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Thermodynamic Characteristics of Protolytic Equilibria of Ethylenediamine-*N,N*'-Diacetic-*N,N*'-Dipropionic Acid

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Abstract—Heat effects of protonation and neutralization of ethylenediamine-*N,N*'-diacetic-*N,N*'-dipropionic acid at 298.15 K and ion force values of 0.1, 0.5, and 1.0 (KNO_3) were measured by the direct calorimetric method. Combined use of the results of thermochemical and potentiometric measurements carried out under the identical experimental conditions permitted to evaluate standard thermodynamic characteristics of the equilibria under study. The results obtained were compared with the corresponding data for related compounds considering the specific features of structure of the diamine complexones.

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Among the complexones having the greatest practical use special place is occupied by the derivatives of ethylenediamine-*N,N,N',N'*-tetraacetic acid. Due to the fortunate combination and reciprocal location of donor centers in the molecule this compound proved to be one of the most effective universal complexones having broad use in various fields of technology, analytical chemistry, and medicine [1]. At the same time this ligand is characterized by low selectivity of complex formation. One of the directions of the improvement of selectivity of complexones with respect to some cations is the increase in number of the methylene groups between the nitrogen atoms and the introduction of functional groups containing electron-donating atoms in this fragment. Another promising way is the reconstruction of carboxylate groups of complexones.

Recently we have studied the protolytic equilibria in water solutions of ethylenediamine-*N,N,N',N'*-tetraacetic [2–10], trimethylenediamine-*N,N,N',N'*-tetraacetic [11–13], 2-hydroxypropylene-1,3-diamine-*N,N,N',N'*-tetraacetic [14, 15], hexamethylenediamine-*N,N,N',N'*-tetraacetic [16], *N*-(β-hydroxyethyl)ethylenediamine-*N,N,N',N'*-triacetic [17, 18], ethylenediamine-*N,N'*-disuccinic [19–21], and ethylenediamine-*N,N,N',N'*-tetrapropionic [22–24] acids.

Here we report on the heat effects of the acid-base interaction in water solutions of ethylenediamine-*N,N'*-diacetic-*N,N'*-dipropionic acid at 298.15 K and the ion force values of 0.1, 0.5, and 1.0 measured by the direct calorimetric method. Potassium nitrate was used as the background electrolyte. The results obtained are listed in Table 1 together with the values of equilibrium constants found previously from the potentiometric measurements at the above mentioned temperature and ion force values [24].

Values ΔH and $\log K$ found at the fixed ion force permit the calculation of the thermodynamic characteristics of corresponding reactions in a standard solution. For the extrapolation of the concentrational heat effects and the protolytic equilibria constants for compound **I** to the zero ion force value equations with one individual parameter were used:

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

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

Here ΔH, ΔH^0, K, K^0 are heat effects and the reaction constants at the final and zero ion force respectively, A is the Debye–Huekkel constant, b and δ are the empiric coefficients, Δz^2 is the difference in charge squares of the reaction products and the reacting particles, $\Psi(I)$ is the ion force function calculated theoretically [25]. The obtained standard thermodynamic characteristics of the dissociation reactions of compound **I** are presented in Table 2 together with the corresponding data for ethylenediamine-*N,N,N',N'*-tetraacetic **II**, *N*-(β-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic **III**, ethylenediamine-*N,N'*-disuccinic **IV**, and ethylenediamine-

Table 1. Thermodynamic characteristics of protolytic equilibria for compound **I** at 298.15 K

$I(KNO_3)$	log K	$-\Delta G$, J mol^{-1}	$-\Delta H$, J mol^{-1}[a]	ΔS, J mol^{-1} K^{-1}
$HL^{3-} + OH^- = L^{4-} + H_2O$				
0.1	3.94±0.03	22489±172	32714±435	–34.3±1.6
0.5	4.02±0.03	22946±172	30603±148	–25.7±0.8
1.0	4.10±0.02	23403±114	28275±134	–16.3±0.6
$H_2L^{2-} + OH^- = HL^{3-} + H_2O$				
0.1	7.69±0.03	43894±172	43043±413	2.9±1.5
0.5	7.68±0.03	43837±172	41175±178	8.9±0.8
1.0	7.68±0.03	43837±172	39088±136	15.9±0.7
$L^{4-} + H^+ = HL^{3-}$				
0.1	9.84±0.03	56166±172	23951±170	108.0±0.8
0.5	9.69±0.03	55310±172	26461±145	96.8±0.8
1.0	9.61±0.02	54854±114	28545±126	88.2±0.6
$HL^{3-} + H^+ = H_2L^{2-}$				
0.1	6.09±0.03	34762±172	13622±103	70.9±0.7
0.5	6.03±0.03	34419±172	15819±94	62.4±0.7
1.0	6.03±0.03	34419±172	17670±93	56.2±0.7
$H_2L^{2-} + H^+ = H_3L^-$				
0.1	3.86±0.03	22033±172	2651±102	65.0±0.7
0.5	3.79±0.03	21633±172	3218±129	61.8±0.7
1.0	3.74±0.05	21348±286	3560±135	59.7±1.1
$H_3L^- + H^+ = H_4L$				
0.1	3.01±0.04	17181±229	2062±337	50.7±1.4
0.5	2.98±0.05	17010±286	2491±310	48.7±1.3
1.0	3.05±0.06	17409±343	3387±324	47.0±1.6
$H_4L + H^+ = H_5L^+$				
0.1	1.79±0.09	10217±514	–	–
0.5	1.79±0.08	10217±457	–	–
1.0	1.82±0.05	10388±286	–	–
$H_5L^+ + H^+ = H_6L^{2+}$				
0.1	1.11±0.19	6336±1085	–	–
0.5	1.08±0.16	6164±914	–	–
1.0	1.09±0.18	6222±1028	–	–

[a] At I 0.5 and 1.0 weighted mean values of heat effects of the reactions with participation of the "betaine" protons from the results obtained by alternative procedures are presented.

N,N,N',N'-tetrapropionic **V** acids found by us previously using the analogous experimental procedures.

On the whole the above-mentioned complexones exhibit analogous acid-base properties. The last two dissociation stages correspond to elimination of the "betaine" protons while the rest ones relate to the carboxy groups. At the same time dissociation of H_4L and H_3L^- (H_3L) results from the elimination of protons from α-carboxy groups of compounds **II**, **III** and β-carboxy groups of the complexones **I**,**IV**,**V** (α-carboxy groups of the acids **I** and **IV** having higher acidity as compared to β-carboxy ones are deprotonated initially due to the formation of the zwitterionic structure H_4L). Consequently, the formation of cationic acids H_5L^+ (H_4L^+) is possible by protonation of α-carboxy groups in compounds **I**–**IV** and β-carboxy group in substance **V**. *S*ome difference in the thermodynamic characteristics of dissociation of the corresponding functional groups in the series of compounds **I**–**V** is connected evidently with the peculiarities of composition of bi- and trifurcate blocks of intramolecular hydrogen bonds N–H···O of the glycinate and β-alaninate type conjugated by the N–H bond [26–29].

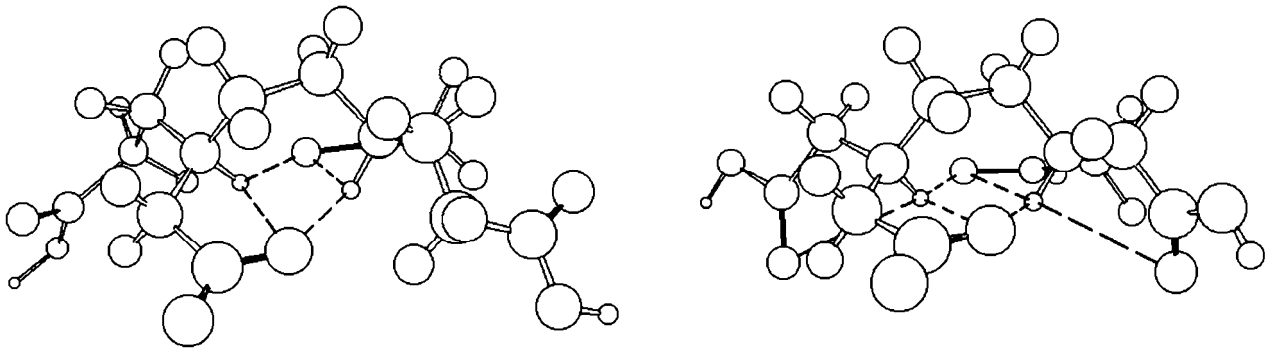
"Betaine" protons of compound **II** form trifurcate intramolecular N–H···O hydrogen bonds with two oxygen atoms of the adjacent acetate fragments and one oxygen atom of the other half of the molecule (Fig. 1). Analogous structure of complexone molecule with the formation of trifurcate NHO-blocks on the whole is conserved in the case of compounds **III**, **IV**. At the same time in the case of products **I** and **V** unlike substances **II**–**IV** no structures containing simultaneously two trifurcate NHO-blocks are found. Both complexones form only two bifurcate NHO-blocks. The decrease in $\Delta_{dis}S^0$ of dissociation of compounds **I**, **V** as compared to **II**–**IV** also may favor the increase in the hydration degree of the corresponding zwitterions due to the increase in the distance between the carriers of positive and negative charges. Analogous variation in the thermodynamic characteristics at the substitution of the glycine fragments by β-alanine ones is observed also (Table 3) in the reactions with participation of amino acids and dipeptides [30–34]. The increase in $\Delta_{dis}S^0$ of dissociation of H_3L^- in going from compound **II** to substance **I** has the exceptional character and on the whole does not contradict the above-described tendency because in these complexones different structures of zwitterions are formed (Fig. 1). Greater hydration of ions arising from the increase in their formal charges (more correctly, from the increase in

Table 2. Standard thermodynamic characteristics of the dissociation reactions of the ethylenediamine-based 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}
Ethylenediamine-*N*,*N*'-diacetic-*N*,*N*'-dipropionic acid				
$H_5L^+ = H_4L + H^+$	1.78±0.09	10.16±0.51	–	–
$H_4L = H_3L^- + H^+$	3.20±0.04	18.27±0.23	1.45±0.34	56.4±1.4
$H_3L^- = H_2L^{2-} + H^+$	4.29±0.05	24.49±0.29	1.80±0.14	76.1±1.1
$H_2L^{2-} = HL^{3-} + H^+$	6.72±0.03	38.36±0.17	12.11±0.10	88.0±0.7
$HL^{3-} = L^{4-} + H^+$	10.69±0.03	61.02±0.17	22.00±0.17	130.9±0.8
Ethylenediamine-*N*,*N*,*N*',*N*'-tetraacetic acid [7–10]				
$H_5L^+ = H_4L + H^+$	1.30±0.08	7.42±0.46	–	–
$H_4L = H_3L^- + H^+$	2.23±0.04	12.73±0.23	–1.51±0.21	47.8±1.0
$H_3L^- = H_2L^{2-} + H^+$	3.17±0.04	18.09±0.23	–6.19±0.25	81.4±1.1
$H_2L^{2-} = HL^{3-} + H^+$	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
N-(β-hydroxyethyl)ethylenediamine-*N*,*N*',*N*' -triacetic acid [17, 18]				
$H_4L^+ = H_3L + H^+$	1.44±0.08	8.22±0.46	–	–
$H_3L = H_2L^- + H^+$	2.78±0.04	15.87±0.23	–1.68±0.17	58.8±1.0
$H_2L^- = HL^{2-} + H^+$	5.79±0.03	33.05±0.17	12.41±0.24	69.2±1.0
$HL^{2-} = L^{3-} + H^+$	10.52±0.03	60.05±0.17	21.95±0.21	127.8±0.9
Ethylenediamine-*N*,*N*'-disuccinic acid [19, 20]				
$H_4L = H_3L^- + H^+$	3.45±0.12	19.69±0.69	5.79±0.16[a]	41.8±0.9[a]
$H_3L^- = H_2L^{2-} + H^+$	4.28±0.05	24.43±0.29	6.40±0.09[a]	52.6±0.8[a]
$H_2L^{2-} = HL^{3-} + H^+$	7.53±0.06	42.98±0.34	20.8±0.1	74.5±1.2
$HL^{3-} = L^{4-} + H^+$	11.12±0.10	63.47±0.57	27.0±0.5	122.5±2.7
Ethylenediamine-*N*,*N*,*N*',*N*'-tetrapropionic acid [23, 24]				
$H_5L^+ = H_4L + H^+$	2.81±0.07	16.04±0.40	–	–
$H_4L = H_3L^- + H^+$	3.61±0.06	20.61±0.34	–	–
$H_3L^- = H_2L^{2-} + H^+$	4.68±0.04	26.71±0.23	–	–
$H_2L^{2-} = HL^{3-} + H^+$	6.86±0.06	39.16±0.34	12.60±0.43	89.1±1.7
$HL^{3-} = L^{4-} + H^+$	10.48±0.04	59.82±0.23	19.55±0.44	135.1±1.8

[a] Values $\Delta_{dis}H$ and $\Delta_{dis}S$ [19] of the dissociation reactions of the carboxy groups of ethylenediaminedisuccinic acid at the ion force 0.12 (KNO_3) are presented.

the number of the charge-carrying functional groups) explains evidently the decrease in $\Delta_{dis}S^0$ values of the corresponding dissociation reactions of complexone **II** as compared to **III**. A significant increase in heat effects $\Delta_{dis}H_3^0$ and $\Delta_{dis}H_4^0$ of dissociation of the "betaine" protons of compound **IV** is connected with the substitution of tertiary amino groups in substances **I**–**III** and **V** by secondary ones in the complexone **IV**. At the same time the variation in the $\Delta_{dis}S_4^0$ of HL^{3-} at the transfer from **II** to **IV** well agrees with the corresponding variations in the $\Delta_{dis}S_2^0$ of dissociation of the "betaine" proton HL^- in going from the iminodiacetic acid [35] to the aspartic [36] and the glutamic [37] ones.



I **II**

Fig. 1. Structure of complexone molecules according to the results of quantum-chemical calculations.

Table 3. Standard thermodynamic characteristics of dissociation of some amino acids and dipeptides

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}
Glycine (aminoacetic acid) [30]				
$H_2L^+ = HL + H^+$	2.35±0.02	13.41±0.11	4.43±0.05	30.1±0.4
$HL = L^- + H^+$	9.78±0.02	55.82±0.11	44.19±0.32	39.0±1.1
β-Alanine (aminopropionic acid) [31]				
$H_2L^+ = HL + H^+$	3.56±0.02	20.32±0.11	5.18±0.06	50.7±0.5
$HL = L^- + H^+$	10.34±0.05	59.02±0.29	47.24±0.32	39.4±1.4
β-Alanylglycine [32]				
$H_2L^+ = HL + H^+$	3.24±0.03	18.49±0.15	1.24±0.15	57.9±0.7
$HL = L^- + H^+$	9.62±0.08	54.91±0.46	47.83±0.21	23.7±1.7
Glycylglycine [33]				
$H_2L^+ = HL + H^+$	3.16±0.01	18.04±0.06	0.61±0.14	58.5±0.5
$HL = L^- + H^+$	8.31±0.01	47.43±0.06	44.19±0.33	10.9±1.1
Glycyl-β-alanine [34]				
$H_2L^+ = HL + H^+$	4.04±0.05	23.06±0.29	1.36±0.18	72.8±1.1
$HL = L^- + H^+$	8.37±0.06	47.78±0.34	42.97±0.28	16.1±1.5
Iminodiacetic acid [35]				
$H_3L^+ = H_2L + H^+$	1.85±0.03	10.56±0.17	3.93±0.42	22.2±1.5
$H_2L = HL^- + H^+$	2.80±0.07	15.98±0.40	3.05±0.33	43.4±1.7
$HL^- = L^{2-} + H^+$	9.80±0.05	55.94±0.29	32.84±0.33	77.5±1.5
Aspartic (aminosuccinic) acid [36]				
$H_3L^+ = H_2L + H^+$	1.91±0.07	10.90±0.40	7.34±0.42	11.9±1.9
$H_2L = HL^- + H^+$	3.97±0.07	22.66±0.40	3.83±0.25	63.2±1.6
$HL^- = L^{2-} + H^+$	10.03±0.05	57.25±0.29	39.02±0.54	61.1±2.0
Glutamic (aminoglutaric) acid [37]				
$H_3L^+ = H_2L + H^+$	2.15±0.02	12.27±0.11	3.28±0.20	30.1±0.8
$H_2L = HL^- + H^+$	4.38±0.02	25.00±0.11	2.39±0.13	75.8±0.6
$HL^- = L^{2-} + H^+$	10.03±0.02	57.25±0.11	40.06±0.23	57.6±0.8

EXPERIMENTAL

Calorimetric measurements were carried out in an ampule calorimeter with the isothermal coating, thermistor transducer, and the automatic registration of temperature variations in time. Heat effects of mixing KOH solution (0.9378 mol kg^{-1} of solution) with 0.0112–0.0174 M complexone solutions in the pH ranges 6.1 → 7.0 and 9.3 → 10.4 and heat effects of mixing HNO_3 solution (0.9284 mol kg^{-1} of solution) with 0.0068-0.0174 M complexone solutions in the pH ranges 3.9 → 3.5, 5.0 → 4.5, 6.6 → 6.0, and 9.4 → 8.8 were measured at 298.15 K and the ion force values 0.1, 0.5, and 1.0 (KNO_3). For the introduction of necessary corrections heats of dilution of KOH and HNO_3 in the solution of the background electrolyte at the corresponding ion force values were also measured.

Calculation of equilibrium compositions showed (Fig. 2) that in the pH ranges 6.1 → 7.0 and 9.3 → 10.4 potassium hydroxide introduced in the solution practically completely is consumed in the neutralization of the betaine proton of H_2L^{2-} and HL^{3-} particles respectively and the neutralization heat effects $\Delta_{neutr}H(H_2L^{2-})$ and $\Delta H_{neutr}H(HL^{3-})$ may be found as the differences of the corresponding mixing and dilution heats.

$$\Delta_{neutr}H = (\Delta_{mix}H_{OH} - \Delta_{dil}H_{OH})/\alpha_{neut}. \quad (3)$$

Here $\Delta_{mix}H_{OH}$ is the heat effect of mixing KOH solution with the solution of compound **I** in the presence of background electrolyte in the corresponding pH range; $\Delta_{dil}H_{OH}$ is the heat effect of the dilution of KOH in the background electrolyte at the same ion force value; α_{neut} is the completeness of neutralization; $\Delta_{neut}H(H_2L^{2-})$ –41175±198 and –39159±206 J mol^{-1}, $\Delta_{neut}H(HL^{3-})$ –30629±159 and –28408±178 J mol^{-1} at the ion force values of 0.5 and 1.0 (KNO_3) respectively.

Evaluated neutralization heat effects permit to calculate the corresponding heat effects of protonation ($\Delta_{prot}H$) and dissociation (Δ_{dis}H) of compound **I.**

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

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

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

Here Δ_wH is the heat effect of the reaction (6); Δ_wH at the necessary ion force values and temperatures are listed in [38]; $\Delta_{prot}H(HL^{3-})$ –15725±446 and –17561±255 J mol^{-1}, $\Delta_{prot}H(L^{4-})$ –26271±430 and –28312±229 J mol^{-1} respectively at the ion force values 0.5 and 1.0 (KNO_3).

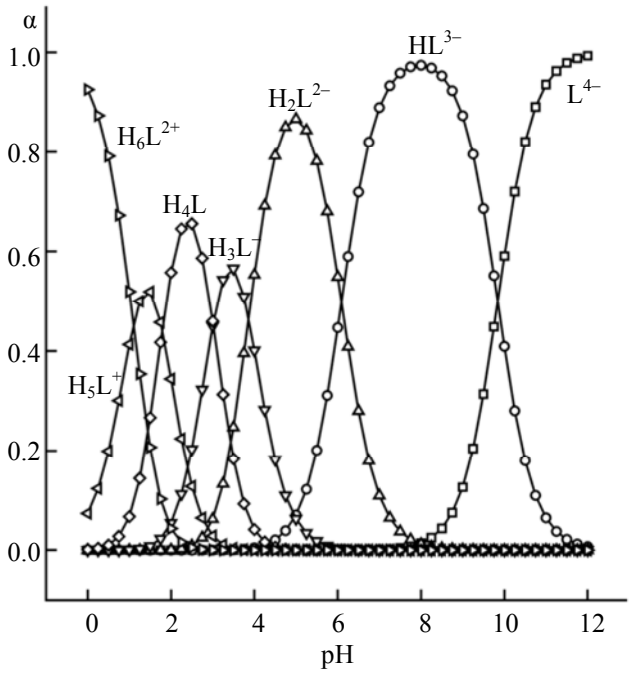


Fig. 2. Diagram of equilibria of compound **I** at 298.15 K and I = 0.1 (KNO_3).

While using second experimental procedure heat effects of protonation $\Delta_{prot}H(HL^{3-})$ and $\Delta_{prot}H(L^{4-})$ can be calculated according to the Eq. (7):

$$\Delta_{prot}H = \Delta_{mix}H_H - \Delta_{dil}H_H. \quad (7)$$

Here $\Delta_{mix}H_H$ are the heat effects of mixing HNO_3 solutions with the solutions of complexone in the pH ranges 6.6 → 6.0 and 9.4 → 8.8; $\Delta_{dil}H_H$ is the heat effect of dilution of HNO_3 solution with background electrolyte; $\Delta_{prot}H(HL^{3-})$ –13622±103, –15823±96, and –17687±100 J mol^{-1}, $\Delta_{prot}H(L^{4-})$ –23951±170, –26485±154 and –28647±151 J mol^{-1} respectively at the ion force values 0.1, 0.5, and 1.0 (KNO_3).

Reaction of the complexone and the nitric acid solutions in the pH range 5.0 → 4.5 is characterized by the following equilibria.

$$HL^{3-} + H+ = H_2L^{2-}, \quad (8)$$

$$HL^{3-} + 2H^+ = H_3L^-, \quad (9)$$

$$H_2L^{2-} + H^+ = H_3L^-. \quad (10)$$

The heat effect of protonation of H_2L^{2-}[$\Delta_{prot}H(H_2L^{2-}) = -\Delta_{dis}H_2$] can be calculated by Eq. (11).

$$\Delta_{mix}H_H - \Delta_{dil}H_H = \{\Delta[H_3L^-]\Delta_{prot}H(H_2L^{2-}) - \Delta[HL^{3-}]\Delta_{prot}H(HL^{3-})\}/c(HNO_3). \quad (11)$$

Here $\Delta[H_3L]$ and $\Delta[HL^{2-}]$ are the variations in the equilibrium concentrations of corresponding particles in the course of the calorimetric experiment; $c(HNO_3)$ is the analytical concentration of nitric acid taking in account its dilution to the volume of the calorimetric liquid. Heat effect of protonation of H_2L^{2-} ion $[\Delta_{prot}H(H_3L^-) = -\Delta_{dis}H_1]$ considering the Eqs. (10), (12), (13) at pH 3.9 → 3.5 may be found analogously.

$$H_2L^{2-} + 2H^+ = H_4L, \quad (12)$$

$$H_3L^- + H^+ = H_4L, \quad (13)$$

$$\Delta_{mix}H_H - \Delta_{dil}H_H = \{\Delta[H_4L]\Delta_{prot}H(H_3L^-) - \Delta[H_2L^{2-}]\Delta_{prot}H(H_2L^{2-})\}/c(HNO_3). \quad (14)$$

Values $\Delta_{prot}H(H_2L^{2-})$ and $\Delta_{prot}H(H_3L^-)$ at the ion force values of 0.1, 0.5, and 1.0 (KNO_3) are listed in Table 1.

Results of quantum-chemical calculations of structures of compounds **I**–**V** are used as the auxiliary data. The calculations were carried out with the help of the MOPAC v.6.0 standard complex of programs [39] by semiempirical AM1 method [40] with the complete optimization of all geometric parameters. More complete information on the structure of mono- and diamine complexones is presented in [27–29].

REFERENCES

1. Dyatlova, N.M., Temkina, V.Ya., and Popov, K.I., *Kompleksony i kompleksonaty metallov* (Complexones and Metal Complexonates), Moscow: Khimiya, 1988.
2. Vasil'ev, V.P., Lymar, V.P., and Lytkin, A.I., *Zh. Neorg. Khim*., 1977, vol. 22, no. 9. p. 2511.
3. Vasil'ev, V.P., Lymar, V.P., and Lytkin, A.I., *Zh. Neorg. Khim*., 1977, vol. 22, no. 10. p. 2652.
4. Vasil'ev, V.P., Kochergina, L.A., and Orlova, T.D., *Zh. Obshch. Khim*., 1978, vol. 48, no. 12, p. 2770.
5. Vasil'ev, V.P., Kochergina, L.A., and Orlova, T.D., *Zh. Obshch. Khim*., 1979, vol. 49, no. 7, p. 1649.
6. Vasil'ev, V.P., Kochergina, L.A., and Orlova, T.D., *Zh. Obshch. Khim*., 1976, vol. 46, no. 10, p. 2192.
7. Vasil'ev, V.P., Kochergina, L.A., and Yastrebova, T.D., *Zh. Obshch. Khim*., 1973, vol. 43, no. 5, p. 975.
8. Vasil'ev, V.P., Kochergina, L.A., and Yastrebova, T.D., *Zh. Obshch. Khim*., 1974, vol. 44, no. 6, p. 1371.
9. Gridchin, S.N. and Kochergina, L.A., *Izv. Vysshikh Uchebnykh Zavedenii, Ser. Khim., Khim. Tekhnol*., 2004, vol. 47, no. 7, p. 36.
10. Gridchin, S.N., *Izv. Vysshikh Uchebnykh Zavedenyy, Ser. Khim.Khim. Tekhnol.,* 2006, vol. 49, no. 9, p. 14.
11. Gridchin, S.N. and Pyreu, D.F., *Zh. Obshch. Khim*., 2008, vol. 78, no. 3, p. 389.
12. Gridchin, S.N., *Zh. Fiz. Khim*., 2008, vol. 82, no. 1, p. 48.
13. Gridchin, S.N., *Zh. Fiz. Khim*., 2005, vol. 79, no. 11, p. 2099.
14. Vasil'ev, V.P., Gridchin, S.N., Kochergina, L.A., and Chernikov, V.V., *Zh. Fiz. Khim*., 1998, vol. 72, no. 5, p. 866.
15. Gridchin, S.N., Kochergina, L.A., Vasil'ev, V.P., and Pyreu, D.F., *Zh. Neorg. Khim*., 2002, vol. 47, no. 7, p. 1125.
16. Gridchin, S.N., *Izv. Vysshikh Uchebnykh Zavedenii, Ser. Khim., Khim. Tekhnol*., 2005, vol. 48, no. 12, p. 51.
17. Gridchin, S.N., *Izv. Vysshikh Uchebnykh Zavedenii, Ser. Khim., Khim,. Tekhnol*., 2008, vol. 51, no. 1, p. 29.
18. Gridchin, S.N., *Zh. Neorg. Khim*., 2008, vol. 53, no. 10, p. 1788.
19. Vasil'ev, V.P., Kozlovskii, E.V., and Ledenkov, S.F., *Teoreticheskie metody opisaniya svoistv rastvorov* (Theoretical Methods of Description of the Solution Properties), Ivanovo: Ivanov. Khim.-Tekhn. Inst., 1987, p. 81.
20. Vasil'ev, V.P., Kozlovskii, E.V., and Ledenkov, S.F., *Zh. Fiz. Khim*., 1987, vol. 61, no. 5, p. 1429.
21. Vasil'ev, V.P., Orlova, T.D., and Ledenkov, S.F., *Zh. Obshch. Khim*., 1989, vol. 59, no. 8, p. 1828.
22. Vasil'ev, V.P., Kochergina, L.A., and Vavilova, S.Yu., *Proyavlenie prirody rastvoritelya v termodinamicheskikh svoistvakh rastvorov* (Revealing of Nature of Solvent in the Thermodynamic Properties of Solutions), Ivanovo: Ivanov. Khim.-Tekhn. Inst., 1989, p. 56.
23. Vasil'ev, V.P., Kochergina, L.A., Ivanova, T.V., Grosheva, S.G., and Kadykova, I.V., *Izv. Vysshikh Uchebnykh Zavedenii, Ser. Khim., Khim. Tekhnol*., 1991, vol. 34, no. 8, p.54.
24. Gridchin, S.N., *Zh. Fiz. Khim*., 2009, vol. 83, no. 1, p. 51.
25. Vasil'ev, V.P., *Termodinamicheskie svoistva elektrolitov* (Thermodynamic Properties of Electrolytes), Moscow: Vysshaya Shkola, 1982.
26. Shkol'nikova, L.M., Poray-Koshitz, M.A., and Dyatlova, N.M., *Zh. Strukt. Khim*., 1986, vol. 27, no. 2, p. 138.
27. Gridchin, S.N. and Bazanov, M.I., *Kvantovo-khimicheskie raschety: struktura i reaktsionnaya sposobnost' organicheskikh i neorganicheskikh molekul* (Quantum Chemical Calculations: Structure and Reactivity of the Organic and Inorganic Molecules), Ivanovo: Ivanov. Gos. Univ., 2005, part 2, p. 11.
28. Gridchin, S.N. and Bazanov, M.I., *Izv. Vysshikh Uchebnykh Zavedenii, Ser. Khim., Khim. Tekhnol*., 2007, vol. 50, no. 2, p.85.
29. Gridchin, S.N. and Bazanov, M.I., *Izv. Vysshikh Uchebnykh Zavedenii, Ser. Khim. Khim. Tekhnol*., 2008, vol. 51, no. 6, p. 23.

30. Vasil'ev , V.P., Kochergina, L.A., Garavin, V.Yu., and Grudochkin, A.V., *Teotericheskie metody opisaniya svoistv rastvorov* (Theoretical Methods of Description of the Solution Properties), Ivanovo: Ivanov. Khim.-Tekhn. Inst., 1987, p. 87.
31. Vasil'ev, V.P., Kochergina, L.A., and Garavin, V.Yu., *Zh. Obshch. Khim*., 1992, vol. 62, no. 1, p. 213.
32. Gridchin, S.N. and Pyreu, D.F., *Zh. Obshch. Khim*., 2007, vol. 77, no. 6, p. 948.
33. Gorboletova, G.G., Gridchin, S.N., and Sazonova, E.S., *Zh. Fiz. Khim*., 2005, vol. 79, no. 8, p. 1390.
34. Gridchin, S.N., Gorboletova, G.G., and Pyreu, D.F., *J. Therm. Anal. Cal.,* 2007, vol. 90, no. 2, p. 607.
35. Vasil'ev, V.P., Kochergina, L.A., Orlova, T.D., and Samoshina, T.D., *Zh. Obshch. Khim*., 1981, vol. 51, no. 2, p. 292.
36. Vasil'ev, V.P., Kochergina, L.A., Iven'kova, S.G., and Kuturov, M.V., *Zh. Obshch. Khim*., 1982, vol. 52, no. 8, p. 1828.
37. Gridchin, S.N., Romodanovskii, P.A., and Pyreu, D.F., *Zh. Fiz. Khim*., 2009, vol. 83, no. 1, p. 156.
38. Lobanov, G.A. and Vasil'ev, V.P., *Izv. Vysshikh Uchebnykh Zavedenii, Ser. Khim., Khim. Tekhnol*., 1969, vol. 12, no. 6, p. 740.
39. Clark, T., *Kompyuternaya khimiya* (Computer Chemistry), Moscow: Mir, 1990.
40. Dewar, M.J.S., Zoelisch, E.G., Healy, E.F., and Stewart, J.J.P., *J. Am. Chem. Soc*., 1985, vol. 107, no. 13, p. 3902.