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

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Abstract—The stability constants of the complexes of 2-hydroxypropylene-1,3-diamine *N,N,N',N'*-tetraacetic acid (H_4L) with Zn^{2+}, Cd^{2+}, and Mn^{2+} ions were determined by the potentiometric method on the background of KCl at 298.15 K and ionic strengths of 0.1, 0.5, and 1.0. The resulting data were extrapolated to the zero ionic strength by a one-parameter equation.

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Published data [1–5] on the stability constants of zinc, cadmium, and manganese(II) hydroxypropylenediamine tetraacetates essentially differ from each other (Table 1). Their analysis does not allow us to determine the most reliable values, and published values relate to a single ionic strength (I 0.1). The inconsistency of the data and the absence of information on the influence of ionic strength on the stability of complexonates have arose the necessity of experimental determination of the stability constants of the complexes at varied ionic strength.

In the present work we determined stability constants for zinc, cadmium, and manganese(II) complexes with 2-hydroxypropylene-1,3-diamine *N,N,N'*, *N'*-tetraacetic acid at 298.15 K and ionic strengths of 0.1, 0.5, and 1.0 (KCl) by potentiometric titration (see figure). The experimental data were processed using the PHMETR program designed for calculation of equilibrium constants with an arbitrary number of reactions on the basis of the measured equilibrium concentration of one of the species [6, 7]. The program is based on the principle of searching for a minimum of the criterion function F by varying in each iteration log β values to be determined, using a modified Hook–Jeeves' algorithm [8, 9]. The criterion function is given by Eq. (1).

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

Here $\log [H^+]_{j,\mathrm{exp}}$ and $\log [H^+]_{j,\mathrm{calc}}$ are the logarithms of the equilibrium concentrations of H^+, measured experimentally and calculated for current log β values. The equilibrium concentrations were calculated according to Brinkley's method [10, 11]. In processing the titration curves were took into consideration side processes (4)–12) occurring in the system along with reactions (2) and (3) that form the metal complexonates under study.

Table 1. Published stability constants of zinc, cadmium, and manganese(II) hydroxypropylenediamine tetraacetates

Method	*T*, K	*I* (background)	log β			Reference
			Zn^{2+}	Cd^{2+}	Mn^{2+}	
			$M^{2+} + L^{4-} \rightleftarrows ML^{2-}$			
Electrophoresis	293.15	0.1 (KNO_3)	13.50	12.50	9.00	[1]
Spectrophotometry	293.15	0.1 (KNO_3)	13.95	12.50	–	[2]
Polarography	293.15	0.1 (KCl)	12.95	11.70	8.20	[3]
Potentiometry	293.15	0.1 (KCl)	11.51	12.60	8.90	[4]
"	298.15	0.1 (KNO_3)	13.70	12.10	9.06	[5]
			$ML^{2-} + H^+ \rightleftarrows MHL^-$			
Potentiometry	298.15	0.1 (KNO_3)	3.58	4.12	5.10	[5]

$$M^{2+} + L^{4-} \rightleftarrows ML^{2-}, \tag{2}$$

$$ML^{2-} + H+ \rightleftarrows MHL^{-}, \tag{3}$$

$$H_4L \rightleftarrows HL^{3-} + H^{+}, \tag{4}$$

$$H_3L^{-} \rightleftarrows H_2L^{2-} \rightleftarrows H^{+}, \tag{5}$$

$$H_2L^{2-} \rightleftarrows HL^{3-} + H^{+}, \tag{6}$$

$$HL^{3-} \rightleftarrows L^{4-} + H^{+}, \tag{7}$$

$$M^{2+} + H_2O \rightleftarrows MOH^{+} + H^{+}, \tag{8}$$

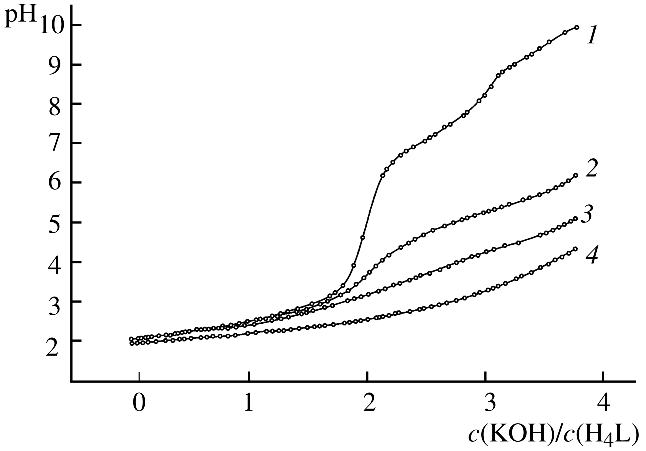
$$M^{2+} + Cl^{-} \rightleftarrows MCl^{+}, \tag{9}$$

$$M^{2+} + 2Cl^{-} \rightleftarrows MCl_2, \tag{10}$$

$$M^{2+} + 3Cl^{-} \rightleftarrows MCl^{3-}, \tag{11}$$

$$M^{2+} + 4Cl^{-} \rightleftarrows MCl^{4-}. \tag{12}$$

Previously we determined the step dissociation constants of H_4L (Table 2) at the same ionic strengths and temperatures [12]. The thermodynamic hydrolysis constants of zinc (pK_0 7.44), cadmium (pK_0 7.92), and manganese (pK_0 10.59) ions were taken from [13], and the summary thermodynamic stability constants of chloride complexes ($\log\beta^0$) were taken from [14]: 0.43 ($ZnCl^+$), 0.61 ($ZnCl_2$), 0.51 ($ZnCl_3^-$), and 0.20 ($ZnCl_4^{2-}$), from [15]: 1.98 ($CdCl^+$), 2.60 ($CdCl_2$), 2.40 ($CdCl_3^-$), and 1.70, and [16]: 0.54 ($MnCl^+$), 0.51 ($MnCl_2$), and –0.12 ($MnCl_3^-$). The stability constants of the zinc, cadmium and manganese(II) complexonates were determined by the results of 7–12 independent titrations at a corresponding ionic strength. The resulting data are presented in Table 2. The pair correlation coefficient [Eq. (13)] of the calculated $\log\beta$ (ML^{2-}) and $\log\beta$ (MHL^-) values span the range 0.34–0.49, which implies correctness of the joint determination of the stability constants of ML^{2-} and MHL^- complexes [17, 18] (it is known that at a better correlation of desired parameters allows experimental data to be adequately fitted even if the estimates for these parameters are erroneous [6, 19]).



Potentiometric titration curves of H_4L at $c(H_4L) = c(M) = 5\times10^{-3}$ M [298.15 K, I 0.5 (KCl)]. (*1*) in absence of metal ions, (*2*) in presence of Mn^{2+} ions, (*3*) in presence of Cd^{2+} ions, (*4*) in presence of Zn^{2+} ions.

$$\rho = \mathrm{Cov}[\log\beta(ML^{2-}), \log\beta(MHL^{-})]/\delta[\log\beta(ML^{2-})]\delta[\log\beta(MHL^{-})]. \tag{13}$$

Here $\mathrm{Cov}[\log\beta(ML^{2-}), \log\beta(MHL^{-})]$ is the co-

Table 2. Values of $\log\beta$ for zinc, cadmium, and manganese(II) complex formation and H_4L dissociation (pK) at 298.15 K and I 0.0, 0.1, 0.5, and 1.0 (KCl)

Reaction	I 0.0	I 0.1	I 0.5	I 1.0
$Zn^{2+} + L^{4-} \rightleftarrows ZnL^{2-}$	15.59±0.05	13.95±0.05	13.20±0.03	13.11±0.05
$Zn^{2+} + HL^{3-} \rightleftarrows ZnHL^{-}$	9.18±0.08	7.95±0.07	7.42±0.06	7.36±0.07
$ZnL^{2-} + H^{+} \rightleftarrows ZnHL^{-}$	4.12±0.04	3.72±0.04	3.68±0.04	3.74±0.02
$Cd^{2+} + L^{4-} \rightleftarrows CdL^{2-}$	13.88±0.06	12.21±0.03	11.64±0.06	11.53±0.04
$Cd^{2+} + HL^{3-} \rightleftarrows CdHL^{-}$	8.23±0.09	6.94±0.06	6.57±0.07	6.40±0.07
$CdL^{2-} + H^{+} \rightleftarrows CdHL^{-}$	4.88±0.05	4.45±0.05	4.39±0.04	4.36±0.04
$Mn^{2+} + L^{4-} \rightleftarrows MnL^{2-}$	10.69±0.06	9.03±0.04	8.66±0.04	8.65±0.04
$Mn^{2+} + HL^{3-} \rightleftarrows MnHL^{-}$	6.02±0.08	4.75±0.05	4.54±0.07	4.46±0.07
$MnL^{2-} + H^{+} \rightleftarrows MnHL^{-}$	5.86±0.04	5.44±0.02	5.34±0.04	5.30±0.04
$H_3L^{-} + H^{+} \rightleftarrows H_4L$	2.06±0.06	1.86±0.06	1.75±0.06	1.73±0.04
$H_2L^{2-} + H^{+} \rightleftarrows H_3L^{-}$	3.23±0.08	2.79±0.06	2.59±0.08	2.47±0.03
$HL^{3-} + H^{+} \rightleftarrows H_2L^{2-}$	7.80±0.06	7.25±0.03	7.11±0.03	7.36±0.06
$L^{4-} + H^{+} \rightleftarrows HL^{3-}$	10.53±0.04	9.72±0.03	9.46±0.04	9.49±0.04

variance of the $\log\beta(ML^{2-})$ and $\log\beta(MHL^{-})$ values; $\delta[\log\beta(ML^{2-})]$ and $\delta[\log\beta(MHL^{-})]$, their rms deviations.

In processing the experimental data we also considered the possibility of formation of MH_2L, $M(OH)L^{3-}$, $MLCl^{3-}$, M_2LCl^{-}, $M_2LCl_2^{2-}$, M_2L, M_2HL^{+}, and $M_2(OH)L^{-}$ complexes.

$$MHL^{-} + H^{+} \rightleftarrows MH_2L, \quad (14)$$

$$MHL^{-} + M^{2+} \rightleftarrows M_2HL^{+}, \quad (15)$$

$$ML^{2-} + M^{2+} \rightleftarrows M_2L, \quad (16)$$

$$ML^{2-} + OH^{-} \rightleftarrows M(OH)L^{3-}, \quad (17)$$

$$M_2L + OH^{-} \rightleftarrows M_2(OH)L^{-}, \quad (18)$$

$$ML^{2-} + Cl^{-} \rightleftarrows MLCl^{3-}, \quad (19)$$

$$MLCl^{3-} + M^{2+} \rightleftarrows M_2LCl^{-}, \quad (20)$$

$$M_2LCl^{-} + Cl^{-} \rightleftarrows M_2LCl_2^{2-}. \quad (21)$$

However, introduction of reactions (14)–(21) in the calculation scheme deteriorates the description, since the criterion function (1) is insensitive to these processes. We can thus conclude that the above complexes are not formed under the experimental conditions. The adequacy of the selected model and the absence of unaccounted reactions (14)–(21) are proved also by a good convergence of the results of processing titration curves obtained for various ratios of initial concentrations of the ligand and metal ions.

The thermodynamic stability constants of the complexonates were calculated by Eq. (22) with a single individual parameter [20].

$$\log\beta - A\Delta z^2\sqrt{I}(1 + 1.6\sqrt{I}) = \log\beta^0 + bI. \quad (22)$$

Here $\log\beta$ and $\log\beta^0$ are the logarithms of the concentration and thermodynamic stability constants, respectively; Δz^2, difference between the squared charges of reaction products and reacting species; A, Debye–Hückel constant; I, ionic strength of the solution; and b, empirical constant describing variation of the dielectric constant of the medium near ions. The $\log\beta^0$ values obtained by extrapolation of the corresponding concentration values to zero ionic strength are given in Table 1.

Comparison with published data shows that our $\log\beta(MnL^{2-})$ value agrees within inaccuracy limits with that reported in [1, 5], our $\log\beta(ZnL^{2-})$ value coincides with that obtained in [2], and the $\log(CdL^{2-})$ value is close to the average of those in [1, 2, 5].

We used the most reliable procedure for processing the experimental data, that allows sidereactions in the system to be considered without any simplifications, as opposed to the out-of-date procedures [1–4]. In [5], potentiometric data were processed by the GAUSS G program [21] that minimizes the sum of the squared errors in the analytical concentrations of hydrogen ions and involves considerable corrections arising in the calculation and resulting in oscillations and lack of convergence [19]. It should also be noted that in the present work, unlike [1–5], the electrode pair was calibrated by the concentration scale. As a result, we need not convert activities of hydrogen ions into their concentrations used for calculation of equilibrium constants. Furthermore, potentiometric measurements were performed at several ionic strengths ranging from 0.1 to 1.0. This allowed us to obtain reliable thermodynamic stability constants of the complexonates studied.

Comparison of the stability constants of zinc, cadmium, and manganese(II) hydroxypropylenediamine tetraacetates with those for the respective complexes of trimetylenediamine *N,N,N',N'*-tetraacetic acid {$\log\beta(ZnA^{2-})$ 15.26, $\log\beta(CdA^{2-})$ 13.90, and $\log\beta(MnA^{2-})$ 9.99 at 293.15 K and I 0.1 (KNO_3) [22]} shows that the former complexes are much less stable than the latter. This finding suggests that the hydroxy group of hydroxypropylenediamine tetraacetic acid does not form an additional chelate bonds with Zn^{2+}, Cd^{2+}, and Mn^{2+} ions, and the difference in the stabilities of these two groups of complexes is connected to the decreased basicity of the nitrogen atoms in H_4L, resulting from the inductive effect of the hydroxy group. Similar results were also obtained earlier in our laboratory [23–27] for some other metal complexonates.

EXPERIMENTAL

2-Hydroxypropylene-1,3-diamine *N,N,N',N'*-tetraacetic acid (H_4L) was synthesized at the Institute of Reagents and md REA (Moscow), and its purity was controlled by potentiometric titration. The content of anhydrous complexon was 97.2% (or 99.9% in terms of $H_4L \cdot 1/2H_2O$). Solutions of KOH and HCl were prepared from chemical grade reagents. The concentrations of working solutions were determined by conventional titrimetric methods.

Complex formation of H_4L with Zn^{2+}, Cd^{2+}, and Mn^{2+} ions was studied by potentiometric titration at 298.15 K and ionic strengths of 0.1, 0.5, and 1.0 (KCl). An exact volume of a complexon solution containing corresponding metal ions, with a preset ionic strength, was placed in a temperature-controlled potentiometric cell. The initial concentration of H_4L was 5×10^{-3} M, and those of metal ions, 3×10^{-3} and

5×10^{-3} M (for Zn^{2+}, Cd^{2+}, and Mn^{2+} ions) and 1×10^{-2} M (for Zn^{2+} and Cd^{2+} ions). The titrant was a standard KOH solution free from carbonates and with a background electrolyte added to avoid variation of the ionic strength during titration due to dilution. The amount of the titrant added was determined gravimetrically (by the decrease in the syringe weight). The curves of H_4L titration with KOH at 298.15 K and I 0.1 (KCl) in the presence of zinc, cadmium, and manganese(II) salts are shown in the figure. The titration curves at the other ionic strengths are similar.

The equilibrium concentration of hydrogen ions was determined by measuring the EMF of the circuit comprising an ESL-43-07 glass electrode and an EVL-1MZ saturated silver chloride electrode. The potential of the glass electrode was monitored by a P-363/3 potentiometer. A pH-340 pH-meter–millivoltmeter was used as zero instrument. The potential was measured with an accuracy of ±0.1 mV. The temperature of the potentiometric cell and electrodes was maintained accurate to ±0.05 K. Before recording each titration curve the potentiometric device was calibrated by standard HCl and KOH solutions containing potassium nitrate for creating a required ionic strength.

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