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Short communication

D_2O–H_2O solvent isotope effects on the enthalpy of 1,1,3,3-tetramethylurea hydration between 278.15 and 318.15 K

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ABSTRACT

The enthalpies of solution of 1,1,3,3-tetramethylurea in H_2O and D_2O were measured at 278.15, 288.15, 298.15, 308.15, and 318.15 K. Standard enthalpies and heat capacities of solution (hydration), along with D_2O–H_2O solvent isotope effects on the quantities studied, were computed. The enthalpies of the solute dissolution as well as corresponding solvent isotope effects were found to be negative in sign and decreasing in magnitude with increasing temperature. It was confirmed that hydrophobic hydration is the predominant type of the solute hydration and it is enhanced in D_2O and weakened on going from 1,1,3,3-tetramethylurea to its cyclic derivative, 1,3-dimethyl-2-imidazolidinone.

1. Introduction

In a previous paper [1], we have determined the D_2O–H_2O solvent isotope effects on the enthalpic and some other thermodynamic characteristics of dissolution (hydration) of *N,N′*-dimethylethyleneurea or 1,3-dimethyl-2-imidazolidinone (hereinafter, DMI) being a liquid-phase molecular cyclic analogue of 1,1,3,3-tetramethylurea (TMU). The latter, as it is known, plays an important role in biochemical process including the manufacture of pharmaceuticals as well as in other various synthetic organic transformations [2–4]. Besides, the interest in both TMU and DMI stems from the desire to study the structural transformations that they cause in the dilute aqueous media [1,5]. The effect is largely associated with the competition between the contributions arising from the hydrophobic and hydrophilic parts of a TMU or DMI molecule in the course of hydration and to their joint action on the structure of the surrounding (protiated or deuterated) solvent.

Up to now, very limited studies on the thermodynamic and physicochemical properties of H/D isotopically distinguishable aqueous solutions of TMU have been carried out [5–11]. Herewith, to the best of our knowledge, the D_2O–H_2O solvent isotope effect on the enthalpy of TMU hydration, $\delta\Delta_{\mathrm{sol}}H^{\circ}(=\delta\Delta_{\mathrm{hydr}}H^{\circ})$, has been estimated only by authors [11] at 298.15 K. They report $\delta\Delta_{\mathrm{sol}}H^{\circ}(H_2O \rightarrow D_2O) = -1.19 \pm 0.11\ \mathrm{kJ\,mol^{-1}}$ (compared to $\delta\Delta_{\mathrm{sol}}H^{\circ} = -0.43 \pm 0.11\ \mathrm{kJ\,mol^{-1}}$ for the $CH_3OH \rightarrow CH_3OD$ substitution in the solvating medium). As it has been mentioned earlier [1,11–13], a combination of such two experimental methods as the precise solution calorimetry and D_2O–H_2O solvent isotope substitution, due to the quantum nature of the isotope effects [14], allows one to establish the role of hydrogen bonding and other types of interparticle interactions (including hydrophobic hydration) in affecting structure that are manifested in the energy-related thermodynamic (enthalpy and heat capacity) characteristics.

Thus, the principal objective of this work is to obtain new information on the enthalpic changes caused by TMU dissolution in ordinary and heavy water at temperatures from 278.15 to 318.15 K (with a step of 10 K). In the present paper we report also detailed results on the D_2O–H_2O solvent isotope effects (below IEs) on the enthalpy as well as heat capacity of TMU hydration and discuss them briefly, comparing with like effects obtained previously [1] for a cyclic analogue of the solute in question.

2. Experimental

TMU (Merck, analytical grade) was initially purified using a drying by Å4 sieves under air-proof conditions for several days; then the sample was twice distilled at reduced pressure ($p \cong 5$ mmHg),

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as described previously [15,16]. In all experiments only the middle fraction of TMU was used. Gas chromatographic analysis showed that final purity of TMU was better than 99.9 mol%; herewith the residual water content, determined with a Karl-Fischer titration, was below 0.01 wt.%. The density and refraction index of the solute purified were 0.96204 g cm^{-3} and 1.44935, at 298.15 K (the reliable data reported in literature are 0.96192 g cm^{-3} and 1.4494 [16]), respectively. Before and after experiments, the freshly prepared sample of TMU was stored in a light-proof vacuum dessicator over P_2O_5. Water was distilled from an alkaline solution of $KMnO_4$ and then redistilled in a quartz still to reach the electric conductivity $\kappa \approx 1.2 \times 10^{-5}$ S m^{-1}. Heavy water D_2O (Izotop Co., St. Petersburg; $\kappa \approx 1.0 \times 10^{-5}$ S m^{-1}) with natural ^{18}O-content was used as such. Its deuterium content being 99.92 ± 0.02 at.% D was tested by measuring its density and comparing the obtained value with that of "reference" ([17], 100 at.% D) heavy water at various temperatures.

The experimental enthalpies of TMU dissolution, $\Delta_{sol}H^m$ (m is the solution molality), in H/D isotopically distinguishable aqueous media were measured at 278.15, 288.15, 298.15, 308.15, and 318.15 K using an automated isoperibol (ampoule-type) calorimeter fitted with a 70 cm^3 titanium vessel and electrical calibration (before each experiment). The detection limit of the apparatus is 10 μK. The temperature instability in the bath is 1 mK in the temperature range from 278 to 333 K. Correction to the presence of solute vapor in incompletely filled ampoules proved negligible because of the low TMU volatility ($T_{b.p.}$ of this solute is equal to 450.5 K [18]). The calorimeter setup and experimental procedure were detailed recently [19].

3. Results

The calorimetric measurements showed that the $\Delta_{sol}H^m$ values in the high dilution region do not depend (within the experimental error) on m those ranging between 0.013 and 0.045 moles of TMU per 1 kg of the solvent (ordinary or heavy water). Therefore, the $\Delta_{sol}H^\circ$ values (*i.e.*, the molar enthalpies of TMU dissolution at infinite dilution) have been calculated as average values $|\Delta_{sol}H^m|_{av}$ over five concentration-depending measurements at each of temperatures, according to the procedure described previously [13,20]. The experimental data on $\Delta_{sol}H^\circ$ for TMU in H_2O and D_2O are listed in Table 1.

The results, shown in the table for the protiated system at 298.15 K, were compared with those reported by others. The value obtained earlier by Rouw and Somsen [22], −24.53 ± 0.01 kJ mol^{-1}, is in satisfactory agreement with our own, while the value reported by Koga and co-workers [23], −22.07 ± 0.05 kJ mol^{-1}, is significantly lower in magnitude than ours. A similar value, $\Delta_{sol}H^\circ = -22.19 \pm 0.05$ kJ mol^{-1}, for TMU in H_2O has been obtained recently by one of us (E.V. Ivanov) with co-authors [11,24], too.[2] However, in the latter case, the D_2O–H_2O solvent IE on $\Delta_{hydr}H^\circ$ being *ca.* −1.2 kJ mol^{-1} at 298.15 K (see Section 1) is found to be very close to that presented in Table 1: $\delta\Delta_{hydr}H^\circ$ ($H_2O \rightarrow D_2O$) = −1.22 ± 0.10 kJ mol^{-1}. In addition, the enthalpic effects of TMU dissolution, $\Delta_{sol}H^\circ$ (H_2O) at 298.15 and 308.15 K, reported by Ahluwalia and co-workers [25] are also systematically less exothermic, differing from ours by *ca.* 0.9 ± 0.1 kJ mol^{-1}, as a whole.

Table 1
Standard enthalpies of solution ($\Delta_{sol}H^\circ$, kJ mol^{-1}), of 1,1,3,3-tetramethylurea in ordinary and heavy water at various temperatures (T, K).

T	H_2O + TMU		D_2O + TMU	
	$10^3 \times m^a$	$-\Delta_{sol}H^{\circ b}$	$10^3 \times m^a$	$-\Delta_{sol}H^{\circ b}$
278.15	17.1–36.2	29.24 ± 0.09	21.8–44.5	31.03 ± 0.07
288.15	15.8–25.7	27.05 ± 0.04	17.0–24.9	28.55 ± 0.08
298.15	21.7–28.3	24.86 ± 0.09	18.6–26.5	26.08 ± 0.05
308.15	18.2–32.3	22.66 ± 0.07	13.8–26.8	23.57 ± 0.06
318.15	14.8–29.7	20.47 ± 0.12	17.9–31.1	21.10 ± 0.07

[a] Concentration (molality) ranges in which the $\Delta_{sol}H^m$ values for TMU were averaged.
[b] Errors represent 95% confidence interval half-width [20,21].

We believe that such a significant scatter in the above-compared data can be explained by the difference in both experimental details and the quality of the preparation of TMU samples (from different manufacturers). Our values (Table 1) appear to be of high accuracy because the TMU sample virtually does not contain the residual water and other impurities. Besides, it should be taken into account that a "commercial" liquid TMU is decomposed partly (due to oxidation), acquiring a slightly yellow tint, from sufficiently long-duration storage.

4. Discussion

As can be seen from data of Table 1, the dissolution of TMU in the H/D isotopologues of water is accompanied by a considerable heat evolution over the whole temperature range studied. With temperature rise, this process becomes decreasingly exothermic. Suffice it to say that the difference in $\Delta_{sol}H^\circ$ for (D_2O + TMU) reaches *ca.* 7.5 kJ mol^{-1}, unlike *ca.* 4.5 kJ mol^{-1} for (D_2O + DMI) [1], on going from 288.15 to 318.15 K. Herewith the $\Delta_{sol}H^\circ$ values decrease in magnitude (*i.e.*, the TMU dissolution becomes less exothermic) when H_2O replaces D_2O, too. A change in the isotope composition of the aqueous medium has a rather slight influence on $\Delta_{sol}H^\circ$, varying this temperature-dependent quantity not more than 6% at 278.15 K and 3% at 318.15 K when the solvent molecules are deuterated. However, taking into account that the uncertainty in the $\Delta_{sol}H^\circ$ determination is not more than 0.6%, it will be a good plan to carry out the subsequent discussion of the IEs in question.

According to inferences [26–29], the large and negative $\Delta_{sol}H^\circ(T)$ values accompanied by a positive slope $(\partial\Delta_{sol}H^\circ/\partial T)_p$ are indicative of a predominantly hydrophobic hydration of the solute. That is, although the interaction of the carbonyl group with the solvent (H_2O or D_2O) proves to be significant [30], at low compositions of aqueous TMU its hydrophobic character (around CH_3 groups) dominates [5,31]. Since the changes in $\Delta_{sol}H^\circ(T)$ observed on going from one solvent (H_2O) to another (D_2O) are numerically equal to those in $\Delta_{hydr}H^\circ(T)$ upon $H_2O \rightarrow D_2O$ isotope substitution [1,29], the more negative $\Delta_{sol}H^\circ(T)$ and more positive $(\partial\Delta_{sol}H^\circ/\partial T)_p$ quantities for the deuterium-substituted solvent (Fig. 1) indicate that, like the previous situation with DMI [1], this type of TMU hydration is enhanced in D_2O.

One can see from Fig. 1 that the sign of IE on $\Delta_{hydr}H^\circ(T)$ is inverted near by 340 K. At higher temperatures, this IE should be increasingly positive. The temperature at the inversion point for TMU is the higher by 6(±4) K than that estimated recently for DMI [1]. It is not surprising due to the more significant isotopic difference in $\Delta_{sol}H^\circ$ between (H_2O + TMU) and (D_2O + TMU) over the whole temperature range studied. We believe that the revealed sign inversion is mainly caused by the isotopic distinction in the rate of thermal predestruction of the water structure. It is well known [9,14,29,31–33] that heavy water is more structured than ordinary water and thus the properties of solutions in D_2O are more sensitive to the solvent-related changes under influence of the solute and temperature. As the latter increases, the structural differences

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[2] Here, it should be noted that if the authors [23] have used TMU (ACROS, ≥99 wt%) as such, in the work [24] this solute (Fluka, ≥99 wt%) was vacuum-distilled.

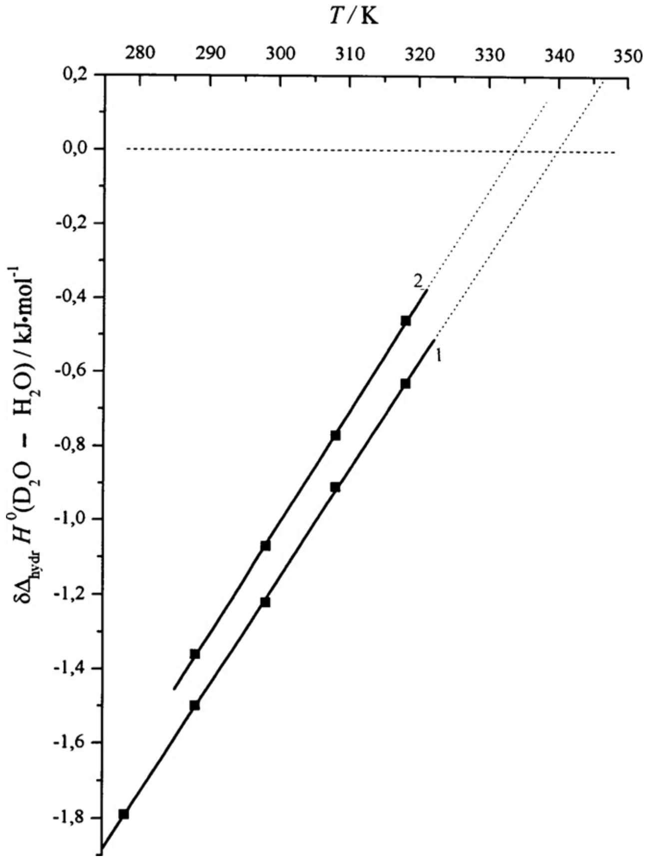

Fig. 1. D_2O–H_2O solvent isotope effects on the enthalpy of dissolution (hydration) of TMU (1) and DMI (2) [1] in the aqueous medium as a function of temperature. The dotted lines are limited by the "hypothetic line of zero-axis isotope effect". (The half-width of the confidence interval for quantities compared are ±0.1 kJ mol^{-1}.)

between H_2O and D_2O become less pronounced and the rising positive enthalpy-isotope contribution caused by a faster (compared to H_2O) destruction of the spatial hydrogen-bond network of heavy water results in weakening the negative enthalpy-isotope effects of TMU hydrophobic hydration, and TMU–water specific interaction as well.

The given conclusion is consistent with the fact that in dilute aqueous solutions of TMU the solute–solute hydrophobic interaction increases with increasing temperature [34]. In this connection, it is interesting too that the second osmotic virial coefficient obtained from the recent small-angle neutron scattering (SANS) experiments in (D_2O + DMI) solutions [5] is temperature independent. In author's opinion, such behavior may suggest that the attractive interaction between DMI molecules is not of the hydrophobic type.

Also, it is noteworthy that the IEs on $\Delta_{\rm hydr}H^\circ$ for both TMU and DMI (see Fig. 1) are roughly equal to the IE on the energy of water–water hydrogen bond, which amounts to -1.0 ± 0.1 kJ mol^{-1} at 298.15 K [14,35]. This indicates that the molecules of both solutes compared are capable of forming the sufficiently strong hydrogen (H- or D-) bonds in aqueous media. Herewith, allowing for the reliable literature data on the vaporization enthalpy being *ca.* 53.36 kJ mol^{-1} (for TMU) [18] and 60.1 ± 0.5 kJ mol^{-1} (for DMI) [36] at 298.15 K, the cyclization of a TMU molecule results in weakening its structure-making effect and hydration, as a whole. At the same time the fact that $\Delta_{\rm hydr}H^\circ({\rm DMI}) \approx \Delta_{\rm hydr}H^\circ({\rm TMU})$ in both H_2O and D_2O may serve as the corroboration of the conclusion [11,37] that the more polar molecules of cyclic analogue are responsible for the higher hydrogen-bond-accepting ability.

The results given in Table 1 made it possible to calculate the standard heat capacities of TMU dissolution, $\Delta_{\rm sol}c_p^\circ$, in the H/D isotopically distinguishable aqueous media. For this purpose, the temperature dependences of $\Delta_{\rm sol}H^\circ$ were approximated by the equation [1,27]:

$$\Delta_{\rm sol}H^\circ(T) = \Delta_{\rm sol}H^\circ(\theta) + \Delta_{\rm sol}c_p^\circ\theta\left(\frac{T}{\theta} - 1\right).$$

Here, $\Delta_{\rm sol}H^\circ(T)$ and T (current temperature, K) are variables, $\Delta_{\rm sol}H^\circ(\theta)$ and $\Delta_{\rm sol}c_p^\circ$ are the enthalpy and heat capacity parameters belonging to a reference temperature θ (K), respectively. The form of the equation assumes that the value of $\Delta_{\rm sol}c_p^\circ$ does not depend on temperature.

The results of approximation by the above equation show that $\Delta_{\rm sol}c_p^\circ(T)$ values being 219 ± 5 J mol^{-1} K^{-1} (compared to 218 ± 13 [25]) and 248 ± 5 J mol^{-1} K^{-1} for (H_2O + TMU) and (D_2O + TMU), respectively, are positive and large as observed usually for hydrophobic-hydrated solutes [26–28,38,39] and become more positive at replacement of H_2O with D_2O. Previously [1], the corresponding values for DMI in ordinary and heavy water was found to be *ca.* 127 and 157 J mol^{-1} K^{-1}. Since $\Delta_{\rm sol}c_p^\circ$ reflects the structural changes in the solvent and intensity of the solvent–solute interactions [1,40], it can be corroborated that the effect of hydrophobic hydration is more pronounced in the deuterated aqueous medium. Herewith the acyclic form of the solute (urea methyl-substituted derivative) is the more hydrophobic one, as it has been emphasized recently by Jancsó and co-workers [5,41], and in our previous works [11–13,37] as well. Also, it is noteworthy the fact that the positive IEs on $\Delta_{\rm sol}c_p^\circ(T)$ for both systems compared (see above) were found to be equal in magnitude being *ca.* 30 J mol^{-1} K^{-1}.

Finally, taking into account the literature value of heat capacity for a pure liquid TMU ($c_p^* \approx 235$ J mol^{-1} K^{-1} at 298.15 K [18])[3], we have estimated the standard or limiting partial molar heat capacities of the specified solute in H_2O and D_2O, $\bar{c}_p^\circ(\equiv \bar{c}_p^\infty) = c_p^* + \Delta_{\rm sol}c_p^\circ$, which proved to be *ca.* 454 J mol^{-1} K^{-1} and 483 J mol^{-1} K^{-1}, respectively, at 298.15 K. For comparison, the values of $\bar{c}_p^\infty$ reported by Phillip et al. [6] are *ca.* 435 J mol^{-1} K^{-1} and 458 J mol^{-1} K^{-1} for (H_2O + TMU) and (D_2O + TMU), respectively, allowing for the fact that $c_p^* \approx 235$ J mol^{-1} K^{-1}, at 298.15 K.

5. Summary

Thus, one can conclude that in highly dilute aqueous (H_2O or D_2O) solutions of TMU hydrophobic hydration is the predominant type of the solute hydration and it is enhanced in heavy (deuterated) water. Herewith, due to distinction in the rate of thermal predestruction of H_2O and D_2O structures, the negative-to-positive sign inversion of the solvent isotope effect on $\Delta_{\rm hydr}H^\circ$ at $T = 340(\pm 3)$ K is observed. The intramolecular cyclization of TMU, to form DMI, result in weakening of its structure-making effect and hydration, as a whole. Also, it is noteworthy that the D_2O–H_2O solvent isotope effect on $\Delta_{\rm hydr}H^\circ$ (298.15 K) for both TMU and DMI is roughly equal to isotope effect on the energy of water–water hydrogen bonds being *ca.* -1.0 kJ mol^{-1}. This indicates that, firstly, the solutes compared are capable of forming the strong hydrogen bonds with aqueous surroundings and, secondly, the more polar molecules of TMU cyclic analogue (DMI) are responsible for the higher hydrogen-bond-accepting ability.

However, to derive more detailed conclusions, additional experimental and theoretical studies should be performed.

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[3] This value has been calculated using the linear temperature dependence of c_p^* with reference to T = 298.15 K.

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