

Short Communication

ENTHALPY CHANGES IN FORMATION REACTIONS OF ZINC AND CADMIUM TRIMETHYLENEDIAMINETETRAACETATES

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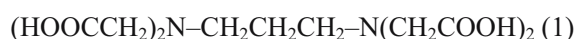
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Calorimetric enthalpy changes in reactions have been measured for the formation of zinc and cadmium trimethylenediaminetetraacetates at 298.15 K and ionic strengths of 0.1, 0.5, 1.0 mol L⁻¹ (KNO₃). The standard thermodynamic parameters of the reactions studied were evaluated from calorimetric and potentiometric measurements under the same conditions. The results obtained were compared with the corresponding data on related compounds.

Keywords: chelates, complexone, enthalpy, entropy, ionic strength

Introduction

Alkylenediaminetetraacetic acids have obtained large recognition. They are widely used in medicine, agriculture, building, galvanic, and metallurgical engineering. Their unique properties offer ample scope for progress of the complexone chemistry. Among the chelating agents of interest is trimethylenediamine-N,N,N',N'-tetraacetic acid (1,3-diaminopropane-N,N,N',N'-tetraethanoic acid, H₄L, TMDTA).



The only work [1] on the thermodynamic parameters of its complexation equilibria is available. That has reported some reaction quantities (Table) for zinc and cadmium trimethylenediaminetetraacetates at 293.15 K and an ionic strength of 0.1 mol L⁻¹ (KNO₃). The influence of the ionic strength on the complexation of TMDTA has not yet been studied. The lack of information on the concentration dependence of the thermodynamic parameters, and the invariety of the data published made it necessary to examine these processes calorimetrically and to determine how ΔH depends on the ionic strength. It therefore seemed useful to measure the relevant reaction enthalpy changes at 298.15 K and various ionic strengths, and to evaluate the standard thermodynamic parameters for zinc and cadmium trimethylenediaminetetraacetates.

Experimental

Trimethylenediamine-N,N,N',N'-tetraacetic acid synthesized at the IREA Research Institute of Chemicals and High-Purity Substances (Moscow) was used. Nitric acid and potassium hydroxide solutions were prepared from reagent grade samples. Zinc, cadmium, and potassium nitrates (analytical grade) were twice crystallized from bidistilled water. The concentrations of working solutions were determined by conventional titrimetric methods.

Enthalpy changes in formation reactions of zinc and cadmium trimethylenediaminetetraacetates have been determined by calorimetry at 298.15 K and ionic strengths of 0.1, 0.5, 1.0 mol L⁻¹. The support electrolyte was potassium nitrate. The heats of mixing 0.2408 M Zn(NO₃)₂ and 0.3999 M Cd(NO₃)₂ solutions with a solution of the complexone ($c=0.01$ mol L⁻¹), which contained the required amount of a background electrolyte and was neutralized with a KOH solution to pH values of 11.8–12.1 were measured. In case of $I=0.1$ mol L⁻¹, these measurements were complemented by the relevant data obtained at pH of 10.9–11.4. The total concentration ratio M(NO₃)₂:TMDTA for the final solution was 0.76–0.92. The heats of dilution for the metal nitrate solutions with a background electrolyte at the corresponding ionic strengths were also measured applying necessary corrections. The measurements were performed in an isothermal jacket calorimeter

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equipped with a KMT-14 thermistor. The calorimetric unit was tested against the heat of solution of crystalline potassium chloride in water. A good agreement between the experimentally measured values and the most reliable literature data [2] showed no significant systematic errors in the calorimeter measurements.

Results and discussion

At pH values of 11.8–12.1, the complexone occurs as completely deprotonated anion L^{4-} . The enthalpy changes in reaction of ML^{2-} complex formation can be found as the difference between the heats of mixing and dilution:

$$\Delta H = \Delta_{\text{mix}}H - \Delta_{\text{dil}}H \quad (2)$$

where $\Delta_{\text{mix}}H$ is the heat of mixing the metal nitrate solution with the complexone solution, $\Delta_{\text{dil}}H$ is the heat of dilution for the metal nitrate solution with the background electrolyte solution. The reaction enthalpy changes obtained for zinc and cadmium trimethylenediaminetetraacetates at 298.15 K and $I=0.1, 0.5, 1.0 \text{ mol L}^{-1}$ (KNO_3) are shown in Table.

A decrease of the initial solution pH values down to 10.9–11.4 makes it necessary to include the dissociation of HL^{3-} species being under these conditions:

$$\Delta H = \Delta_{\text{mix}}H - \Delta_{\text{dil}}H + \Delta_{\text{dis}}H \cdot \Delta[\text{HL}^{3-}]/c_M \quad (3)$$

where $\Delta_{\text{dis}}H = 23.52 \pm 0.26 \text{ kJ mol}^{-1}$ found at 298.15 K and $I=0.1 \text{ mol L}^{-1}$ (KNO_3) using a calorimetric procedure [3] is the enthalpy change in HL^{3-} dissociation process; $\Delta[\text{HL}^{3-}]$ is change in equilibrium concentration of this species; c_M is total concentration of the metal in the final solution. The ΔH values obtained at 298.15 K and $I=0.1 \text{ mol L}^{-1}$ (KNO_3) are -12.56 ± 0.26 and $-23.78 \pm 0.27 \text{ kJ mol}^{-1}$ for zinc and cadmium complexonates, respectively.

The reaction enthalpy changes at zero ionic strength were determined by extrapolating the ΔH values found at the fixed ionic strengths using one-parameter Eqs [4, 5]:

$$\Delta H - \Delta z^2 \Psi(I) = \Delta H^0 + bI \quad (4)$$

where ΔH , ΔH^0 denote the enthalpy changes at the finite and zero ionic strengths, respectively; b is an empirical coefficient; Δz^2 is the difference between the squared charges of reaction products and reacting species; and $\Psi(I)$ is a function of ionic strength deduced theoretically [4, 5]. The ΔG^0 and ΔS^0 values were calculated from the ΔH^0 and $\log K^0$ values. The thermodynamic stability constants were evaluated using the following Eqs [5, 6].

$$\log K - A_\gamma \Delta z^2 I^{1/2} / (1 + 1.6I^{1/2}) = \log K^0 + \delta I \quad (5)$$

where K^0 , K denote the thermodynamic and stoichiometric stability constants, respectively; A_γ is the Debye parameter; δ is an empirical coefficient. The stoichiometric stability constants have been found at 298.15 K and $I=0.1, 0.5, 1.0 \text{ mol L}^{-1}$ (KNO_3) using a potentiometric procedure described previously [7, 8]. The thermodynamic parameters obtained are presented in Table 1. This table also contains the corresponding parameters [9–15] for ethylenediamine- N,N,N',N' -tetraacetic (EDTA), 2-hydroxypropylene-1,3-diamine- N,N,N',N' -tetraacetic (HPDTA), imino- N,N -diacetic (IDA) and β -hydroxyethylimino- N,N -diacetic (HEIDA) acids.

These data shows that the complexes with HPDTA and TMDTA are significantly less stable than the corresponding complexes with EDTA, probably because a six-membered chelate cycle is formed in the HPDTA and TMDTA complexes in place of the five-membered cycle in the EDTA complexes. The lower stability of HPDTA complexes compared to TMDTA complexes suggest that the hydroxy group of hydroxypropylenediaminetetraacetic acid is not involved in the formation of an extra chelate bond with Zn^{2+} and Cd^{2+} ions. The difference in stability between TMDTA and HPDTA complexes is related to the decreased basicity of the ligand nitrogen because of the induction effect of the hydroxy group and the formation of $\text{N} \cdots \text{H} - \text{O} - \text{C}$ cycles [16] in HPDTA molecule.

The formation of complexonates ZnL^{2-} and CdL^{2-} is characterized by a negative value of ΔH , the absolute value significantly decreases in the series of $\text{EDTA} > \text{TMDTA} > \text{HPDTA}$. This can be attributed to weakening of the $\text{M}-\text{N}$ bond when going from EDTA to HPDTA. A similar decrease in ΔH is observed when going from IDA to HEIDA. These iminodiacetic acids are the structural elements of EDTA, TMDTA and HPDTA. The ΔS values for the formation reactions of TMDTA complexonates are similar to entropy changes during analogous reactions of HPDTA and EDTA. A significant decrease in ΔS , which is observed when going from EDTA, TMDTA, and HPDTA complexes to bis-complexes of IDA and HEIDA, is consistent with the absence of a carbon chain between nitrogen atoms in the latter, which makes the formation of alkylenediamine chelate cycles impossible.

Significant positive entropy changes in the complexonate formation reactions are related to the release of a large number of water molecules from the hydrate shells of the starting ions, which significantly exceeds the decrease in the number of species due to complexation. The decrease in ΔS , which is observed when the ionic strength of solution increases, is attributed to the ordering of the system due to the orientation of polar solvent molecules around background

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Table 1 Thermodynamic parameters for zinc and cadmium complexonates

<i>T</i> /K	<i>I</i> *	log <i>K</i>	-Δ <i>G</i> /kJ mol ⁻¹	-Δ <i>H</i> /kJ mol ⁻¹	Δ <i>S</i> /J mol ⁻¹ K ⁻¹	Ref.
Zn²⁺+L⁴⁻↔ZnL²⁻ (TMDTA)						
298.15	0.0	16.77±0.04	95.72±0.23	8.99±0.17	290.9±1.0	this
	0.1	15.14±0.04	86.42±0.23	12.41±0.17	248.2±1.0	work
	0.5	14.29±0.04	81.56±0.23	14.83±0.14	223.8±0.9	
	1.0	14.23±0.04	81.22±0.23	16.38±0.15	217.5±0.9	
293.15	0.1	15.26	85.64	9.50	259.7	[1]
Zn²⁺+L⁴⁻↔ZnL²⁻ (HPDTA)						
298.15	0.0	15.59	88.99	4.58	283.1	[9]
	0.1	13.94	79.57	8.06	239.9	
	0.5	13.22	75.50	10.47	218.0	
	1.0	13.09	74.72	12.14	209.9	
Zn²⁺+L⁴⁻↔ZnL²⁻ (EDTA)						
293.15	0.1	16.50	92.60	20.29	246.7	[10]
293.15	0.17	16.49	92.55	23.47	235.6	[11]
298.15	0.1	16.56	94.54	23.43	238.5	[12]
Zn²⁺+2L²⁻↔ZnL₂²⁻ (IDA)						
298.15	0.0	13.21	75.40	24.23	171.6	[13]
	0.2	12.21	69.69	26.28	145.6	
	0.5	12.01	68.55	27.91	136.3	
	1.0	11.95	68.21	29.12	131.1	
Zn²⁺+2L²⁻↔ZnL₂²⁻ (HEIDA)						
298.15	0.0	12.84	73.29	16.43	190.7	[14]
	0.3	11.74	67.01	18.77	161.8	
	0.5	11.64	66.44	19.19	158.5	
	1.0	11.58	66.10	19.70	155.6	
Cd²⁺+L⁴⁻↔CdL²⁻ (TMDTA)						
298.15	0.0	14.99±0.05	85.56±0.29	19.93±0.16	220.1±1.1	this
	0.1	13.34±0.04	76.14±0.23	23.34±0.16	177.1±0.9	work
	0.5	12.59±0.04	71.86±0.23	25.54±0.12	155.4±0.9	
	1.0	12.51±0.05	71.40±0.29	26.98±0.16	149.0±1.1	
293.15	0.1	13.90	78.01	22.76	188.5	[1]
Cd²⁺+L⁴⁻↔CdL²⁻ (HPDTA)						
298.15	0.0	13.86	79.11	12.90	222.1	[9]
	0.1	12.25	69.92	16.34	179.7	
	0.5	11.60	66.21	18.94	158.6	
	1.0	11.55	65.93	20.61	152.0	
Cd²⁺+L⁴⁻↔CdL²⁻ (EDTA)						
293.15	0.1	16.46	92.37	37.87	185.9	[10]
293.15	0.17	16.45	92.34	42.18	171.1	[11]
298.15	0.1	16.58	94.64	42.18	175.7	[12]
298.15	0.0	18.11	103.36	36.60	223.9	[15]
	0.5	15.64	89.25	42.11	158.1	
	1.0	15.45	88.17	43.78	148.9	
	1.5	15.44	88.10	44.39	146.6	

* Potassium nitrate was used as the background electrolyte

electrolyte ions. The entropy change in the formation reactions for zinc complexonates is 1.3–1.4 times the corresponding values for cadmium complexonates. This can be explained by the fact that cadmium ions in aqueous solutions are hydrated significantly lower than zinc ions.

For the reactions of EDTA, TMDTA, and HPDTA, the similar relationship between the thermodynamic parameters and the ionic strength of solution are observed. This indicates that the change in the core of alkylendiaminetetraacetic acid has no significant effect on the complexation of zinc and cadmium with these complexones in aqueous solutions and that the modification of the alkylene bridge only affects the numerical values of $\log K$ and ΔH because of a decrease in basicity of nitrogen atoms when going from EDTA to HPDTA.

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