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Enthalpies of solution in water of urotropine as function of concentration and temperature

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Abstract Enthalpies of solution of Hexamethylenetetramine in water at several molal concentrations and at four temperatures (278.15, 288.15, 298.15, and 308.15) K were determined. The values of enthalpy of solution at infinite dilution were combined with the enthalpy of sublimation to get the corresponding enthalpies of hydration. The change in heat capacity at infinite dilution was calculated.

Keywords Aquеous solutions · Solution enthalpy · Hydration enthalpy · Urotropine

Introduction

Hexamethylenetetramine (HMT, Hexamine, Urotropine) is an antibacterial agent widely used for the treatment of urinary tract infections [1], which is also frequently used in chemical synthesis, chemical industry, and in the explosives and plastics manufacture [2–5]. The HMT is a cage-like molecule that has shown special behavior in aqueous solution. Several physical chemistry studies suggest that HMT is a structure making agent [6–10]. However, thermodynamic studies at low concentration, of less than 0.05 mol kg^{-1}, are scarce; in the literature, data are found for partial molar volumes at molar concentrations above 0.05 mol L^{-1} [6] and it is only possible to find data of enthalpies of solution at 298.15 and 303.15 K (-21.33 kJ mol^{-1} at 0.100 mol kg^{-1} [10] and -20.49 kJ mol^{-1} [11], respectively).

This article deals with the study of HMT in aqueous solutions at molal concentrations below 0.05 mol kg^{-1} getting the calorimetric determination of the solution enthalpy. The enthalpy of solution was determined at 278.15, 288.15, 298.15, and 308.15 K and the dependence with temperature allowed the calculation of heat capacity. The hydration enthalpy was also calculated.

Experimental

The Hexamethylenetetramine, HMT, was reagent grade obtained from Sigma Co. with purity higher than 99.4% and was used as received. The water was doubly distilled according to the literature recommendations [12] and was degassed before used. The conductivity of the water was 2 μS cm^{-1}. All the solutions were prepared by weight using an Ohaus Analytical Plus balance.

The determinations of enthalpy of solution were carried out using an isoperibol solution calorimeter. The experimental setup and the calibration procedure have been described elsewhere [13, 14]. The measurements of molar enthalpy of solution, $\Delta_{\mathrm{sol}}H_m$, were carried out over the molality range from 0.007 to 0.05 mol kg^{-1}. The uncertainty in the molar enthalpy of solution determinations was less than 1%.

Results

The values of $\Delta_{\mathrm{sol}}H_m$ of HMT in water at different molal concentrations and at 278.15, 288.15, 298.15, and 308.15 K

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are shown in Table 1 and in Fig. 1. The experimental uncertainty of solution enthalpy measurements, $\sigma_{\Delta H}$, calculated according to [14], is also shown. It is not possible to compare the data of this study with the literature values because those authors have not reported either the uncertainty of the measurements or the concentration values.

The molal enthalpies at infinite dilution, $\Delta_{\mathrm{sol}}H_m^{\infty}$, were calculated by weighted least squares regression. The values of $\Delta_{\mathrm{sol}}H_m^{\infty}$ and their uncertainties are given in Table 2, and in the Fig. 2, the dependence with temperature is also shown.

Hydration enthalpies

The enthalpy of hydration, $\Delta_{\mathrm{hyd}}H_m^0$, was calculated as the difference between the enthalpy of solution at infinite dilution, $\Delta_{\mathrm{sol}}H_m^{\infty}$, and the enthalpy of sublimation, $\Delta_{\mathrm{s}}^{\mathrm{g}}H_m^0$, according to the equation:

$$\Delta_{\mathrm{hyd}}H_m^0 = \Delta_{\mathrm{sol}}H_m^{\infty} - \Delta_{\mathrm{s}}^{\mathrm{g}}H_m^0 + RT\,(1 - \alpha T) \tag{1}$$

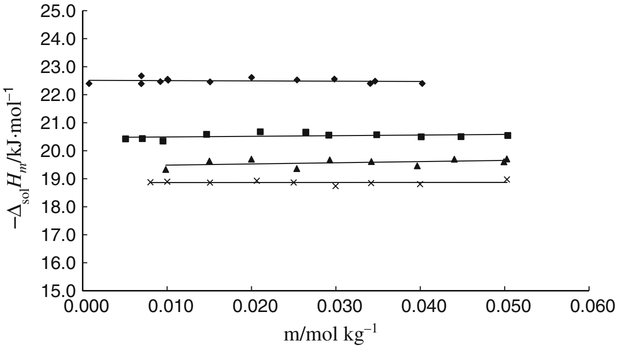

Fig. 1 Enthalpy of solution of HMT in water at: *filled diamonds*, 278.15 K; *filled squares*, 288.15 K; *filled triangles*, 298.15 K; and *times*, 308.15 K

where α is the thermal expansion of the solvent. The last term in Eq. 1 accounts for the correction of the experimental thermodynamic quantities to the standard state used in the definition of the solvation enthalpy [15]. The values of $\Delta_{\mathrm{hyd}}H_m^0$ at 278.15, 288.15, 298.15, and 308.15 K are shown in Table 2, and in Fig. 3, the dependence on

Table 1 Enthalpies of solution of HMT in water as a function of molal concentration and at 278.15, 188.15, 298.15, and 308.15 K

m/mol kg^{-1}	$\Delta_{\mathrm{sol}}H_m$/kJ mol^{-1}	$\sigma_{\Delta H}$/kJ mol^{-1}	m/mol kg^{-1}	$\Delta_{\mathrm{sol}}H_m$/kJ mol^{-1}	$\sigma_{\Delta H}$/kJ mol^{-1}
278.15 K			298.15 K		
0.02001	−22.62	0.04	0.00985	−19.33	0.09
0.00920	−22.47	0.06	0.02000	−19.70	0.01
0.03465	−22.48	0.03	0.04992	−19.60	0.02
0.00695	−22.39	0.14	0.03964	−19.46	0.01
0.01014	−22.52	0.03	0.02928	−19.67	0.17
0.01509	−22.46	0.01	0.01502	−19.63	0.05
0.01006	−22.55	0.74	0.04403	−19.70	0.01
0.00075	−22.39	0.07	0.03421	−19.61	0.15
0.02540	−22.53	0.03	0.02537	−19.36	0.01
0.02983	−22.56	0.02	0.05025	−19.71	0.21
0.03408	−22.40	0.02			
0.04024	−22.40	0.03			
0.00696	−22.67	0.02			
288.15 K			308.15 K		
0.02104	−20.68	0.02	0.05026	−18.97	0.03
0.02916	−20.56	0.03	0.02500	−18.86	0.01
0.04011	−20.50	0.12	0.01002	−18.90	0.01
0.05037	−20.54	0.00	0.03998	−18.81	0.02
0.00508	−20.42	0.03	0.03417	−18.84	0.09
0.00707	−20.43	0.02	0.00803	−18.87	0.03
0.03484	−20.57	0.02	0.02996	−18.74	0.01
0.04483	−20.50	0.01	0.02063	−18.93	0.01
0.02644	−20.66	0.02	0.01509	−18.86	0.06
0.00952	−20.35	0.16			
0.01468	−20.58	0.20			

Table 2 Thermodynamic properties of HMT in water at 278.15, 188.15, 298.15, and 308.15 K

T/K	$\Delta_{\mathrm{sol}}H_m^{\infty}$/kJ mol^{-1}	$\Delta_{\mathrm{sol}}C_{\mathrm{p},m,2}$/J mol^{-1} K^{-1}	C_{p}^0/J mol^{-1} K$^{-1\mathrm{a}}$	$C_{\mathrm{p},2}^0$/J mol^{-1} K^{-1}	$\Delta_{\mathrm{s}}^{\mathrm{g}}H_m^0$/kJ mol$^{-1\mathrm{b}}$	$\Delta_{\mathrm{hyd}}H_m^0$/kJ mol^{-1}
278.15	−22.56 ± 0.05	239.09	140.04	379.13	79.39	−99.65
288.15	−20.54 ± 0.07	159.97	146.15	306.12	79.24	−97.48
298.15	−19.50 ± 0.17	80.85	152.26	233.10	79.08	−96.30
308.15	−18.94 ± 0.06	1.73	158.41	160.13	78.92	−95.57

[a] Reference [18]; [b] reference [14]

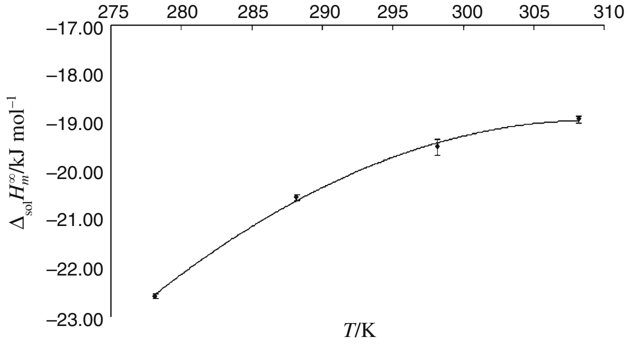

Fig. 2 Molar enthalpies at infinite dilution, $\Delta_{\mathrm{sol}}H_m^{\infty}$ as a function of temperature for HMT in water

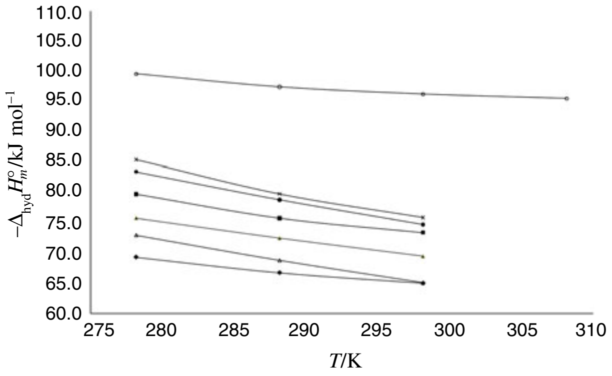

Fig. 3 Enthalpies of hydration as a function of temperature for several amines: *open circles* HMT, this work; *times* (n-Bu)$_2$NH, [17]; *filled circles* (sec-Pr)$_2$NH, [17]; *filled squares* (n-Pr)$_2$NH, [17]; *filled triangles* (iso-Pr)$_2$NH, [17]; *open triangles* (iso-Bu)$_2$NH, [17]; *filled diamonds* Et$_2$NH, [17]

temperature is shown. Data of $\Delta_{\mathrm{s}}^{\mathrm{g}}H_m^0$for HMT and for α of water were taken from [16] and [17], respectively.

Heat capacities

The dependence of $\Delta_{\mathrm{sol}}H_m^{\infty}$with temperature can be adjusted to the following equation: [18, 19]

$$\Delta_{\mathrm{sol}}H_m^{\infty} = a + b\,(T - 273.15\,\mathrm{K}) + c\,(T - 273.15\,\mathrm{K})^2 \tag{2}$$

where T is the temperature in Kelvin and a, b, and c are the empirical parameters. The values of a, b, and c were calculated by the method of least squares and their values are −23,850 ± 98/J mol^{-1}, 279 ± 15/J mol^{-1} K^{-1}, and −3.96 ± 0.36/J mol^{-1} K^{-2}, respectively. The change in heat capacity in going from the pure compound to the infinite dilute solutions, $\Delta_{\mathrm{sol}}C_{\mathrm{p},m,2}$, can be obtained by differentiating Eq. 2 with respect to temperature so that $\Delta_{\mathrm{sol}}C_{\mathrm{p},m,2} = b + 2c\,(T - 273.15)$. The values of $\Delta_{\mathrm{sol}}C_{\mathrm{p},m,2}$ for HMT in water at different temperatures are shown in Table 2. Comparison between heat capacity C_{p}^0 for the pure HMT and $\Delta_{\mathrm{sol}}C_{\mathrm{p},m,2}$ is made according to following equation:

$$C_{\mathrm{p},2}^0 = C_{\mathrm{p}}^0 + \Delta_{\mathrm{sol}}C_{\mathrm{p},m,2} \tag{3}$$

where $C_{\mathrm{p},2}^0$ is the partial molal heat capacity. The value of $C_{\mathrm{p},2}^0$ calculated from Eq. 3 are shown in Table 2. The values of C_{p}^0 were taken from [20]. The uncertainty of the results does not allow the calculation of temperature derivatives of $\Delta_{\mathrm{sol}}C_{\mathrm{p},m,2}$, but in general negative values of $\partial\Delta_{\mathrm{sol}}C_{\mathrm{p},m,2}/\partial T$can be obtained [19].

Discussion

As can be seen from Table 1, the process of dissolution of HMT in water is highly exothermic. With increasing temperature, the process becomes less exothermic. This behavior has been reported for other amino-derivates in the literature: for example, Bergström and Olofsson [21] measured the enthalpies of solution of Et$_3$N, Pr$_2$NH, c-HexNH$_2$, and HexNH$_2$ as a function of temperature and calculated $\Delta_{sol}H_m^{\infty}$; Batov and Ivanov [22, 23] measured enthalpies of solution of *N*,*N*-dimethylethyleneurea and 1,1,3,3-tetramethylurea, as a function of temperature and also calculated the dependence of $\Delta_{\mathrm{sol}}H_m^{\infty}$ on temperature. Franks and Watson [19] obtained $\Delta_{\mathrm{sol}}H_m^{\infty}$ of dialkylamines as function of temperature. In Fig. 3, some of these data are shown along with the data obtained for HMT. Thus, the behavior observed for HMT in this study can be explained in terms of predominance of hydrophobic interactions between the alkyl groups and the surrounding water along with the hydrophilic interactions because of nitrogen atoms capable of participating in hydrogen bonding.

The enthalpy of hydration is related with the energy required to make a cavity in liquid water and is determined by solute–solvent interactions. On the other hand, the enthalpy of solution is determined by the balance of solute–solute and solute–solvent interactions. The hydration enthalpies of HMT shown in Table 2 are more exothermic than the corresponding solution enthalpies, with similar behavior having been found with alcohols and other mixed solutes [24]. These results are consistent with the fact that, in dilute aqueous solutions, the hydrophobic hydration due to CH_2–groups of HMT is dominant over the interaction by hydrogen bonding between lone pairs of nitrogen and water.

Values of $\Delta_{\mathrm{sol}}C_{\mathrm{p},m,2}$ for a solution process reflect the properties of the pure compound as well as those for the solvated compound, including the effects on the solvent [18]. Franks and Watson [19] have related positive values of $\Delta_{\mathrm{sol}}C_{\mathrm{p},m,2}$ with the formation of hydrogen-bonded structures which increase the structure of the water around the solvent. The positive value of $\Delta_{\mathrm{sol}}C_{\mathrm{p},m,2}$ and the high value of $C^{0}_{\mathrm{p},2}$ for HMT suggest the formation of the structures like "icebergs" which gradually "melt" with increasing temperature.

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