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Complex Formation of Cobalt(II) and Nickel(II) with 2-Hydroxypropylene-1,3-diamine-*N,N,N',N'*-tetraacetic Acid

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Abstract—The complex-formation equilibria of 2-hydroxypropylene-1,3-diamine-*N,N,N',N'*-tetraacetic acid (H_4L) with Co^{2+} and Ni^{2+} ions were studied. The stability constants of the complexes CoL^{2-}, $CoHL^-$, NiL^{2-}, and $NiHL^-$ were estimated; the resulting data were compared with respective data for related compounds.

Reported [1–4] stability constants of cobalt(II) and nickel(II) hydroxypropylenediaminetetraacetates diverge considerably. Their analysis does not allow us to establish the most reliable values. In [1–3], the possible formation of protonated complexonates was not taken into account. The formation of $NiHL^-$ and $CoHL^-$ complexes was considered in [4] only, but the experimental data therein were treated by the GAUSS G program [5] which makes use of the Gauss–Newton method for minimizing the sum of squared errors in the analytical concentration of hydrogen ions. This program characteristically involves large corrections, which leads to oscillations and lack of divergence [6]. Therefore, the $\log \beta_{ML}$ and $\log \beta_{MHL}$ values obtained in [4] can hardly be considered reliable. The controversy in published data and the practical importance of the compounds studied prompted us to experimental determination of the stability constants of cobalt(II) and nickel(II) hydroxypropylenetetraacetates.

In the present work, the complex-formation equilibria of H_4L with Co^{2+} and Ni^{2+} ions were studied potentiometrically and spectrophotometrically at 298.15 K and ionic strength I 0.5 (KNO_3). The potentiometric data were treated using a PHMETR program designed for calculation of constants of equilibria involving arbitrary number of reactions by the measured equilibrium concentration of one of the particles [7, 8]. The program operates by minimizing the criterial function F by varying each iteration of the target $\log \beta_j$ values by a modified Hook–Jeevs algorithm [9, 10]. The criterial function has equation (1).

$$F = \Sigma\ (\log [H^+]_{i,\mathrm{exp}} - \log [H^+]_{i,\mathrm{calc}})^2 \longrightarrow \min, \quad (1)$$

Here $\log [H^+]_{i,\mathrm{exp}}$ and $\log [H^+]_{i,\mathrm{calc}}$ are the logarithms of the equilibrium concentrations of H^+, measured and calculated at current $\log \beta_j$ values. The equilibrium concentrations were calculated by the Brinkley procedure [11, 12].

In treatment of the titration curves we took into account, along with complex formation [schemes (2) and (3)], acid–base interaction. The step dissociation constants of H_4L at the same ionic strength and temperature we determined earlier [13]. The hydrolysis constants of Co^{2+} and Ni^{2+} were taken from [14].

$$M^{2+} + L^{4-} \rightleftarrows ML^{2-}, \quad (2)$$

$$M^{2+} + HL^{3-} \rightleftarrows MHL^-. \quad (3)$$

The calculation results suggest formation in the solution of mononuclear complexonates ML^{2-} and MHL^-. Inclusion in the calculation scheme of the possible formation of polynuclear complexes deteriorates the results, since the criterial function is insensitive to these forms. We thus can conclude that H_4L does not form polynuclear compolexes under the experimental conditions. Further evidence for the validity of the chosen model and lack of unaccounted processes comes form the fact that the results of treatment of the titration curves obtained at various ratios of the initial concentrations of the ligand and metal ions well fit each other. The resulting stability constants of cobalt(II) and nickel(II) hydroxypropylenediaminetetraacetates at 298.15 K and I 0.5 (KNO_3) are listed in the table.

Calculation of the stability constants from combined spectrophotometric and potentiometric data was performed by the FTPH program [15] which minimizes the criterial function F [Eq. (4)].

$$F = \Sigma_k\Sigma_i(A_{ki,\mathrm{exp}} - A_{ki,\mathrm{calc}})^2 + \Sigma_i(\log [H^+]_{i,\mathrm{exp}} - \log [H^+]_{i,\mathrm{calc}})^2. \quad (4)$$

Here A_{ki} in the optical density (k is the wavelength

Stability constants of cobalt(II) and nickel(II) hydropypropylenediaminetetraacetates [298.15 K, *I* 0.5 (KNO_3)]

Process	log K^a	log K^b
$Co^{2+} + L^{4-} \rightleftarrows CoL^{2-}$	14.07±0.06	14.15±0.02
$Co^{2+} + HL^{3-} \rightleftarrows CoHL^-$	7.58±0.09	7.66±0.05
$CoL^{2-} + H^+ \rightleftarrows CoHL^-$	3.01±0.04	3.01±0.02
$Ni^{2+} + L^{4-} \rightleftarrows NiL^{2-}$	16.08±0.08	16.26±0.10
$Ni^{2+} + HL^{3-} \rightleftarrows NiHL^-$	9.35±0.11	9.55±0.15
$NiL^{2-} + H^+ \rightleftarrows NiHL^-$	2.77±0.06	2.79±0.10

[a] Determined by potentiometry.

[b] Determined by spectrophotometry.

number and *i* and the experimental point number) reduced to a 1-cm cell, measured and calculated at current log β_j values. The program allows data treatment in the case of close spectral characteristics and fairly high stability of colored complex species [15]. The calculation results show that, like with potentiometric titration data, the systems in hand are mathematically described by a scheme including ML^{2-} and MHL^- complexes. The resulting log β_j values nicely fit the potentiometric titration data (see table).

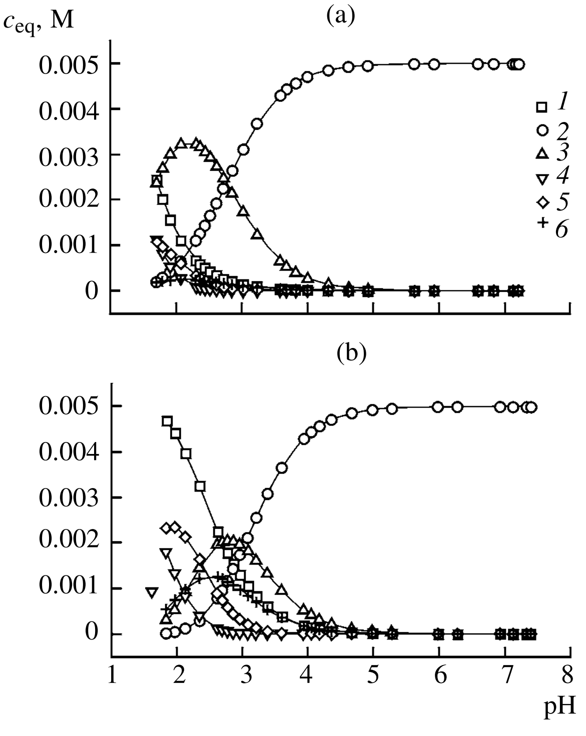

Fig. 1. Diagram of equilibrium particle distribution in the systems (a) Ni^{2+}–H_4L–H_2O and (b) Co^{2+}–H_4L–H_2O [c_{H_4L} = c_M 5×10^{-3} M, 298.15 K, *I* 0.5 (KNO_3)]. Equilibrium concentrations (c_{eq}) of (*1*) M^{2+}, (*2*) ML^{2-}, (*3*) MHL^-, (*4*) H_4L, (*5*) H_3L^-, and (*6*) H_2L^{2-}.

Figure 1 shows the diagrams of equilibrium particle distribution vs. pH in the systems Ni^{2+}–H_4L–H_2O and Co^{2+}–H_4L–H_2O at a metal : ligand concentration ratio of 1 : 1. As seen, H_4L formes with Ni^{2+} and Co^{2+} stable complexonates over a wide pH range. At pH > 5, the Co^{2+} ions are almost completely bound in the complex CoL^{2-}, whereas at pH < 4 the protonated complex $CoHL^-$ is formed in the solution. The same pattern is observed with nickel(II) complexonates with the only difference that respective ranges are shifted to lower pH values, on account of the fact that nickel(II) complexonates are more stable than cobalt(II) complexonates.

The stability constants of cobalt(II) and nickel(II) hydroxypropylenediaminetetraacetates, determined in the present work, are consistent with those reported in [1, 2]. However, our values should be considered as the most probable, since we made use of the most reliable method of data treatment, allowing one to account for side reactions without any simplifications. Moreover, in the present work we calibrated the electrode pair by the concentration scale, which required no recalculation of the activities of H^+ ions into their concentrations used in calculation of equilibrium constants.

Comparison of the stability constants of cobalt(II) and nickel(II) hydroxypropylenediaminetetraaxetates with those for trimethylenediamine- *N,N,N',N'*-tetraacetic {log $\beta(CoL^{2-})$ 15.54, log $\beta(NiL^{2-})$ 18.15 at *I* 0.1 (KNO_3) and 293.15 K [16]} and ethylenediamine-*N,N,N',N'*-tetraacetic {log $\beta(CoL^{2-})$ 16.31, log $\beta(NiL^{2-})$ 18.62 at *I* 0.1 (KNO_3) and 293.15 K [17]} complexes shows that the former complexes are much less stable. It thus be concluded that the hydroxyl functional group in H_4L is not involved in chelate formation with Co^{2+} and Ni^{2+} ions, and the lower stability of cobalt(II) and nickel(II) hydroxypropylenediaminetetraacetates derives from the fact that the inductive effect of the OH group reduces the basicity of the nitrogen atoms in the ligand.

EXPERIMENTAL

2-Hydroxypropylene-1,3-diamine-*N,N,N',N'*-tetraacetic acid was synthesized at the Institute of Ultrapure Reagents and Preparations, Moscow. The content of dry substance was 97.2% (99.9% per H_4L–$1/2H_2O$). Solutions of KOH and HNO_3 were prepared with chemically pure grade reagents. The concentrations of the solutions were determined titrimetrically. Cobalt(II) and nickel(II) nitrates of chemically pure grade were twice recrystallized from twice distilled water, and their concentrations were determined trilonometrically.

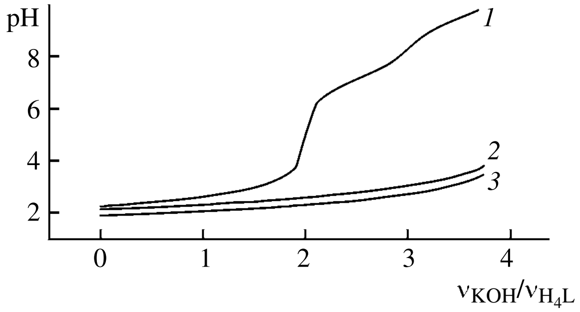

Fig. 2. Potentiometric titration curves of H_4L (c_{H4L} 5×10^{-3} M) [298.15 K, *I* 0.5 (KNO_3)]. (*1*) in the absence of metal ions, (*2*) in the presence of Co^{2+} ions (c_{Co} 10^{-2} M), and (*3*) in the presence of Ni^{2+} ions (c_{Ni} 10^{-2} M).

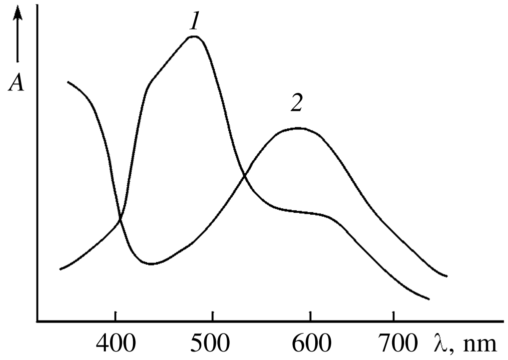

Fig. 3. Absorption spectra in the systems (*1*) Co^{2+}–H_4L–H_2O and (*2*) Ni^{2+}–H_4L–H_2O [c_{H_4L} 5×10^{-3}, c_M 4×10^{-3} M, 298.15 K, *I* 0.5 (KNO_3)].

Complex formation of H_4L with Co^{2+} and Ni^{2+} was studied by potentiometric titration at 298.15 K and ionic strength *I* 0.5 (KNO_3). An exact volume of the H_4L solution containing alkali metal ions and with required ionic strength was placed into a thermostated potentiometric cell. The initial concentration of H_4L was 5×10^{-3} M, and the initial concentrations of metal ions were 3×10^{-3}, 5×10^{-3}, and 10^{-2} M. The titrant was the standard carbonate-free KOH solution with a background electrolyte added to maintain the ionic strength of the solution constant in the course of titration; the quantity of the titrant added was determined gravimetrically. The titration curves of H_4L with KOH at 298.15 K and *I* 0.5 (KNO_3) in the presence of cobalt(II) and nickel(II) salts are shown in Fig. 2.

The equilibrium concentration of hydrogen ions was determined by measuring the emf of a chain including an ESL-43-07 glass electrode and an EVL-1MZ silver–silver chloride electrode. The potential of the glass electrode was controlled with an R-363/3 potentiometer. The zero instrument was a pH-340 pH-meter–millivoltmeter. The potentials were measured to an accuracy of ±0.1 mV. The temperature of the potentiometric cell and electrodes were maintained to an accuracy of ±0.1 K with a UTU-2 thermostat.

The potentiometric cell was calibrated with standard solutions of NNO_3 and KOH containing potassium nitrate for adjusting required ionic strengh.

Spectrophotometry was performed at 298.15 K and *I* 0.5 (KNO_3) on a Specord M-400 two-beam spectrophotometer. The absorption spectra of a series of H_4L solutions containingcorrepoding metal nitrate was measured at 350–900 nm (Fig. 3). The Ni^{2+}–H_4L–H_2O system gives two absorption bands at λ_1 569–577 and λ_2 375–380 nm. The Co^{2+}–H_4L–H_2O system gives an absorption band at 480–485 nm. The position and intensity of the band are nicely consistent with those reported in [2].

The stability constants of nickel(II) and cobalt(II) hydroxypropylenediaminetetraacetates at 298.15 K and *I* 0.5 (KNO_3) were determined be measuring the optical densities of a series of solution with a constant concentration of H_4L and corresponding metal nitrate (c_{H_4L} 5×10^{-3}, c_M 4×10^{-3} M) at pH 2.0–11.8. The pHs of the solutions were adjusted with KOH solution and controlled potentiometrically. The optical densities of a series of solutions with fixed pH 11.6 at a constant concentration of H_4L (c_{H_4L} 3.5×10^{-3} M) and varied concentration of corresponding metal ion (c_{Ni} 2×10^{-3} 5×10^{-3}, c_{Co} 2×10^{-3} 4×10^{-3} M). The spectrophotometric measurements were performed at λ_1 572 and λ_2 375 nm for Ni^{2+}–H_4L–H_2O and λ 480 nm for Co^{2+}–H_4L–H_2O.

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