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PECULIARITIES OF THERMOCHEMICAL INVESTIGATIONS OF ACID–BASE EQUILIBRIA IN COMPLEXON SOLUTIONS

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Abstract

The enthalpies of acid–base interactions in solutions of the complexons iminodiacetic acid, nitryltriacetic acid, ethylenediaminetetraacetic acid and their phosphorylated analogues were determined with an isothermal-shell calorimeter with automatic temperature recording in a background of different electrolytes in the temperature range 283–328 K.

The concepts of Gurney were used to analyse the thermodynamic characteristics of the reactions.

Keywords: complexon, protolytic equilibria, thermodynamics

Introduction

Numerous questions relating to the thermodynamics of protolytic equilibria, and in particular a large number of acid–base reactions involving chemical compounds of different nature (amines, amino acids, complexons, and organic and inorganic acids), have so far been considered only generally; this does not correspond to the great practical and scientific significance of these compounds.

The enthalpies of acid–base interactions in solutions of the complexons iminodiacetic acid (IDA), nitryltriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA) and their phosphorylated analogues have been determined in our laboratory [1–5].

These measurements were performed by calorimetry in order to study the effects of temperature and ionic strength on the heats of the investigated reactions and also to obtain reliable thermodynamic characteristics.

The thermodynamic parameters of the stepwise dissociation processes may permit determination of the overall reaction proceeding and can be used in thermodynamic calculations and to obtain the standard enthalpies of formation of these compounds.

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Experimental

The heat effects of the acid–base reactions of the compounds used were measured in an isothermal-shell calorimeter with automatic temperature recording in a background of different electrolytes in the temperature interval 283–328 K. The temperature was kept constant to within ±0.002 K, the time being measured within $1\cdot10^{-3}$ s.

For determination of the ionization constants of the investigated compounds, use was made of the results of potentiometric titrations at 298.15 K and different ionic strengths, which corresponded exactly to the values in the thermochemical experiments.

The conditions of the thermochemical experiments were optimized with the RRSU program on a PC 486 DX2.

The enthalpy changes for the dissociation of cation-acids, complexons with carboxyl-containing groups and their phosphorylated analogues were determined by two independent methods: 1) from experimental data relating to the protonation heats of anionic species; 2) from experimental results on heats of neutralization of weak acids with alkali solutions in different pH regions [1–3].

The study also involved determination of the heat effects of ligand protonation accompanying formation of the corresponding cation-acid. In some cases, interaction of an anion with a proton is complicated by complex formation with alkali metal cations from the 'background'.

Taken together, the data obtained for the heats of dissolution and the results of bomb calorimetry on the heats of the combustion of the substances furnished the key-values in their thermodynamics: the standard enthalpies of formation of the cation-acid and dissociation products in aqueous solution.

Materials: Chemically pure complexons (IDA, NTA and EDTA) and their phosphorylated analogues [1, 4, 8] were used.

Lithium, sodium and potassium nitrates, and sodium chloride and perchlorate were used as supporting electrolytes.

Results and discussion

The heat effects of the reactions were extrapolated to zero ionic strength according to the following equation:

$$\Delta_r H - \Delta z^2 \Psi(I) = \Delta_r H^o + iI \qquad (1)$$

where $\Delta_r H$ and $\Delta_r H^o$ are the enthalpies at finite and zero ionic strength (I); $\Psi(I)$ is the theoretically calculated function of I; i is an empirical coefficient; and Δz^2 is the difference in square charges of the reactants [7].

The magnitude of the empirical coefficient i in Eq. (1) was shown to correlate with the reciprocal sum of the thermochemical radii of the ions of the supporting electrolyte. Thus, Eq. (1) can be represented as follows:

$$\Delta_r H - \Delta z^2\Psi(I) = \Delta_r H^0 + \left[k_1 + \frac{k_2}{r_+ + r_-}\right] I \qquad (2)$$

where k_1 and k_2 are coefficients depending on the type of proton transfer and on the individual properties of the system [1, 9].

It was found (Fig. 1) that the points satisfactorily fitted the straight lines with coordinates $\Delta_r H + \Psi(I)$ *vs.* I. These lines intercepted the ordinate at heat effect values corresponding to zero ionic strength. The heat effects at finite ionic strength were essentially different, particularly at large values of I. However, the standard heat effect values obtained with different supporting electrolytes were constant. They did not depend on specific properties of the electrolytes. Equation (2) may be used to predict values and characters of heat effects in other electrolyte solutions for which the sums $(r_+ + r_-)$ are known.

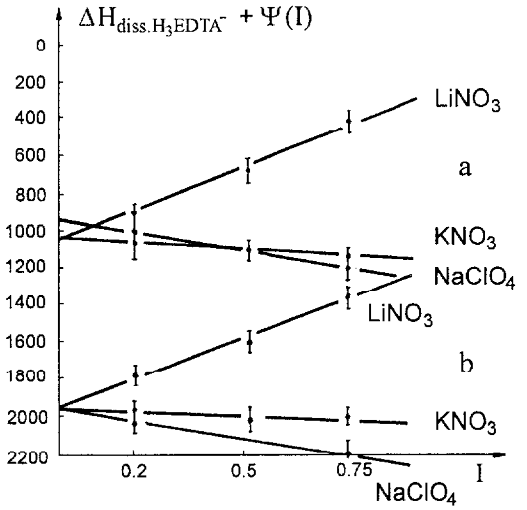


Fig. 1 Extrapolation of H_3EDTA^- dissociation heats to zero ionic strength at 288 K (a) and 308 K (b)

The thermodynamic characteristics of dissociation of series of compounds were found by joint use of the results of thermochemical and potentiometric measurements on the dissociation constants. They are given in Table 1.

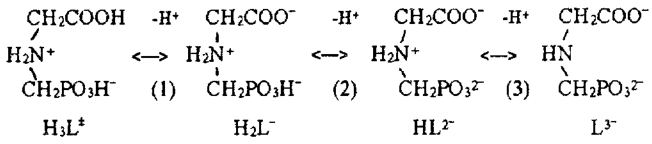
To analyse the thermodynamic characteristics of the reactions, the Gurney concepts were used [6]; these allow a consideration of various chemical processes from the same aspect. A comparison of the temperature-dependent and

Table 1 Standard thermodynamic characteristics of acid–base equilibria in solutions of complexons (phosphonomethylglycine ($H_3L^{\pm}$) and iminodimethylene-phosphonic acid ($H_4L^{\pm}$); their temperature-dependent and temperature-independent contributions

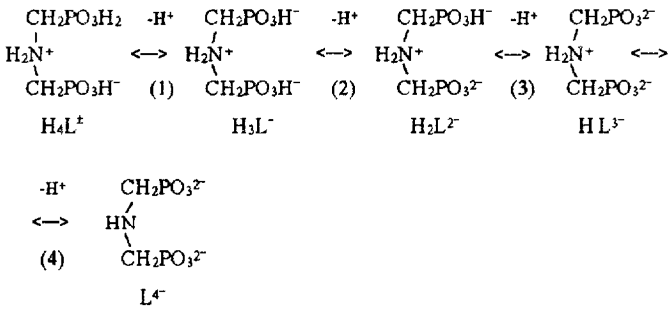
T/ K	ΔG^o/	ΔH^o/	ΔG^o_{dep}/	$-\Delta H^o_{dep}$/	$\Delta G^o_{indep}=\Delta H^o_{indep}$	$-\Delta S^o$/	$-\Delta S^o_{dep}$/
	kJ mol^{-1}					kJ mol^{-1} K^{-1}	
		$H_3L^{\pm} \Leftrightarrow H_2L^- + H^+$ *)					
288	13.15±0.1	3.39±0.17	14.78	4.58	7.97	33.8±0.7	67.2
298	13.52±0.1	1.69±0.10	16.09	5.72	7.41	39.7±0.5	73.1
308	13.93±0.1	0.25±0.10	17.12	6.86	7.11	44.4±0.5	77.8
318	14.40±0.1	–1.14±0.10	18.09	8.07	6.93	48.9±0.5	82.3
		$H_2L^- \Leftrightarrow HL^{2-} + H^+$ **)					
288	32.11±0.1	–0.60±0.13	32.31	10.01	9.41	113.5±0.6	146.9
298	33.28±0.1	–2.70±0.13	33.89	12.04	9.34	120.6±0.5	154.0
308	34.52±0.1	–4.45±0.15	35.18	14.10	9.65	126.5±0.6	159.9
		$HL^{2-} \Leftrightarrow L^{3-} + H^+$ ***)					
288	60.51±0.1	26.26±0.30	33.50	10.38	36.64	118.9±1.1	152.3
298	61.71±0.1	25.33±0.32	34.20	12.15	37.48	122.0±1.1	155.4
308	62.95±0.1	24.29±0.33	34.94	14.00	38.29	125.4±1.1	158.8
		$H_4L^{\pm} \Leftrightarrow H_3L^- + H^+$ **)					
288	7.55±0.55	–4.41±0.34	16.49	5.09	–0.68	41.6±2.2	75.0
298	7.99±0.57	–6.06±0.31	17.72	6.29	0.23	47.2±2.1	80.6
308	8.48±0.59	–8.74±0.29	19.64	7.87	–0.87	55.9±2.1	89.3
		$H_3L^- \Leftrightarrow H_2L^{2-} + H^+$ **)					
288	30.31±0.1	–1.47±0.16	31.61	9.79	8.32	110.2±0.7	143.6
298	31.45±0.1	–3.88±0.132	33.42	11.87	7.99	118.6±0.6	152.0
308	32.67±0.1	–5.81±0.16	34.82	13.95	8.14	124.8±0.6	158.2
		$H_2L^{2-} \Leftrightarrow HL^{3-} + H^+$ **)					
288	37.08±0.1	–2.22±0.08	37.35	11.57	9.35	136.4±0.5	169.8
298	38.47±0.1	–4.07±0.08	38.74	13.76	9.69	142.7±0.5	176.1
308	39.93±0.1	5.93±0.09	40.09	16.06	10.13	148.9±0.5	182.3
		$HL^{3-} \Leftrightarrow L^{4-} + H^+$ ***)					
288	65.04±0.1	24.48±0.30	38.31	11.87	36.35	140.7±1.1	174.1
298	66.44±0.1	23.80±0.31	38.81	13.79	37.57	143.1±1.1	176.5
308	67.90±0.1	22.43±0.30	39.81	15.95	38.38	147.5±1.0	180.9

*) dissociation of proton from carboxyl group
**) dissociation of proton from methylenephosphonic group
***) dissociation of proton from amino group

Dissociation of phosphonmethilglicine



Dissociation of iminodimetilenphosphonic acid



temperature-independent contributions to the Gibbs energy and enthalpy change yields the criterion of the change in sign of the process, i.e. it permits prediction of the temperature Θ at which $\Delta_r H=0$.

Preliminary studies have shown that the temperature dependence of the ionization constants of weak acids in the general form may be represented as a parabola. The temperature corresponding to the extremum of the $pK=f(T)$ curve may be calculated according to the equation

$$\Theta = 298.15 - \frac{\Delta_r H_{298.15}}{\Delta_r C_p} \qquad (3)$$

where $\Delta_r H_{298.15}$ and $\Delta_r C_p$ are the enthalpy and heat capacity changes in the dissociation process. Experimental data from numerous studied systems reveal that this relation holds true. The temperature Θ for acetic acid dissociation was found to be 298 K; it is also near this value for the dissociation of carboxy-containing complexons such as IDA, NTA, PhMG and others. The temperature Θ for the proton dissociation of phosphorus-containing groups is essentially different from room temperature.

The enthalpy change may be represented as the sum of temperature-dependent and temperature-independent contributions.

The differences between the constituents characterizing the energies of interaction of a proton with nitrogen-, oxygen- and phosphorus-containing groups are significant. It was observed (Table 1) that the dissociation of a betaine proton is accompanied by a large absolute value of $\Delta_r H$ (25 kJ mol^{-1}). However, for the dissociation process of a proton linked to oxygen, $\Delta_r H$ is not high: it does not exceed 1.7 kJ mol^{-1}.

At some temperature, the thermal effect of the ionization process becomes zero (pK$_{\min}$). In accordance with this condition, the following equation may be written:

$$|\Delta_r H^o_{\text{indep.}}| + |\Delta_r H^o_{\text{dep.}}| = 0 \tag{4}$$

and hence the values of $|\Delta_r H^o_{\text{indep}}|$ and $|\Delta_r H^o_{\text{dep.}}|$ must be compared. Thus, the correlation between the temperature-dependent and temperature-independent contributions to the enthalpy change may be the criterion of the change in sign of the dissociation heats. If $|\Delta_r H^o_{\text{indep}}| >> |\Delta_r H^o_{\text{dep.}}|$, then a change in sign would be impossible. In contrast, if $|\Delta_r H^o_{\text{indep}}| = |\Delta_r H^o_{\text{dep.}}|$, then temperature increase may lead to a change in sign. As a rule, in this case the heat capacity change $\Delta_r C_p$ for the reaction would approach 120 J mol^{-1}K^{-1}. The experimental data fully confirmed this (Table 1).

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