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Magnesium and Calcium Complexation with 2-Hydroxypropylene-1,3-Diamine-*N*,*N*,*N*',*N*'-Tetraacetic Acid

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Abstract — Stability constants and heats of formation of magnesium and calcium hydroxypropylenediaminetetraacetates are determined, and the standard thermodynamic characteristics of the complexation equilibria are estimated.

2-Hydroxypropylene-1,3-diamine-*N*,*N*,*N*',*N*'-tetraacetic acid (H_4L) shows promise as a versatile chelating agent. However, to our knowledge, the thermochemistry of formation of the corresponding magnesium and calcium complexes is not studied yet. Practical significance of these complexes makes urgent the thermodynamic characterization of complexation of H_4L with Mg^{2+} and Ca^{2+}.

Therefore, in this study we determined the stability constants K of these complexes by potentiometric titration at 298 K and ionic strength of 0.1, 0.5, and 1.0 M (KNO_3). The heats of formation ΔH were measured by direct calorimetry under the same experimental conditions (see table).

Potentiometric data were processed using PHMETR program package destined for calculation of the equilibrium constants of arbitrary number of reactions from the measured concentration of one of species [1]. The program minimizes the criterial function F by varying log K in each iteration step using the modified Hook–Jeeves algorithm [2, 3]. The criterial function takes the form (1).

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

Here $[H^+]_{j,\mathrm{exp}}$ and $[H^+]_{j,\mathrm{calc}}$ are the experimental equilibrium concentrations of H^+ and those estimated for current K. The equilibrium concentrations are estimated by the Brinkley method [4, 5]. The titration curves were processed taking into account acid–base interactions inaddition to the complexation. Previously [6] we determined the step dissociation constants of H_4L at the same ionic strengths and temperatures using the procedure described in [7] (hydrolysis constants of the metal ions were taken from [8]). The calculation revealed formation of mononuclear complexes CaL^{2-} and MgL^{2-} in solution. The criterial function appeared to be insensitive to inclusion of protonated and binuclear complexes into consideration, suggesting that such species are not formed under the experimental conditions. The adequacy of the model is confirmed also by good reproducibility of the results obtained at different initial metal to ligand concentration ratios. The stability constants of magnesium and calcium hydroxypropylenediaminetetraacetates were determined from 8–12 replicate titration experiments at each ionic strength. Our results are consistent within the error limits with the log K values obtained with potassium chloride as a supporting electrolyte [9].

Our results are also well consistent with the published data on the stability constants of magnesium and calcium hydroxypropylenediaminetetraacetates [10, 11]. The stability constants obtained in this work can be recommend as the most reliable values, since we used the most efficient procedure for processing titration curves, taking into consideration side reactions and requiring no simplifications, in contrast to out-of-date graphical methods used in [11–14]. Tompson and Kundra [10] processed the experimental data using the GAUSS G program [15], which minimizes the sum of squared errors of the analytical concentration of H^+. This program is characterized by the need in large correction factors, resulting in oscillations and poor reproducibility [16]. Furthermore, data obtained in [10, 11] are referred to a single ionic

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Thermodynamic characteristics of formation of magnesium and calcium hydroxypropylenediaminetetraacetates at 298 K

I, M	$\log K$	$-\Delta G$, kJ mol^{-1}	ΔH, kJ mol^{-1}	ΔS, J mol^{-1} K^{-1}
		$Mg^{2+} + L^{4-} = MgL^{2-}$		
0.0	6.57 ± 0.06	37.50 ± 0.34	30.14 ± 0.33	226.9 ± 1.6
0.1 (KNO_3)	4.92 ± 0.06	28.08 ± 0.34	26.94 ± 0.33	184.5 ± 1.6
0.5 (KNO_3)	4.25 ± 0.03	24.26 ± 0.17	24.64 ± 0.22	164.0 ± 0.9
1.0 (KNO_3)	4.16 ± 0.06	23.75 ± 0.34	23.95 ± 0.18	160.0 ± 1.3
		$Ca^{2+} + L^{4-} = CaL^{2-}$		
0.0	8.47 ± 0.06	48.35 ± 0.34	–3.71 ± 0.23	149.7 ± 1.4
0.1 (KNO_3)	6.82 ± 0.04	38.93 ± 0.23	–7.00 ± 0.09	107.1 ± 0.8
0.5 (KNO_3)	6.01 ± 0.05	34.31 ± 0.29	–8.18 ± 0.23	87.6 ± 1.2
1.0 (KNO_3)	5.85 ± 0.06	33.39 ± 0.34	–8.81 ± 0.22	82.4 ± 1.4

strength (I 0.1 M), while in this work, the experiments were carried out at three ionic strengths covering the range from 0.1 to 1.0 M, which allows more reliable interpretation of the calorimetric data.

In the pH range 10.6–10.7, the ligand is partly protonated in the solution to form HL^{3-} species, and the formation of the ML^{2-} complexes is accompanied by occurring side acid–base reactions. On mixing $M(NO_3)_2$ and H_4L solutions in the calorimetric cell, reactions (2)–(4) occur.

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

$$M^{2+} + HL^{3-} \rightleftarrows ML^{2-} + H^+, \quad (3)$$

$$H^+ + L^{4-} \rightleftarrows HL^{3-}. \quad (4)$$

The enthalpy of reaction (3) can be considered as an algebraic sum of the enthalpies of reactions (2) and (4). Therefore, the heat of mixing of magnesium nitrate and H_4L solutions can be estimated by Eq. (5).

$$\Delta_{mix}H = \alpha_{MgL}\Delta H_{MgL} + \alpha_{HL}\Delta H_{HL} + \Delta_d H. \quad (5)$$

Here $\Delta_{mix}H$ is the heat of mixing of $Mg(NO_3)_2$ and H_4L solutions per mole of Mg^{2+}; $\Delta_d H$, heat of dilution of the $M(NO_3)_2$ solution with the supporting electrolyte solution; ΔH_{Mg} and ΔH_{HL}, enthalpies of reactions (2) and (4), respectively (ΔH_{HL} was determined by us previously [6]); and α_{MgL} and α_{HL}, fractions of MgL^{2-} and HL^{3-} formed during the calorimetric experiment (per mole of Mg^{2+}). The decrease in pH in the course of the experiment was within 0.2 unit; α_{MgL} ranged from 0.985 to 0.989, and $\alpha_{HL}\Delta H_{HL} \leq 1.6$ kJ mol^{-1}.

On mixing $Ca(NO_3)_2$ and H_4L solutions, the degree of formation of the Ca complex α_{CaL} was 0.998–1.000. Since calcium forms an unstable nitrate complex, the experimental $\Delta_d H$ was corrected for the heat of decomposition of $CaNO_3^+$ [Eq. (6)].

$$\Delta_{mix}H = \alpha_{CaL}\Delta_{CaL} + \alpha_{HL}\Delta H_{HL} + \Delta_d H - \alpha_{CaNO_3}\Delta H_{CaNO_3}. \quad (6)$$

Here ΔH_{CaNO3} is the enthalpy of formation of the complex $CaNO_3^+$ [17].

From $\log K$ and ΔH at a fixed ionic strength (see table), we can estimate the standard thermodynamic characteristics of the equilibria under study. To extrapolate the stability constants and enthalpies to zero ionic strength, we used Eqs. (7) and (8) with one individual parameter [18].

$$\log K - A\Delta z^2 I^{1/2}/(1 + 1.6I^{1/2}) = \log K_0 + bI, \quad (7)$$

$$\Delta H - \Delta z^2 \Psi(I) = \Delta H_0 + \delta I. \quad (8)$$

Here $\log K$, $\log K_0$, ΔH, and ΔH_0 are the stability constants and reaction enthalpies at current and zero ionic strengths, respectively; b and δ, empirical coefficients; Δz^2 is the difference of squared charges of the products and reactants; A, constant in the Debye–Hückel equation; and $\Psi(I)$, theoretical function of the ionic strength [18].

The differences in the thermodynamic characteristics of formation of the calcium and magnesium complexes with H_4L are caused essentially by the sizes of the metal cations. Because of higher charge density, the magnesium cation exhibits stronger polarizing capacity. The enthalpies of formation of the Mg and Ca complexes are opposite in the sign, demonstrating similar dependences on the ionic strength. The formation of MgL^{2-} and XaL^{2-} complexes is accompanied by large positive entropy changes (ΔS_{MgL} and ΔS_{CaL}) associated with the liberation of a large number of water molecules from the hydration shells of the initial ions, which considerably exceeds the effect of decreasing number of species due to complexation. In this case, ΔS_{MgL} is nearly twice as large as ΔS_{CaL}, which is not surprising, since the radius of Mg^{2+} is much smaller than that of Ca^{2+}, and the magnesium

cations are hydrated to a greater extent. A decrease in ΔS of formation of the Mg and Ca complexes with increasing ionic strength can be attributed to the ordering of the system by virtue of the orientation of polar molecules of the solvent in the vicinity of ions of the supporting electrolyte.

EXPERIMENTAL

In the work we used 2-hydroxypropylene-1,3-diamine-*N*,*N*,*N*',*N*'-tetraacetic acid synthesized at the Institute of Chemicals and Ultrapure Substances (Moscow). Its purity was confirmed by potentiometric titration. The content of anhydrous chelating agent was 97.2% (or 99.9% recalculated to $H_4L \cdot 0.5H_2O$). Solutions of KOH and HNO_3 were prepared from the chemicals of chemically pure grade. The nitrates of calcium (chemically pure grade) and magnesium (analytically pure grade) were recrystallized twice from double-distilled water. The concentration of the working solutions was determined by common titration methods.

The stability constants of the complexes of H_4L with Mg(II) and Ca(II) were determined by potentiometric titration at 298 K and ionic strength of 0.1, 0.5, and 1.0 M (KNO_3). An exact volume of the H_4L solution containing Mg or Ca ions and supporting electrolyte was placed in the temperature-controlled potentiometric cell. The initial H_4L concentration was 5×10^{-3} M and that of the metals, 5×10^{-3} and 10^{-2} M. Titration was carried out with standard carbonate-free KOH solutions (0.0764–0.0772 M) containing the supporting electrolyte of the same concentration. The amount of the standard solution added was determined gravimetrically.

pH was measured with an ESL-43-07 glass electrode vs. an EVL-1MZ saturated silver chloride reference electrode. The potential of the glass electrode was measured with a P-363/3 potentiometer. A pH-340 pH meter–millivoltmeter was used a null instrument. The potentials were measured to within 0.1 mV. The temperature of the potentiometric cell and electrodes was controlled to within 0.05 K. Prior to each measurement, the potentiometric system was calibrated with standard HNO_3 and KOH solutions containing potassium nitrate to adjust the desired ionic strength.

The enthalpy of formation of Ca and Mg hydroxypropylenediaminetetraacetates were determined calorimetrically at 298.15 K and ionic strength I of 0.1, 0.5, and 1.0 M (KNO_3). The experiments were carried out in an ampule-ype isothermal calorimeter equipped with a KMT-14 thermistor sensor and automatic recorder. The heats of mixing of the solutions of $Mg(NO_3)_2$ (0.8165 m) and $Ca(NO_3)_2$ (0.8243 m) with 5×10^{-3} M H_4L solution containing estimated amount of the supporting electrolyte and neutralized with KOH to pH 10.6–10.7 were measured. To introduce necessary corrections, we also determined the heats of dilution of the metal nitrate solutions with the supporting electrolyte solution at fixed ionic strengths.

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