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Complexation in the System Paramagnetic Ion (Tm^{3+})–Diamagnetic Ion (Mg^{2+})–Carboxylic Acid

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Abstract — The dependence of the NMR chemical shift in the system containing complexes of a paramagnetic cation PL and PL_2 on the concentration of a diamagnetic salt was simulated. The complexation in the system paramagnetic ion (Tm^{3+})–diamagnetic ion (Mg^{2+})–carboxylic acid (acetic, propionic, *n*-butyric) was studied experimentally. The effect of the second cation on the calculated complexation constants was detected.

Although complexation in multicomponent systems was considered in numerous papers [1–3], a substantiated procedure for quantitative evaluation of the complexation parameters in such systems is still lacking. Moreover, some papers give several sets of equilibrium constants equally well fitting the experimental data within the same stoichiometric scheme [4]. Even when advanced physicochemical methods are applied to equilibrium chemical systems with several ions present simultaneously, the information derived from the measurements largely depends on the availability of methods for mathematical processing of the results [5–10]. The ambiguity in evaluation of the complexation constants can also be due to inadequacy of physicochemical models describing the processes that occur in the system with complexation [11, 12]. Thus, the mutual influence of ions in such systems is still poorly inderstood. This problem is also interesting from the viewpoint of development of mathematical methods for processing experimental results.

It should be noted that we already considered this problem in our previous papers [13–15]. In this work, we simulated the effect of diamagnetic salts on the chemical shifts induced by paramagnetic ions and experimentally studied, using ^{1}H NMR spectroscopy, the mutual effect of two simultaneously present cations on complexation with aliphatic carboxylic acids.

We chose systems containing simultaneously paramagnetic ions of a rare-earth element (Tm^{3+}) and diamagnetic Mg^{2+} ions. Such systems are of interest for biochemistry and for development of rare-earth spectroscopic probing procedures [16–18].

We considered the following equilibria of complexation of paramagnetic (P) and diamagnetic (D) ions:

$$P + L \rightleftarrows PL, \qquad (1)$$

$$PL + L \rightleftarrows PL_2, \qquad (2)$$

$$D + L \rightleftarrows DL. \qquad (3)$$

The observed relative proton chemical shift was calculated in the superpositional approximation for fast (on the NMR time scale) ligand exchange:

$$\delta_{ob} = \sum_i \delta_i N_i. \qquad (4)$$

Here N_i and δ_i are the mole fraction and relative chemical shift of *i*th ligand species. Complexes PL and PL_2 are characterized by the chemical shifts δ_1 and δ_2, and equilibria (1) and (2), by constants K_1 and K_2. Equilibrium (3) is characterized by the constant K_d, and the relative chemical shift of DL is zero.

Using reference data for the activity coefficients of ions participating in equilibria (1)–(3), we constructed the dependences of the observed chemical shifts on the concentration of the diamagnetic salt. The simulated dependences of the observed chemical shifts in the system containing 0.2 M ligand and 0.6 M paramagnetic cation salt are shown in Fig. 1. The results show that the complexation of the ligand with a diamagnetic cation does not result in increase in the observed chemical shift with increasing concentration of the diamagnetic salt. This is true for any known concentration dependences of the activity coefficients of rare-earth ions, Group I and II metal halides, and organic ligands.

Figure 2 shows the simulated dependences demonstrating how the ratio of the concentrations of the rare-earth ion (C_p) and ligand (C_L) affects the observed

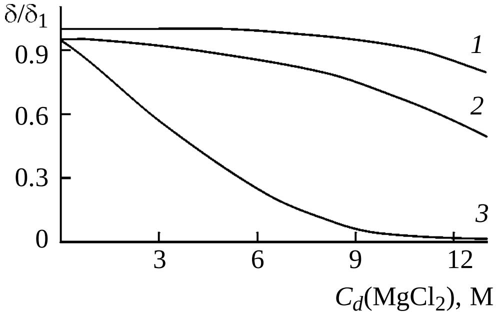

Fig. 1. Influence of the complexation constants K_1 and K_d on the observed chemical shifts. K_1: (*1, 3*) 900 and (*2*) 1000; K_d: (*1, 2*) 0.001 and (*3*) 0.1; δ_2/δ_1: (*1*) 1.2 and (*2, 3*) 1.0; K_2 100.

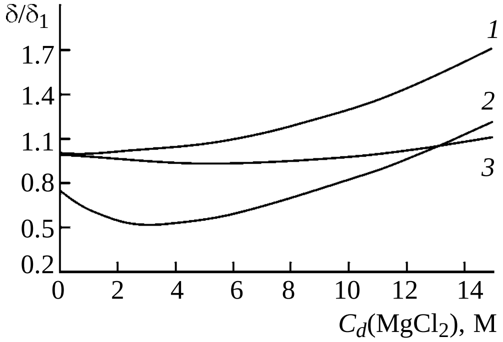

Fig. 2. Influence of the concentration ratio of the paramagnetic ion and ligand on the observed chemical shifts, C_L, M: (*1, 3*) 0.2 and (*2*) 0.5; C_p, M: (*1, 3*) 0.6 and (*2*) 0.2; K_1: (*1*) 10 000 and (*2, 3*) 1000; K_2: (*1*) 50 and (*2, 3*) 10; K_d 0; δ_2/δ_1: (*1, 2*) 1.2 and (*3*) 1.0.

chemical shifts. It should be noted that previously [19, 20] we examined the influence exerted by the concentration of a diamagnetic salt on the observed chemical shift induced by the paramagnetic ion of a rare-earth element and obtained similar dependences. It was suggested that, at high ligand concentrations, with increasing concentration of the diamagnetic salt, the increase in the chemical shifts is determined by structural changes in the coordination sphere of the ligand, rather than by the effect of the solution ionic strength as follows from the simulation results.

Thus, the effect of diamagnetic additives on the spectral characteristics of rare-earth complexes deserved further study.

Using ^{1}H NMR spectroscopy, we studied complexation in the system containing a paramagnetic ion (Tm^{3+}), a diamagnetic ion (Mg^{2+}), and a carboxylic acid (acetic, propionic, or *n*-butyric).

By combining the equations of material balance with respect to metal (C_p, C_d) and ligand (C_L) and the expressions for the equilibrium constants K_1 and K_d, we obtain expression (5) for the observed chemical shift of the system:

$$\delta_{ob} = \frac{1}{C_L}\left\{\delta_L[L^-] + \delta_{HL}\left(C_L - [L^-] - \sum_i^N \frac{K_iC_i[L^-]}{1 + K_i[L^-]}\right) + \sum_i^N \delta_i \frac{K_iC_i[L^-]}{1 + K_i[L^-]}\right\}. \qquad (5)$$

Here δ_L and δ_{HL} are the relative chemical shifts of the protonated and deprotonated forms of the ligand, respectively.

From the dependence $\delta_{ob} = f(\text{pH})$, we preliminarily calculated the acid dissociation constants K_a and the chemical shifts of the protonated and deprotonated species of acetic, propionic, and *n*-butyric acids from the chemical shifts of the acid α-protons (Fig. 3): $\delta_L(C_2H_4O_2)$ 0.67, $\delta_{HL}(C_2H_4O_2)$ 0.89, $\delta_L(C_3H_6O_2)$ 0.95, $\delta_{HL}(C_3H_6O_2)$ 1.19, $\delta_L(C_4H_8O_2)$ 0.94, and $\delta_{HL}(C_4H_8O_2)$ 1.16 ppm. The following dissociation constants were obtained: $K_a(C_2H_4O_2)$ 2.27×10^{-5}, $K_a(C_3H_6O_2)$ 2.14×10^{-5}, and $K_a(C_4H_8O_2)$ 2.09×10^{-5} M.

We restricted the consideration to 1 : 1 complexes of the paramagnetic ion, since, when 1 : 2 complexes were included, the stability constants obtained for them differed by more than two orders of magnitude from those of the PL complexes.

We have calculated the complexation constants of Tm^{3+} with carboxylic acids from the observed ^{1}H NMR chemical shifts of the α-protons of the carboxylic acid, $\delta_{ob} = f(C_p/C_L)$ (Fig. 4), by numerical solution of Eq. (5) ($N = 1$).

Addition of diamagnetic Mg^{2+} salts caused no changes in the ^{1}H NMR spectra of carboxylic acids. We also calculated the complexation constants of Tm^{3+} and Mg^{2+} (present simultaneously) with carboxylic acids by Eq. (5) ($N = 2$) from the ^{1}H NMR signals of α-protons: $\delta_{ob} = f(C_p/C_L, C_d/C_p)$ (Fig. 4).

The determination errors for complexation constants were found as described in [21, 22].

Our results show that the difference (Δ) between the complexation constants obtained for the systems containing Tm^{3+} only and Tm^{3+} + Mg^{2+} (paramagnetic and diamagnetic ions simultaneously) exceeds the error in determination of the complexation constant of the paramagnetic ion, inherent in model (5) and amounting to 1%. The results are listed in the table.

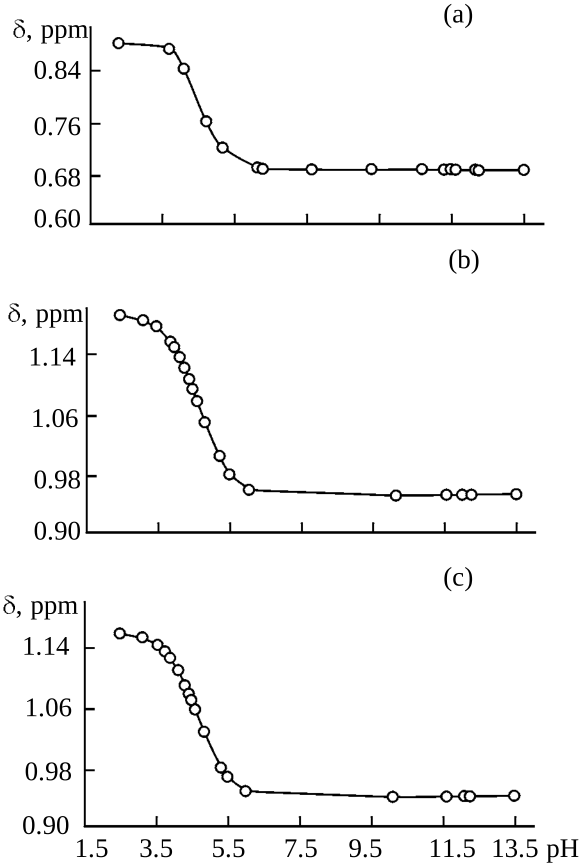

Fig. 3. Observed chemical shift of α-protons of (a) acetic, (b) propionic, and (c) *n*-butyric acids as a function of pH.

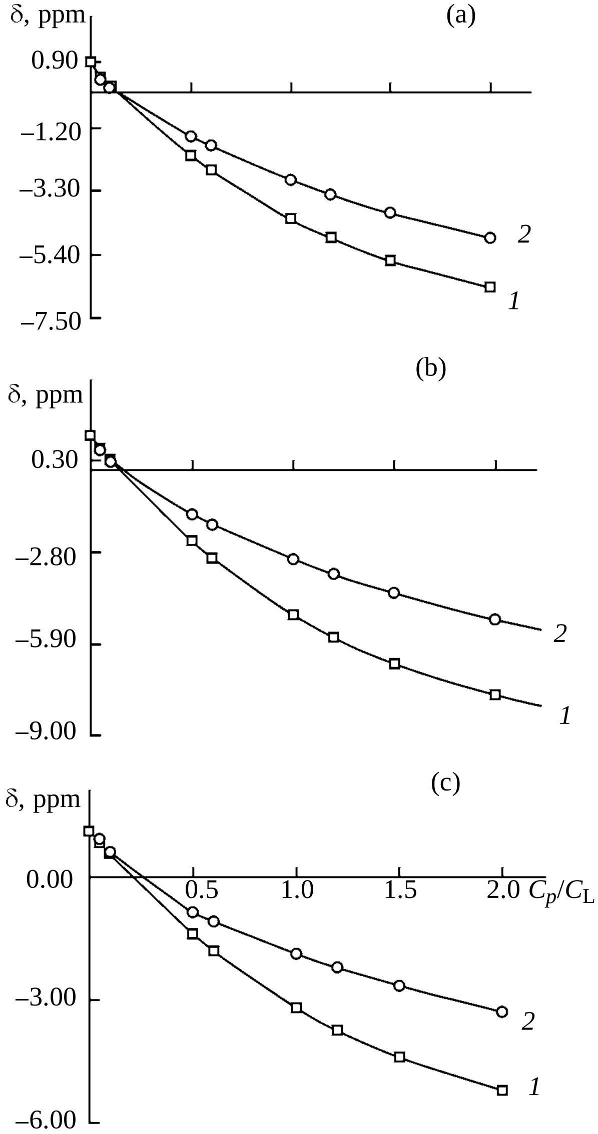

Fig. 4. Paramagnetic shifts of the signals of α-protons of (a) acetic, (b) propionic, and (c) butyric acids, induced by the Tm^{3+} ion, in the ^1H NMR spectra recorded (*1*) in the absence and (*2*) in the presence of Mg^{2+} ions.

Thus, we have simulated the observed chemical shift in the system containing the complexes PL and PL_2 in relation to the concentration of a diamagnetic salt. The complexation in the system paramagnetic ion (Tm^{3+})–diamagnetic ion (Mg^{2+})–carboxylic acid was studied experimentally. It was found that the complexation constants in the system containing two cations are lower than those of the cations taken separately. This effect may be due to specific features of the solution structure.

EXPERIMENTAL

The ^1H NMR spectra of solutions of acids and complexes in D_2O were taken on a BS-587A NMR spectrometer with a fixed working frequency of 80 MHz, with *tert*-butyl alcohol as internal reference. The solution pH was adjusted with deuterated alkali, NaOD. Complexation was studied at constant pH 4. The pH was measured in a temperature-controlled cell at 25±0.5°C with an EV-74 universal pH meter using a Radelkis OP-080P combined electrode [combined silver chloride electrode (1 M KCl) and glass electrode]; the accuracy was ±0.05 pH unit. The chemical shifts were determined with an accuracy of 0.01 ppm. The concentrations of the components (M) were as follows: $TmCl_3$, 0.0025–0.15; $MgCl_2$, 0.25; and carboxylic acids, 0.05. The concentrations of solutions of the diamagnetic and paramagnetic metal ions were determined by complexometric titration with Na_2EDTA. The ligand concentrations were determined by acid–base titration with NaOH. The ionic strength was constant in all the experiments and equal to 5; it was supported with KCl.

Complexation constants of Tm^{3+} and Mg^{2+} with carboxylic acids, according to ^1H NMR data

Cation	M_i^{n+} + L^-	L^- + Tm^{3+} + Mg^{2+}	Δ, %
Acetic acid			
Tm^{3+}	198.54	148.91	25
Mg^{2+}		18.25	
Propionic acid			
Tm^{3+}	201.52	179.35	11
Mg^{2+}		39.85	
n-Butyric acid			
Tm^{3+}	178.89	157.42	12
Mg^{2+}		40.78	

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