formation of triacetate complexes of rare-earth metals, even though the ratio of the equilibrium concentrations of acetate and rare-earth metal ions was sometimes no less than 60. Under such conditions the accumulation of triacetate complexes of rare-earth metals can be rather significant and their mole fraction can exceed 60% [16].

Second, the acid dissociation constants of ligands taken for a required ionic strength but determined at a different composition of background electrolyte are often used. For example, Partanen et al. found [17–19] that the dissociation constants of acetic acid, determined for its aqueous solutions with similar background electrolytes (NaCl, KCl, and LiCl), vary considerably at equal ionic strengths.

Third, most authors neglect complex formation with background electrolyte anions, even though the accumulated fraction of such complexes is obviously significant. In this connection illustrative are the results of Wood et al. [20] whose proved that adequate formation functions and thermodynamic stability constants of Nd^{3+} acetate complexes in aqueous solutions of NaCl (0.1 mol kg^{-1}) can only be obtained if the formation of $NdCl^{2+}$ and $NdCl^{2+}$ complexes is taken into account.

Fourth, specific interparticle interactions and effect of ionic strength on the stability constants of complexes are accounted for in terms of different models, namely, those of Pitzer [21], Broensted–Guggenheim–Scatchard [22], Debye–Huckel and Gosh–Bjerrum [23, 24], Bromley [25], and Helgeson [26].

In the last few years, high-resolution NMR spectroscopy on various nuclei [27] has found expanding application as an alternative to the classical potentiometry for determination of ionic equilibrium constants. At the same time, the commonly accepted NMR practice involves a number of serious methodical drawbacks: No information on the effect of ionic strength, composition of electrolyte, internal standards, and contents of uncontrollable amounts D_2O in samples on chemical shifts is available. A variety of experimental conditions, the absence of unified procedures and recommendations not infrequently result in considerable scatter in measured constants. In this connection critical analysis of the modern practice of application of NMR spectroscopy to ionic equilibria, development of an NMR titration method and general recommendations are of doubtless interest. The urgency of this problem has been recognized by IUPAC, under which a special project no. 2001-038-2-500 has been developed [28].

Note that systems containing simultaneously paramagnetic rare-earth metal atoms and diamagnetic salts are topical to study, since magnetic resonance experiments involving simple and complex compounds of rear-earth metals as selective shifting and relaxation reagents are carried out in practice in biological media and aqueous and aqueous-organic solutions in the presence of diamagnetic salts as components of media under study. Furthermore, at present there is no unambiguous theory allowing for predicting the direction and values of changes in magnetic resonance parameters (paramagnetic chemical shift in NMR spectra, relaxation time, and width of ESR lines) in such systems.

Buikliskii et al. found [29, 30] that observable paramagnetic shifts in NMR spectra change with changing concentration of diamagnetic salts (background electrolytes). So far this effect was not explained appropriately though an attempt was undertaken [31, 32] to explain the fact that observable paramagnetic shifts in ^{1}H NMR spectra change with the concentration of diamagnetic salts by changes in the activity coefficients of reacting ions.

Note that thermodynamically most rigorous theories of interparticle interactions of Pitzer, Brønsted–Guggenheim–Scatchard, Bromley, and Helgeson are practically impossible to apply for treatment of ^{1}H NMR data, because the parametric coefficients of the corresponding equations have been tabulated not for all simple ions in aqueous solutions, whereas for solutions in heavy water they are completely absent from the literature. Noteworthy is also the fact that most authors take no account of changes in acid–base equilibria involving ligand when passing from aqueous solutions to solutions in D_2O, though the need in it was repeatedly pointed out [33, 34].

It is also necessary to note that taking account of the influence of ionic strength and composition of background electrolyte on the complex formation constants and magnetic resonance parameters, determined by NMR, makes the greatest difficulty in attempts of adequate application of high-resolution NMR for studying weak complex formation. Background electrolytes with concentrations higher than 2 M are scarcely used in potentiometry or spectrophotometry and are commonly used in high-resolution NMR.

We have studied rare-earth metal chloride–propionic acid–$MgCl_2$ systems by ^{1}H NMR spectroscopy and attempted to take the most account of interparticle specific interactions and competitive complex formation when calculating stability constants for propionate complexes of rare-earth metals. As the dissociation constant of propionic acid in D_2O on $NaNO_3$ background is absent from the literature, we preliminarily determined this constant in a 5.0 M $NaNO_3$ solution in D_2O, as well as the chemical shifts of protonated δ_{HL} and deprotonated δ_L forms for α and β protons of propionic acid. Corrections for the deuteration effect were calculated by formula (1).

$$pD = pH + X. \qquad (1)$$

Various X values are used in Eq. (1): 0.40 [33–40]), 0.38 [41], and 0.50 [42]. We took X 0.40, since it is used in the overwhelming majority of works.

Equation (1) reflects the isotope effect of deuterium on the ionization constants of protolytes. For example, for acetic acid the pK value of 5.14 was found by NMR spectroscopy in heavy water at 20°C and ionic strength $I = 0$ [43]. Comparison of this value with ΔH 0.41 kJ mol^{-1} and pK 4.756, recommended by IUPAC for the dissociation of acetic acid at zero ionic strength in usual water, gives the isotope coefficient X of 0.384. This value is close to the correction coefficient of 0.38 for the dissociation of alcohol and water hydroxy groups [41]. For various classes of organic compounds the coefficient reflecting the isotope effect spans the range 0.38–0.64 [44].

The isotope effect of deuteration on the stability constants of complexes can be estimated. Direct correlation (2) between $\log K$ for Sm^{3+} and Eu^{3+} mono- and dicarboxylates and the acid dissociation constant of the ligand has been found in [45–47].

$$\log K = 0.512(\pm 0.008)pK_a. \qquad (2)$$

As the isotope effect of solvent deuteration increases pK_a (for example, by ~0.4 for acetic acid), the corresponding stability constants ($\log K$) of rare-earth metal acetates in heavy water will be overestimated by ~0.21–0.22 units.

Assuming that the observed chemical shifts are additive and correlate with pD (Fig. 1) and using the CPESSR (Complex Formation Parameters of Equilibria in Solution with Solid Phases) program complex for simulating complicated equilibria [48], we found chemical shifts and dissociation constants for propionic acid independently for the α and β protons: $\delta_{HL}(\alpha)$ 2.19, $\delta_L(\alpha)$ 1.95, p$K_a(\alpha)$ 5.08 ± 0.01; $\delta_{HL}(\beta)$

Table 1. Paramagnetic shifts of β-proton signals of propionic acid in ^{1}H NMR spectra, induced by rare-earth metal ions, ppm

μ	Dy^{3+}	Dy^{3+} + Mg^{2+}	Er^{3+}	Er^{3+} + Mg^{2+}	Yb^{3+}	Yb^{3+} + Mg^{2+}	Tm^{3+}	Tm^{3+} + Mg^{2+}
0	–0.16	–	–0.17	–	–0.17	–	–0.16	–
0.05	0.81	0.55	–0.31	–0.16	–0.31	–0.16	–0.34	–0.17
0.10	1.75	1.14	–0.45	–0.25	–0.46	–0.25	–0.51	–0.27
0.50	8.50	5.32	–1.45	–0.89	–1.48	–0.91	–1.74	–0.98
0.60	9.93	6.22	–1.66	–1.02	–1.71	–1.05	–2.00	–1.14
1.00	14.56	9.32	–2.35	–1.49	–2.42	–1.53	–2.86	–1.68
1.20	16.27	10.59	–2.61	–1.69	–2.68	–1.72	–3.20	–1.92
1.50	18.24	12.25	–2.91	–1.94	–2.98	–1.98	–3.61	–2.23
2.00	20.42	14.42	–3.25	–2.26	–3.31	–2.31	–4.11	–2.66
2.50	21.77	16.06	–3.46	–2.51	–3.52	–2.56	–4.44	–3.00
3.00	22.66	17.32	–3.60	–2.70	–3.65	–2.75	–4.68	–3.27

0.85, $\delta_L(\beta)$ 0.78, $pK_a(\beta)$ 5.09 ± 0.01. Further we used the average pK_a value of 5.085 ± 0.020.

With the resulting chemical shifts of the protonated and deprotonated forms of the acid and the dissociation constants, we calculated the complex formation constants and limiting paramagnetic shifts of acid protons for rare-earth metal ion–propionic acid–diamagnetic salt systems, based on ^{1}H NMR data [$\delta = f(\mu)$, where μ is the rare-earth metal ion-to-acid concentration ratio (Table 1)]. Note that Dy^{3+} induced downfield paramagnetic shifts in ^{1}H NMR spectra into, whereas Er^{3+}, Tm^{3+}, and Yb^{3+}, upfield.

The stability constants of complexes of rare-earth metal ions with propionate ions $LnProp^{2+}$ (1 : 1) and $LnProp_2^+$ (1 : 2) ($Prop^-$ is propionate ion) and nitrate ions $LnNO_3^{2+}$ [49], monochloride complexes $LnCl^{2+}$ [50, 51], and magnesium propionate complexes $MgProp^+$ (1 : 1) [52] were included in the equilibrium stoichiometry matrix for the CPESSP program complex. The stability constants of the complexes $MgProp_2$, $MgNO_3^+$, $MgCl^+$ [52–54], $Ln(NO_3)^{2+}$ [49, 50], $LnCl_2^+$ [50, 51], $LnProp_3$ [5–7], and NaProp [52] were not included in the equilibrium stoichiometry matrices because of the extremely low stability of these complexes.

It should be noted that the published non-varied stability constants of complexes, included in the equilibrium stoichiometry matrix, as well as those of neglected complex forms were preliminarily extrapolated to the experimental ionic strength created by the background electrolyte $NaNO_3$, using JESS (Joint Expert Speciation System) [55–57].

The calculations showed that the stability constants of the rare-earth metal monopropinate complexes, estimated on the basis of induced chemical shifts of α protons of propionic acid are several times less accurate than those estimated on the basis of induced chemical shifts of β protons, probably, because the α-proton signals are significantly broaden with increasing concentration of the paramagnetic rare-earth metal ion. Therefore, in what follows we consider the calculation results obtained from the dependence of the chemical shifts of propionic β protons on the rare-earth metal ion-to-acid concentration ratio (Table 1).

The calculated constants and limiting paramagnetic shifts are given in Tables 2 and 3. For comparison,

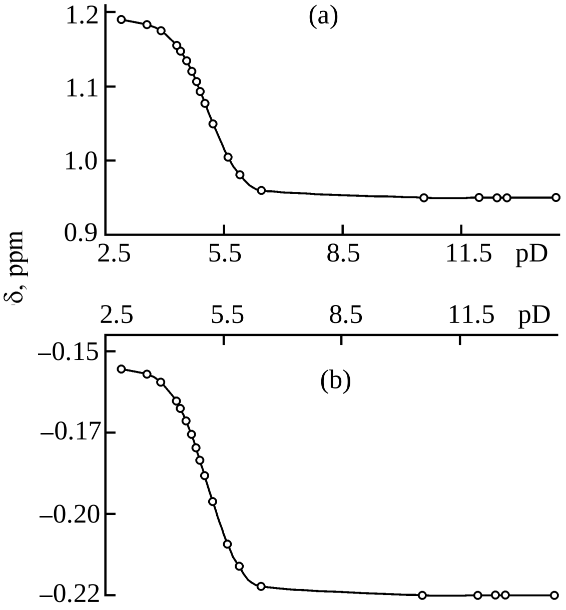

Fig. 1. Plots of the observed chemical shifts of the (a) α- and (b) β-proton signals of propionic acid (against *tert*-butanol methyl proton signals) vs. pD.

Table 2. Logarithms of the stability constants of the propionate complexes in the $LnCl_3$–Hprop–$MgCl_2$ system (5.0 M $NaNO_3$, 298 K)

$LnCl_3$ + HProp + $NaNO_3$			$LnCl_3$ + HProp + $NaNO_3$ + $MgCl_2$			$LnCl_3$ + HProp + $NaNO_3$ + $MgCl_2$ (account for $LnCl^{2+}$)		
ion	$\log K_c$	$\log K_m$	ion	$\log K_c$	$\log K_m$	ion	$\log K_c$	$\log K_m$
DyProp^{2+}	3.64 ± 0.02	3.51 ± 0.02	DyProp^{2+}	3.51 ± 0.02	3.38 ± 0.02	DyProp^{2+}	3.46 ± 0.02	3.33 ± 0.02
DyProp$_2^+$	2.58 ± 0.07	2.45 ± 0.07	DyProp$_2^+$	–	–	DyProp$_2^+$	–	–
			MgProp$^+$	2.37 ± 0.02	2.24 ± 0.02	MgProp$^+$	2.31 ± 0.02	2.18 ± 0.02
ErProp^{2+}	3.81 ± 0.03	3.68 ± 0.03	ErProp^{2+}	3.69 ± 0.02	3.56 ± 0.02	ErProp^{2+}	3.66 ± 0.02	3.53 ± 0.02
ErProp$_2^+$	2.71 ± 0.09	2.58 ± 0.09	ErProp$_2^+$	–	–	ErProp$_2^+$	–	–
			MgProp$^+$	2.31 ± 0.03	2.18 ± 0.03	MgProp$^+$	2.28 ± 0.03	2.15 ± 0.03
TmProp^{2+}	3.51 ± 0.03	3.38 ± 0.03	TmProp^{2+}	3.40 ± 0.02	3.27 ± 0.02	TmProp^{2+}	3.38 ± 0.02	3.25 ± 0.02
TmProp$_2^+$	2.47 ± 0.07	2.34 ± 0.07	TmProp$_2^+$	–	–	TmProp$_2^+$	–	–
			MgProp+	2.34 ± 0.03	2.21 ± 0.03	MgProp+	2.30 ± 0.02	2.17 ± 0.02
YbProp^{2+}	3.57 ± 0.03	3.44 ± 0.03	YbProp^{2+}	3.41 ± 0.02	3.28 ± 0.02	YbProp^{2+}	3.40 ± 0.02	3.27 ± 0.02
YbProp$_2^+$	2.61 ± 0.11	2.48 ± 0.11	YbProp$_2^+$	–	–	YbProp$_2^+$	–	–
			MgProp$^+$	2.38 ± 0.03	2.25 ± 0.03	MgProp$^+$	2.35 ± 0.02	2.22 ± 0.02

Table 3. Limiting paramagnetic shifts of β protons of the propionate complexes of rare-earth metal ions, ppm mol^{-1}

Ion	$LnCl_3$ + HProp + $NaNO_3$	$LnCl_3$ + HProp $NaNO_3$ + $MgCl_2$	$LnCl_3$ + HProp + $NaNO_3$ + $MgCl_2$ (account for $LnCl^{2+}$)
DyProp^{2+}	554	570	520
DyProp^{2+}	900	–	–
ErProp^{2+}	–80	–82	–75
ErProp^{2+}	–600	–	–
TmProp^{2+}	–101	–108	–93
TmProp^{2+}	–890	–	–
YbProp^{2+}	–82	–89	–76
YbProp^{2+}	–500	–	–

we also included in Table 2 complex formation constants for the case that the $LnCl^{2+}$ complexes are included in the equilibrium stoichiometry matrices. The constants for dipropionate complexes are less accurate than those for monocarboxylate complexes because of the low accumulation degree of the former complexes. However, these values were included in the equilibrium stoichiometry matrices, since the statistic criteria of convergence of the calculations (CPESSP) were considerably improved. We failed to obtain reliable complex formation constants for 1 : 2 rare-earth metal propionate complexes when processing data for systems containing Mg^{2+} ions, as their accumulation degree of these conditions was low because of the competitive effect of Mg^{2+} ions. The error in the limiting paramagnetic shifts did not exceed 5%.

Table 2 also lists the logarithms of the stability constants K_m reduced by Eq. (3) to the molal scale [58].

$$\log K_m = \log K_s + \Sigma\nu \log \rho. \qquad (3)$$

Here K_s is the stability constant on the molar scale; Σν, sum of the stoichiometric coefficients of the reaction; ρ, molarity–molality conversion factor equal to 1.3609 for a 5 M $NaNO_3$ solution in heavy water and calculated from the density data for $NaNO_3$ solutions in heavy water [59].

Table 3 also lists the limiting paramagnetic shifts for the systems, calculated with account for the $LnCl_2^+$ complexes.

It is seen from the distribution diagrams (Figs. 2–4) that the fraction of accumulated chloride and nitrate complexes of rare-earth metals at the used concentration of diamagnetic salts is significant. Therefore, the inclusion of nitrate and chloride ions as basic particles in the equilibrium stoichiometry matrices was justified and essentially improved the statistic convergence criteria of CPESSP calculations. The dipropionate complex forms of rare-earth metal ions are not presented in the diagrams, as the mole fraction α of their accumulation did not exceed 3–4%.

The logarithms of the calculated stability constants of monocarboxylale complexes of certain investigated

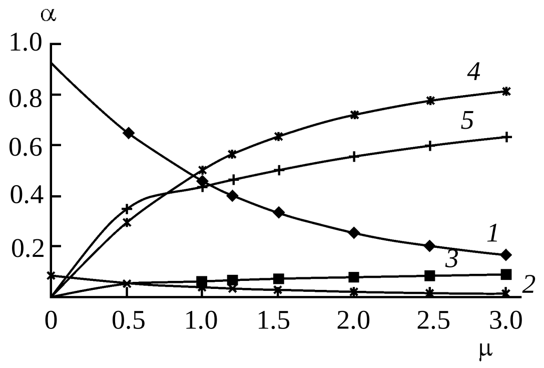

Fig. 2. Distribution of complex forms in the $HProp^+$ + $DyCl_3$ + $NaNO_3$ system as a function of μ. (*1*) HProp, (*2*) $Prop^-$, (*3*) Dy^{3+}, (*4*) $DyProp^{2+}$, (*5*) $DyNO_3{}^{2+}$.

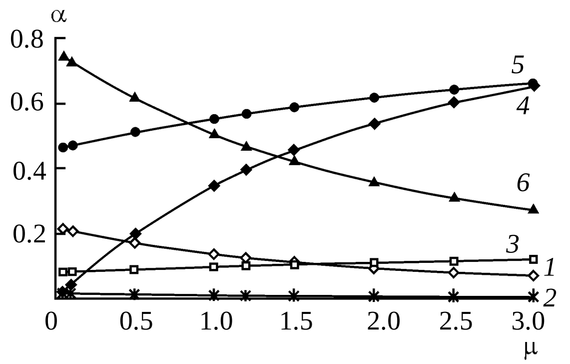

Fig. 3. Distribution of complex forms in the system $HProp^+$ + $DyCl_3$ + $MgCl_2$ + $NaNO_3$ as a function of μ. (*1*) HProp, (*2*) $Prop^-$, (*3*) Dy^{3+}, (*4*) $DyProp^{2+}$, (*5*) $DyNO_3{}^{2+}$, and (*6*) $MgProp^+$.

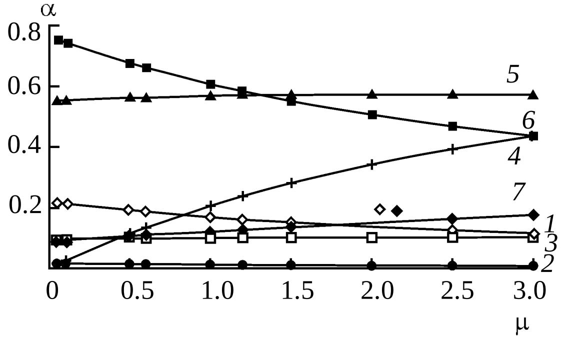

Fig. 4. Distribution of complex forms in the $HProp^+$ + $DyCl_3$ + $MgCl_2$ + $NaNO_3$ system (with account for $DyCl^{2+}$) as a function of μ. (*1*) HProp, (*2*) $Prop^-$, (*3*) Dy^{3+}, (*4*) $DyProp^{2+}$, (*5*) $DyNO_3{}^{2+}$, (*6*) $MgProp^+$, and (*7*) $DyCl^{2+}$.

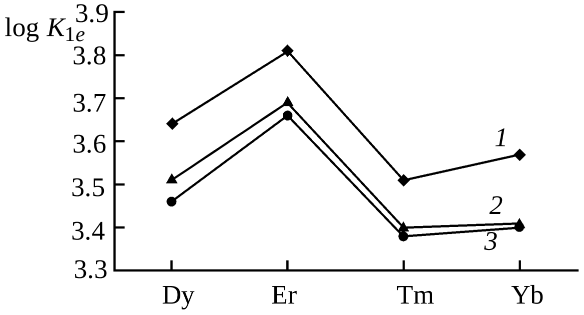

Fig. 5. Values of $\log K_{©}$ for monopropinate complexes of the rare-earth metal series. (*1*) $LnCl_3$ + $HProp^+$ $NaNO_3$, (*2*) $LnCl_3$ + $HProp^+$ $NaNO_3$ + $MgCl_2$, (*3*) $LnCl_3$ + $HProp^+$ + $NaNO_3$ + $MgCl_2$ (with account for $LnCl_2^+$).

rare-earth metals in the $LnCl_3$–propionic acid and $LnCl_3$–propionic acid–$MgCl_2$ systems are given in Fig. 5. Inclusion of chloride complexes of rare-earth metals results in different values (Figs. 5, 2, and 3) of the calculated stability constants.

The resuling data show that the formation constants of 1 : 1 complexes of rare-earth metals with propionic acid decrease by 30-65% on introduction of $MgCl_2$ in the $LnCl_3$–propionic acid system. Previously we revealed the tendency of the stability constants of rare-earth metal complexes to decrease in the presence of Mg^{2+} and Ca^{2+} salts [60–63]. However, in these works we took no account of complex formation with background electrolyte anions, and the above effect was less significant than in the present work.

Hence, adequate description of equilibria and calculation of reliable complex formation parameters based on NMR experiments with high concentrations of background electrolyte are only possible if particle interactions are taken into account as thoroughly as possible.

In our opinion, the decreasing stability constants and changes in the induced limiting paramagnetic shifts of carboxylate complexes of rare-earth metals at the simultaneous presence of Mg^{2+} ions can be explained by several reasons.

(1) Decrease of the entropy component and increase of the endothermic effect of desolvation of aqua ions of rare-earth metals and ligands and coordination of ligands in the coordination sphere of rare-earth metal ions [45, 64–66]. This is caused by the fact that magnesium ions enhance structural ordering of liquid water [67, 68].

(2) Decrease of the water activity upon complex formation in aqueous solution [Eq. (4)], caused by Mg^{2+} ions.

$$\mathrm{Ln(H_2O)}_k^{3+} + i\mathrm{L(H_2O)}_x \rightleftarrows [\mathrm{Ln(H_2O)}_{k-n}\mathrm{L}_i\mathrm{(H_2O)}_{ix-m}]^{3-i} + (n + m)\mathrm{H_2O}. \quad (4)$$

Here n, m = 1 – 6 [45], k = 8 [69], i = 1 – 2, L is Prop^-.

The equilibrium (4) constant takes form (5).

$$K = \frac{a\{[\mathrm{Ln(H_2O)}_{k-n}\mathrm{L}_i\mathrm{(H_2O)}_{ix-m}]^{3-i}\}a^{m+n}\mathrm{(H_2O)}}{a[\mathrm{Ln(H_2O)}_k^{3+}]a^i[\mathrm{L(H_2O)}_x^-]}. \quad (5)$$

(3) Complex formation of f metals in aqueous solutions with the majority of inorganic and simple organic ligands is commonly described by the Eigen–Tamm–Wilkinson mechanism [45, 70] in terms of equilibrium reactions (6).

$$\mathrm{Ln}^{3+}_{\mathrm{aq}} + \mathrm{Ln}^{n-}_{\mathrm{aq}} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} \mathrm{Ln}^{3+}_{\mathrm{aq}} + \mathrm{Ln}^{n-}_{\mathrm{aq}} \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} [\mathrm{Ln}^{3+}\mathrm{(H_2O)L}^{n-}]_{\mathrm{aq}} \underset{k_{43}}{\overset{k_{34}}{\rightleftarrows}} \mathrm{LnL}^{(3-n)+}_{\mathrm{aq}}. \quad (6)$$

The first stage is diffusion-controlled formation of a solvent-separated ion pair $\mathrm{Ln}^{3+}_{\mathrm{aq}}\mathrm{L}^{n-}_{\mathrm{aq}}$; the following stage is formation of an outer-sphere complex $[\mathrm{Ln}^{3+}\mathrm{(H_2O)L}^{n-}]_{\mathrm{aq}}$ which then forms an intra-sphere complex $\mathrm{LnL}^{(3-n)+}_{\mathrm{aq}}$.

Since the induced limiting paramagnetic shifts of carboxylate complexes of rare-earth metals decrease in the presence of Mg^{2+} ions, and the coordination structures of carboxylale complexes of rare-earth metals are unlikely to differ from each other in the presence and in the absence of Mg^{2+} ions, the difference in the stability constants of the complexes can be caused by increased life time of water molecules in the coordination sphere of the paramagnetic aqua ion. The Mg^{2+} ion is known [67, 68] to strengthen considerably the structure of liquid water, limiting the translation mobility of water molecules and hydrated ions, which decreases the corresponding self-diffusion coefficients [71]. As a result, the rate constants k_{12} and k_{34} of the first and the third stages of reaction (6) can decrease. Decreased k_{12} and k_{34} can decrease the corresponding stability constants of rare-earth carboxylate complexes [45], whereas decreased k_{34} can be responsible for decreased induced limiting paramagnetic shifts of such complexes.

Thus, we have studied complex formation of propionic acid with yttrium-group rare-earth metal ions in aqueous solutions in the absence and presence of diamagnetic Mg^{2+} cations at a high concentration of background electrolyte, using ^{1}H NMR spectroscopy in combination with mathematical simulation. The necessity of accounting for complex formation of paramagnetic cations with anions of diamagnetic salt and background electrolyte, as well as for changes in acid–base equilibria of ligand at a high concentration of background electrolyte in $\mathrm{D_2O}$ solutions has been demonstrated.

EXPERIMENTAL

The ^{1}H NMR spectra were obtained on a Tesla BS-587A spectrometer at 80 MHz. The chemical shifts were measured accurate to 0.02 ppm against the methyl signal of *tert*-butanol used as internal reference. The ^{1}H NMR spectra of propionic acid were analyzed in terms of a weakly bound A_3X_2 spin system. The paramagnetic chemical shifts induced by rare-earth metal ions in the ^{1}H NMR spectrum of propionic acid were fixed as centers of spin multiplets of the corresponding protons, because paramagnetic additives of rare-earth metal ions caused a noticeable signal broadening.

The pH values were measured on a Beckman Model-4500 digital pH-meter in a temperature-controlled cell at 25°C using a Volta-pH-3002 combined electrode (St. Petersburg State University, Potential Production Association) with an accuracy of ±0.01 pH units. The electrode was calibrated in aqueous solutions by titration of a solution of HCl with a solution of NaOH [72, 73]. The glass electrode was calibrated using the GLEE program [74].

Chemical grade crystal hydrates of rare-earth metals chlorides $\mathrm{LnCl_3}$ (Ln = Dy, Er, Tm, Yb), $\mathrm{MgCl_2}$, and *tert*-butanol were used. Chemical grade propionic acid was doubly distilled over freshly calcined $\mathrm{Na_2SO_4}$ as a dehydrating agent. The water content of the acid was controlled by potentiometric titration and refractometry.

The concentration of $\mathrm{LnCl_3}$ and $\mathrm{MgCl_2}$ solutions in $\mathrm{D_2O}$ (99.8%, Sigma) was determined by complexometry with sodium ethylenediamine tetraacetate. The concentrations used were 0.0025–0.1500 for $\mathrm{LnCl_3}$, 0.25 for $\mathrm{MgCl_2}$, and 0.05 M for propionic acid. The solutions were prepared at a constant ionic strength of 5.0 M created by chemical grade $\mathrm{NaNO_3}$. In ^{1}H NMR experiments, the solutions were thermostated with an accuracy of ±0.05°.

The dissociation constant of propionic acid in heavy water was measured by NMR titration by adding microamounts of concentrated solutions of DCl (Sigma) or NaOD (Sigma) free of $\mathrm{CO_2}$. In the NMR titration of the acid solution in the presence or in the absence of Mg^{2+} ions with paramagnetic rare-earth metal ions, the pH values of the solutions was maintained constant (pH 4.00) with deuterated acid and alkali solutions. Paramagnetic ions were taken in excess to provide prevalence of 1 : 1 complexes in the NMR titration.

ACKNOWLEDGMENTS

The authors are grateful to P. Hans (Protonic Soft, Great Britain) for providing the GLEE program and to L.D. Petit (Academic Soft, Great Britain) for providing IUPAC SC Database materials.

The work was financially supported by the Russian Foundation for Basic Research (project no. 03-03-32 296).

REFERENCES

1. Choppin, G.R., *J. Less-Common Metals,* 1986, vol. 126, no. 3, p. 307.
2. De Baar, H.J.W., Bacon, M.P., Brewer, P.G., and Brilund, K.W., *Geochim. Cosmochim. Acta,* 1985, vol. 49, no. 10, p. 1943.
3. Wood, S.A., *Eng. Geol.,* 1993, vol. 34, nos. 3–4, p. 229.
4. Sholkovitz, E.R., *Aquat. Geochem.,* 1995, vol. 1, p. 1.
5. Powell, J.E., Kolat, R.S., and Paul, G.S., *Inorg. Chem.,* 1964, vol. 3, no. 4, p. 518.
6. Aziz, A., Lyle, S.J., and Newbery, J.E., *J. Inorg. Nucl. Chem.,* 1971, vol. 33, no. 6, p. 1757.
7. Bukietynska, K., Mondry, A., and Osmeda, E., *J. Inorg. Nucl. Chem.,* 1981, vol. 43, no. 6, p. 1321.
8. Martell, A.E. and Smith, R.M., *Critical Stability Constants,* vol. 3: *Other Organic Ligands,* New York: Plenum, 1977, p. 312.
9. Moeller, T., *Lanthanides and Actinides,* Bagnall, K.W., Ed., vol. 7, London: Univ. Manchester Press, 1972, p. 275.
10. Martell A.E. and Smith, R.M., *Critical Stability Constants,* vol. 5: Suppl. 1, New York: Plenum, 1982, p. 412.
11. Smith, R.M. and Martell, A.E., *Critical Stability Constants,* vol. 6. Suppl. 2, New York: Plenum, 1982, p. 528.
12. Perrin, D.D., *IUPAC Chemical Data Series 22. Stability Constants of Metal-Ion Complexes,* Suppl. 2(B). *Organic Ligands,* Oxford: Pergamon, 1982.
13. *NIST Standart Reference Database 46. Version 6.0,* Martell, A.E. and Smith, R.M., Eds., Gaithersburg: Natl. Inst. Stand. and Technol., 2001.
14. Deberdt, S., Castet, S., Dandurand, J.L., Harrichoury, J.G., and Louiset, I., *Chem. Geol.,* 1998, vol. 151, nos. 1–4, p. 349.
15. Deberdt, S., Castet, S., Dandurand, J.L., and Harrichoury, J.G., *Chem. Geol.,* 2000, vol. 167, nos. 1–2, p. 75.
16. Zanonato, P.L., Di Bernardo, P., Bismondo, A., Rao, L., and Choppin, G.R., *J. Solution. Chem.,* 2001, vol. 30, no. 1, p. 1.
17. Partanen, J.I., Karki, M.H., and Juusola, P.M., *Acta Chem. Scand.,* 1995, vol. 49, no. 2, p. 865.
18. Partanen, J.I., *Acta Chem. Scand.,* 1998, vol. 52, no. 3, p. 985.
19. Partanen, J.I. and Juusola, P.M., *Fluid Phase Equilibria,* 2000, vol. 169, no. 2, p. 149.
20. Wood, S.A., Wesolowski, D.J., and Palmer D.A., *Chem. Geol.,* 2000, vol. 167, nos. 1–2, p. 231.
21. Pitzer, K.S., *J. Phys. Chem.,* 1973, vol. 77, no. 2, p. 268.
22. Scatchard, G., *Equilibrium in Solutions,* Cambridge: Harvard Univ. Press, 1976, p. 208.
23. Belevantsev, V.I., Mironov, I.V., and Peshchevitskij, B.I., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk,* 1981, no. 2, issue 6, p. 23.
24. Mironov, I.V. and Peshchevitskij, B.I., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk,* 1981, no. 6, issue 3, p. 54.
25. Bromley, L.A., *Am. Int. Chem. Eng. J.,* 1973, vol. 19, p. 313.
26. Helgeson, H.C. and Kirkham, D.H., *Am. J. Sci.,* 1974, vol. 274, no. 10, p. 1199.
27. Popov, K.I., *Cand. Sci. (Chem.) Dissertation,* Moscow, 2003.
28. Popov, K.I., *Chem. Intern.,* 2002, vol. 24, no. 6, p. 19.
29. Buikliskii, V.D. and Panyushkin, V.T., *Zh. Obshch. Khim.,* 1987, vol. 57, no. 10, p. 2262.
30. Buikliskii, V.D., Panyushkin, V.T., and Soldatenko, I.A., *Zh. Obshch. Khim.,* 1990, vol. 60, no. 11, p. 2143.
31. Vashchuk, A.V., Panyushkin, V.T., and Fedorenko, N.L., *Zh. Obshch. Khim.,* 1994, vol. 64, no. 1, p. 119.
32. Panyushkin, V.T., Sukhno, I.V., and Vodopetova, N.L., *Zh. Obshch. Khim.,* 2003, vol. 73, no. 4, p. 541.
33. Glassoe, P.K. and Long, F.A., *J. Phys. Chem.,* 1960, vol. 64, no. 1, p. 188.
34. Sawyer, D.T. and Brannan, J.R., *Inorg. Chem.,* 1966, vol. 5, no. 1, p. 65.
35. Mikkelsen, K. and Nielsen, S.O., *J. Phys. Chem.,* 1960, vol. 64, no. 5, p. 632.
36. Burai, L., Ren, J., Kovacs, Z., Brucher, E., and Sherry, A.D., *Inorg. Chem.,* 1998, vol. 37, no. 1, p. 69.
37. Geraldes, C., F.G.C., Brucher, E., Cortes, S.,

Koenig, S.H., and Dean Sherry, A., *J. Chem. Soc., Dalton Trans.*, 1992, no. 16, p. 2517.

38. Burai, L., Kiraly, R., Lazar, I., and Brucher, E., *Eur. J. Inorg. Chem.*, 2001, no. 4, p. 813.
39. Giroux, S., Rubini, P., Henry, B., and Aury, S., *Polyhedron*, 2000, vol. 19, no. 13, p. 1567.
40. Sherry, A.D., Ren, J., Huskens, J., Brucher, E., Toth, E., Geraldes, C.F.G.C., Castro, M.M.C.A., and Cacheris, W.P., *Inorg. Chem.*, 1996, vol. 35, no. 16, p. 4604.
41. Fife, T.H. and Bruice, T.C., *J. Phys. Chem.*, 1961, vol. 65, no. 6, p. 1079.
42. Carvalho, R. A., Peters, J. A., and Geraldes, C.F.G.C., *Inorg. Chim. Acta*, 1997, vol. 262, no. 2, p. 167.
43. Pettit, L.D. and Powell, K., *IUPAC Stability Constant Database*, Otley: Acad. Software (UK), 1997.
44. Blasko, A., Bunton, C.A., Bunel, S., Ibarra, C., and Moraga, E., *Carbohyd. Res.*, 1997, vol. 298, p. 163.
45. Choppin, G.R., *J. Alloys Comp.*, 1997, vol. 249, nos. 1–2, p. 1.
46. Choppin G.R., *J. Less-Common Metals.*, 1983, vol. 93, no. 3, p. 323.
47. Choppin, G.R., *J. Alloys Comp.*, 1995, vol. 223, no. 2, p. 174.
48. Sal'nikov, Yu.I., Glebov, A.A., and Devyatov, F.V., *Poliyadernue kompleksy v rastvorakh* (Polynuclear Complexes in Solutions), Kazan: Kazan. Gos. Univers., 1989.
49. Millero, F.J., *Geochim. Cosmochim. Acta*, 1992, vol. 56, no. 15, p. 3123.
50. Haas, J.R., Shock, L.E., and Sassani, D., *Geochim. Cosmochim. Acta*, 1995, vol. 59, no. 21, p. 4329.
51. Luo, Yu-Ran and Byrne, R.H., *J. Solution Chem.*, 2001, vol. 30, no. 9, p. 837.
52. Woolard, C.A., *Computer Simulation of the Trace Metal Speciation in Seawater, Ph.D. Thesis*, Cape Town: Cape Town Univ., 1995.
53. Fein, J.B., *Geochim. Cosmochim. Acta*, 1991, vol. 55, no. 4, p. 955.
54. Skipper, N.T., Neilson, G.W., and Cummings, S.C., *J. Phys.: Condensed Matter.*, 1989, vol. 1, no. 22, p. 3489.
55. May, P.M. and Murray, K., *Talanta*, 1991, vol. 38, no. 8, p. 1409.
56. May, P.M. and Murray, K., *Talanta*, 1991, vol. 38, no. 8, p. 1419.
57. May, P.M. and Murray, K., *Talanta*, 1993, vol. 40, no. 6, p. 819.
58. Wanner, H. and Osthols, E., *Standards and Conventions for TDB Publications*, Le Seine-St.: Issy-les-Moulineaux, 2000.
59. Riddel, J.D., Lokwood, D.J., and Trich, D.E., *Can. J. Chem.*, 1972, vol. 50, no. 21, p. 2951.
60. Vashchuk, A.V., Sukhno, I.V., and Panyushkin, V.T., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 12, p. 1941.
61. Vashchuk, A.V., Sukhno, I.V., and Panyushkin, V.T., *Koord. Khim.*, 1998, vol. 24, no. 9, p. 719.
62. Vashchuk, A.V., Sukhno, I.V., and Panyushkin, V.T., *Koord. Khim.*, 1999, vol. 25, no. 7, p. 556.
63. Panuyshkin, V.T., Sukhno, I.V., and Arutunyan M.M., *J. Mol. Liq.*, 2001, vol. 92, no. 3, p. 235.
64. Mishchenko, K.P. and Poltoratskii, G.M., *Termodinamika i stroenie vodnykh i nevodnykh rastvorov elektrolitov* (Thermodynamics and Structure of Aqueous and Nonaqueous Solutions of Electrolytes), Leningrad: Khimiya, 1976.
65. Arutyunyan, M.M., Sukhno, I.V., Buz'ko, V.Yu., and Panyushkin, V.T., *Koord. Khim.*, 2004, vol. 30, no. 2, p. 135.
66. Arutyunyan, M.M., Sukhno, I.V., Buz'ko, V.Yu., and Panyushkin, V.T., *Zh. Fiz. Khim.*, 2003, vol. 77, no. 9, p. 1547.
67. Guardia, E., Sese, G., Padro, J.A., and Kalko S.G., *J. Solution Chem.*, 1999, vol. 28, no. 10, p. 1113.
68. Ohtaki, H., *Monatsh. Chem.*, 2001, vol. 132, no. 11, p. 1237.
69. Choppin, G.R., *J. Alloys Comp.*, 1997, vol. 249, nos. 1–2, p. 9.
70. Eigen, M. and Tamm, K., *Z. Electrochim.*, 1962, vol. 66, no. 93, p. 107.
71. Endom, L., Hertz, H.G., Thul, B., and Zeidler, M.D., *Ber. Bunsen-Ges. Phys. Chem.*, 1967, vol. 71, nos. 9–10, p. 1008.
72. Motekaitis, R.J. and Martell, A.E., *The Determination and Use of Stability Constants*, New York: VCH, 1988.
73. Braibanti, A., Bruschi, C., Fisicaro, E., and Pasquali, M., *Talanta*, 1986, vol. 33, no. 3, p. 471.
74. Gans, P. and O'Sullivan, B., *Talanta*, 2000, vol. 51, no. 1, p. 33.