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Thermodynamic Characteristics of Protolytic Equilibria of Trimethylenediamine-*N,N,N′,N′*-tetraacetic Acid

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Abstract—The thermal effects of the neutralization of betainic protons of trimethylenediamine-*N,N,N′,N′*-tetraacetic acid (H_4L) at 298.15 K and ionic strength of 0.3, 0.5, and 1.0 (KNO_3) were directly measured by calorimetry. The standard thermodynamic characteristics of the protolytic equilibria of H_4L were calculated from a combination of thermochemical and potentiometric data obtained under identical experimental conditions. The results obtained were compared with the corresponding data for related compounds taking into account the specific structure of diamine complexones.

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Thanks to a favorable combination and mutual arrangement of donor centers in the molecule of trimethylenediamine-*N,N,N′,N′*-tetraacetic acid **I**, this compound is one of the most promising versatile complexones.

$$(HOOCCH_2)_2NCH_2CH_2CH_2N(CH_2COOH)_2$$

Nevertheless, the thermodynamic characteristics of equilibria involving **I** are studied inadequately. In particular, the published values of the thermal effects of dissociation of betaine protons in the complexone are essentially inconsistent: $\Delta_{dis}H_3$ 22.7, $\Delta_{dis}H_4$ 29.6 kJ mol^{-1} at 298.15 K and I 0.5 (Na ClO_4) [1]; $\Delta_{dis}H_3$ 18.5, $\Delta_{dis}H_4$ 21.6 kJ mol^{-1} 293.15 K and 0.1 (KNO_3) [2]. Furthermore, measurements in [1, 2] were performed at a single ionic strength (I). The influence of the ionic strength on the protolytic equilibria of **I** were not considered. The lack of data on the concentration dependence of the thermodynamic characteristics, the inconsistency of the published data, and the practical importance of this complexone stimulated us to measure calorimetrically the thermal effects of the neutralization of betaine protons in **I** at several ionic strengths and to determine the standard thermodynamic characteristics of protolytic equilibria of this complexone.

In this study we measured by the direct calorimetric method the thermal effects of the acid–base transformations of **I** in aqueous solutions at 298.15 K and I 0.3, 0.5, and 1.0 (KNO_3). The results are given in Table 1. The table also contains the equilibrium constants determined potentiometrically at the same values of the ionic strength and temperature. The procedure of potentiometric measurements and treatment of the experimental data is described in [3].

The values of ΔH and log K found at fixed ionic strengths allow calculation of thermodynamic characteristics of the corresponding reactions in a standard solution. For the extrapolation of the concentration thermal effects and constants of the protolytic equilibria of **I** to zero ionic strength, we used equations with one individual parameter [4]:

$$\Delta_{dis}H - \Delta z^2\Psi(I) = \Delta_{dis}H^0 + bI, \quad (1)$$

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

where ΔH, ΔH^0, K, and K^0 are the thermal effects and equilibrium constants at finite and zero ionic strengths, respectively; A, constant of the Debye–Hückel theory; b and Δ, empirical coefficients; Δz^2, difference between the squared charges of the reaction products and reacting species; $\Psi(I)$, theoretically

calculated function of the ionic strength [4]. The obtained standard thermodynamic characteristics of the reactions of dissociation of **I** are given in Table 2, together with the corresponding values for 2-hydroxypropylene-1,3-diamine-*N,N,N′,N′*-tetraacetic (**II**), ethylenediamine-*N,N,N′,N′*-tetraacetic (**III**), and ethylenediamine-N,*N′*-disuccinic (**IV**) acids determined previously in our laboratory [5–11].

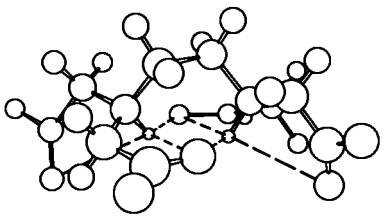
The betaine proton is takes off the H_2L^{2-} form of **III** considerably more readily than from the related forms of **I** and **II**. This may be due to the possibility of formation of "twisted" conformations of the complexones derived from ethylenediamine, via mutual approach of two imino carboxylate fragments and closure of cross N–H···OOC bonds of the glycinate type [12–15], which results in weakening of the N–H bond. The structure of the "twisted" conformation of the H_2L^{2-} anion of ethylenediaminetetraacetic acid is shown in the figure as an example. At the same time, compounds **I** and **II** form stable conformation inly of the "open" structure (Table 3), because increased length of the aliphatic chain between the nitrogen atoms prevents formation of such cross bonds. This fact may be responsible for a considerable decrease in the entropy of the corresponding reactions in going from **III** and **IV** to **I** and **II**. A decrease in $\Delta_{dis}H^0$ of dissociation of betaine protons in going from **I** to **II** is apparently caused by weakening of the N–H

Table 1. Thermodynamic characteristics of protolytic equilibria of trimethylenediamine-*N,N,N′,N′*-tetraacetic acid at 298.15 K

$I(KNO_3)$	log K	$-\Delta G$, J mol^{-1}	$-\Delta H$, J mol^{-1}	ΔS, J mol^{-1} K^{-1}
$H_2L^{2-} + OH^- = HL^{3-} + H_2O$				
0.3	5.88±0.04	33563±229	35128±189	–5.2±1.0
0.5	5.87±0.04	33506±229	34472±197	–3.2±1.0
1.0	5.90±0.05	33677±286	32867±183	2.7±1.1
$HL^{3-} + OH^- = L^{4-} + H_2O$				
0.3	3.71±0.04	21177±229	32346±179	–37.5±1.0
0.5	3.77±0.04	21519±229	31962±187	–35.0±1.0
1.0	3.74±0.04	21348±229	31147±184	–32.9±1.0
$HL^{3-} + H^+ = H_2L^{2-}$				
0.3	7.84±0.04	44750±229	21658±442	77.5±1.7
0.5	7.84±0.04	44750±229	22428±446	74.9±1.7
1.0	7.81±0.05	44579±286	23853±237	69.5±1.2
$L^{4-} + H^+ = HL^{3-}$				
0.3	10.01±0.04	57137±229	24440±438	109.7±1.7
0.5	9.94±0.04	56737±229	24938±442	106.7±1.7
1.0	9.97±0.04	56908±229	25573±237	105.1±1.1

Table 2. Standard thermodynamic characteristics of the reactions of dissociation of betaine protons in some diamine complexones

Process	pK^0	$\Delta_{dis}G^0$, kJ mol^{-1}	$\Delta_{dis}H^0$, kJ mol^{-1}	$-\Delta_{dis}S^0$, J mol^{-1} K^{-1}
Trimethylenediamine-*N,N,N′,N′*-tetraacetic acid				
$H_2L^{2-} = HL^{3-} + H^+$	8.47±0.03	48.35±0.17	19.27±0.45	97.5±1.6
$HL^{3-} = L^{4-} + H^+$	11.07±0.03	63.19±0.17	22.02±0.44	138.1±1.6
2-Hydroxypropylene-1,3-diamine-*N,N,N′,N′*-tetraacetic acid [5, 6]				
$H_2L^{2-} = HL^{3-} + H^+$	7.79±0.04	44.47±0.23	15.68±0.25	96.5±1.1
$HL^{3-} = L^{4-} + H^+$	10.51±0.03	59.99±0.17	20.11±0.24	133.8±1.0
Ethylenediamine-*N,N,N′,N′*-tetraacetic acid [7–9]				
$H_2L^{2-} = HL^{3-} + H^+$	6.80±0.04	38.81±0.23	16.86±0.25	73.6±1.1
$HL^{3-} = L^{4-} + H^+$	11.05±0.03	63.07±0.17	22.59±0.17	135.8±0.8
Ethylenediamine-N,*N′*-disuccinic acid [10, 11]				
$H_2L^{2-} = HL^{3-} + H^+$	7.53±0.06	43.0±0.3	20.8±0.1	74.5±1.2
$HL^{3-} = L^{4-} + H^+$	11.12±0.10	64.8±0.7	27.0±0.5	122.5±2.7



"Twisted" conformation of the H_2L^{2-} ion of ethylenediaminetetraacetic acid (according to quantum-chemical calculations).

bond due to formation of N–H···OH bonds of the nitrilohy-droxyethyl type [14–16], and close values of $\Delta_{dis}S^0$ suggest similar structure and solvation of the corre-sponding zwitterions in aqueous solution. Considerably increased $\Delta_{dis}H_3^0$ and $\Delta_{dis}H_4^0$ in the case of **IV** are due to replacement of the tertiary nitrogen atoms in **I–III** by secondary ones in **IV**. A similar change in the thermal effect of the dissociation of the betaine proton is also observed in monoamine complexones in going from *N*-(β-hydroxyethyl)imino-*N,N*-diacetic ($\Delta_{dis}H_2^0$ 20.34 kJ mol^{-1} [17]), nitrilo-*N,N,N*-triacetic ($\Delta_{dis}H_3^0$ 19.53 kJ mol^{-1} [18, 19]), and *N,N*-bis(carboxymethyl)aspartic ($\Delta_{dis}H_4^0$ 20.38 kJ mol^{-1} [20]) acids to imino-*N,N*-diacetic ($\Delta_{dis}H_2^0$ 32.84 kJ mol^{-1} [21]) and imino-*N,N*-disuccinic ($\Delta_{dis}H_4^0$ 25.92 kJ mol^{-1} [22]) acids.

EXPERIMENTAL

Trimethylenediamine-*N,N,N′,N′*-tetraacetic acid was prepared in the Institute of Chemical Reagents and Ultrapure Chemical Substances (IREA, Moscow).

Table 3. Heats of formation of molecules and ions of **I–II**

Form	$-\Delta_f H$, kJmol^{-1}			
	I	**II**	**III**	**III**[a]
H_6L^{2+}	99.24	112.21	–149.95	–140.25
H_5L^{+}	659.77	895.29	599.07	639.98
H_4L	1126.92	1362.10	1124.83	1164.45
H_3L^{-}	1414.57	1634.90	1372.94	1357.25
H_2L^{2-}	1441.64	1643.81	1391.14	1396.45
HL^{3-}	1194.53	1400.68	1134.32	–
L^{4-}	687.31	879.85	573.00	–

[a] Data refer to the "twisted" conformation of **III** and to open conformations of the other complexones.

The purity of the compound was checked by potentiometric titration; it was as high as 99.4%. KOH solutions were prepared from the chemically pure grade alkali. The concentrations of the working solutions were determined by common titration methods. Analytically pure grade KNO_3 used for supporting the required ionic strength was recrystallized two times from double-distilled water before use.

The calorimetric measurements were performed in an ampule calorimeter with an isothermal shell, a thermistor temperature sensor, and automatic recording of the temperature variation in time [5]. At 298.15 K and ionic strengths of 0.3, 0.5, and 1.0 (KNO_3), we measured the thermal effects of mixing a KOH solution (2.9736 mol kg^{-1} solution) with 0.0071–0.0114 M solutions of the complexone in the ranges pH 7.0–7.8 and 9.6–10.5. To make the required corrections, we also measured the heats of dilution of KOH in the supporting electrolyte solutions of the corresponding ionic strengths.

Calculation of the equilibrium compositions shows that, at pH 7.0–7.8 and 9.6–10.5, potassium hydroxide added to the solution virtually fully reacts with the betainic proton to form HL^{3-} and HL^{4-}, respectively, and the thermal effects of the neutralization with the formation of HL^{3-} and HL^{4-} (Table 1) can be found as differences between the corresponding heats of mixing and dilution:

$$\Delta_{neut}H = (\Delta_{mix}H - \Delta_{dil}H)/\alpha. \quad (3)$$

Here $\Delta_{mix}H$ is the thermal effect of mixing of a KOH solution with a solution of **I** in the presence of a supporting electrolyte in the corresponding pH range; $\Delta_{dil}H$ is the thermal effect of dilution of a KOH solution in the supporting electrolyte at the same ionic strength; and α is the degree of completion of the neutralization. From the thermal effects of the neutralization reactions, it is possible to calculate the corresponding thermal effects of the protonation of trimethylenediaminetetraacetic acid (Table 1):

$$-\Delta_{prot}H(HL^{3-}) = \Delta_{dis}H_3 = \Delta_{neut}H(H_2L^{2-}) + \Delta_wH, \quad (4)$$

$$-\Delta_{prot}H(L^{4-}) = \Delta_{dis}H_4 = \Delta_{neut}H(HL^{3-}) + \Delta_wH, \quad (5)$$

$$H_2O = H^+ + OH^-, \quad (6)$$

where $\Delta_w H$ is the thermal effect of reaction (6); the values of $\Delta_w H$ at the required ionic strengths and temperature are given in [23].

As auxiliary data we used the results of a quantum-chemical calculation of the structure of isolated molecules and ions of **I–III**. The calculation was performed using standard MOPAC v.6.0 software [24] by the AM1 semiempirical method [25], with full optimization of all the geometric parameters. More detailed information on the structure of a series of mono- and diamine complexones is given in [14, 15].

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