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D_2O–H_2O solvent isotope effects on the enthalpy of 1,3-dimethylpropyleneurea hydration at temperatures from (278.15 to 313.15) K and atmospheric pressure

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ABSTRACT

The enthalpies of solution of 1,3-dimethylpropyleneurea in ordinary (H_2O) and heavy (D_2O) water were measured at (278.15, 283.15, 288.15, 298.15, and 313.15) K and atmospheric pressure. 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 solution as well as corresponding solvent isotope effects were found to be negative and decreasing in magnitude with increasing temperature. It was established that the hydration (mainly of a hydrophobic type) is enhanced in D_2O and on going from 1,3-dimethylethyleneurea (1,1,3,3-tetramethylurea) to 1,3-dimethylpropyleneurea, whereas the enthalpy-isotope effects become less appreciable in the latter case.

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1. Introduction

It is known that the interaction-related thermodynamic characteristics of a binary aqueous solution convey information about structurally averaged or supramolecular properties of the system and its components. Although thermodynamics does not yield directly the structural and energetic aspects of the intermolecular interaction, one can derive meaningful inferences from the partial molar properties such as enthalpy and heat capacity of solution (hydration) indirectly [1–6]. Meanwhile, in going from one solvent to another, the changes of molecular shape and local liquid structure are usually so substantial that enthalpy or other characteristics of the solute have to be considered virtually on an individual basis for each solvating medium compared. Some of the difficulties are avoided if the considered properties of the solute are examined in H_2O and D_2O, and the corresponding solvent isotope effects then give useful information on both the energy and structure differences between ordinary and heavy water and the interactions between the solute and H/D isotopically distinguishable solvents [7–16].

Based on the results of previous investigations [9,11–16], an experimental approach including a combination of solution isothermal calorimetry and H_2O–D_2O (solvent) isotope substitution methods allows one to establish at the molecular level the role of both hydrogen-bonding and hydrophobic hydration in structure-forming effects, which are manifested in the enthalpy and heat capacity characteristics. Here, the point is that the replacement of H_2O by D_2O in aqueous solutions is dictated by the fact that deuteration, inducing the changes in vibrational (mainly, librational) and hindered-translational motions as well as donor-accepting abilities of water molecules, brings about the formation of deuterium bonds in an aqueous medium that are stronger but more susceptible to destruction under the influence of the solute and temperature, compared with the similar protium bonds [9,17–20].

Earlier [15,16], we have discussed the temperature-dependent D_2O–H_2O solvent isotope effects (hereinafter, IEs) on standard enthalpies of solution (hydration), $\Delta_{\text{sol}}H^{\infty}(\Delta_{\text{hydr}}H^{\circ})$, for 1,1,3,3-tetramethylurea (TMU) and its cyclic derivative, 1,3-dimethyl-2-imidazolidinone or 1,3-dimethylethyleneurea (DMEU) (see Fig. 1). These solutes being efficient aprotic dipolar solvents in the pure state play an important role in various synthetic organic (biochemical) transformations, including the manufacture of pharmaceuticals [21–23]. As it was established, the hydrophobic hydration is enhanced in D_2O and weakened on going from TMU to DMEU; herewith the capability to form hydrogen bonds with aqueous surroundings becomes less pronounced at replacement of DMEU by TMU.

Allowing for these facts, it appeared fairly interesting to assess the influence of further lengthening of the hydrocarbon chain attached to N atoms in the ring of a DMEU molecule, at

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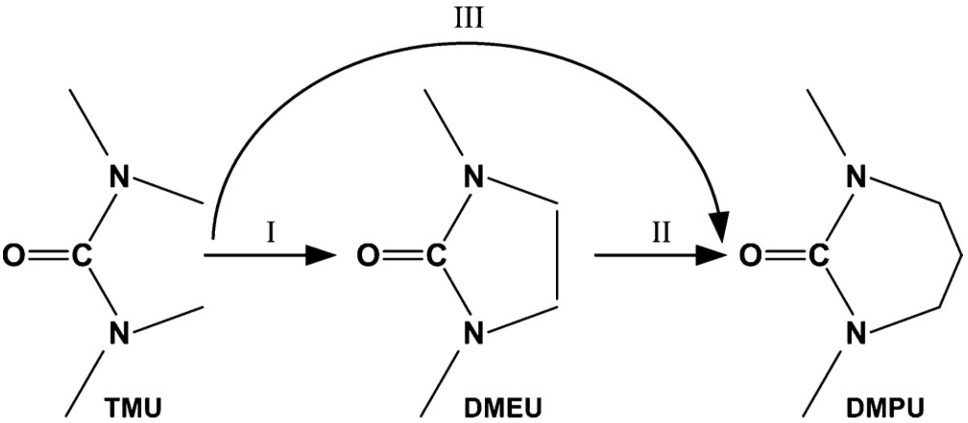

Fig. 1. Schematically simplified molecular structures of 1,1,3,3-tetramethylurea (TMU), 1,3-dimethylethyleneurea (DMEU) and 1,3-dimethylpropyleneurea (DMPU), together with the corresponding structural transitions. (Open-ended line at a nitrogen atom means the presence of a methyl group.)

forming a 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone or 1,3-dimethylpropyleneurea (DMPU) molecule (see Fig. 1), on the enthalpy/heat-capacity effects of the solute solvation in H_2O and D_2O. Since DMPU has an unusually high oxygen donor strength ($D_s \approx 34$),[1] high permittivity ($\varepsilon = 36.12$) and a large dipole moment ($\mu = 14.11 \times 10^{-30}$ C m) [24–26], this aprotic dipolar solvent, like DMEU, is an "ideal" replacement for the strong-hydrophobic but carcinogenic hexamethylphosphotriamide [24]. Meanwhile limited studies on thermodynamic properties of aqueous DMPU have been carried out hitherto [24,26–28] and only the paper [28] contains the results of calorimetric measurements for DMPU in ordinary water at four temperatures, from (293.15 to 313.15) K. The enthalpy and heat capacity characteristics of DMPU dissolution (hydration) in heavy water have not been investigated at all.

Thus, the principal objective of this work is to obtain new information on the enthalpy and heat capacity changes induced by a process of DMPU dissolution (hydration) in H_2O and D_2O at (278.15, 283.15, 288.15, 298.15 and 313.15) K and at atmospheric pressure. In the present paper we report also detailed results on the corresponding IEs and discuss them, comparing with like effects obtained previously for DMEU [15] and TMU [16].

2. Experimental

DMPU ($C_6H_{12}N_2O$: CAS [7226-23-5]) was purchased from Fluka with purity better than 99.0% as checked by GLC and water (H_2O) content less than 0.03 wt%. The solute specimen was additionally purified according to the procedure [28]: using a thermally activated 0.3-nm molecular sieves (under N_2 atmosphere) for several days with following vacuum distillation at *ca.* 340 K and $p \sim 2$ mmHg. The distillate had a specific conductance (κ) of 4.3×10^{-8} S cm^{-1} as well as density (ρ) and refraction index (n_D) being 1.06006 g cm^{-3} and 1.4878, respectively, at 298.15 K (the data reported in literature are: κ (S cm^{-1}) = 4.73×10^{-8} [29], ρ (g cm^{-3}) = 1.0600 [24], 1.059220 [27], and 1.0596 [29] and n_D = 1.4874 [24], 1.4873 [27], and 1.4881 [29]). GLC-analysis showed that final purity of DMPU was 99.9% and more; herewith the residual water content, determined with a Karl Fischer titration, was *ca.* 0.005 wt%. Before and after measurements, the DMPU sample was stored in a dark vacuum dessicator over P_2O_5. Water of natural isotope composition was twice distilled up to $\kappa = 1.3 \times 10^{-6}$ S cm^{-1}. Heavy water (Izotop Co., St. Petersburg; 99.9 at% D; $\kappa = 1.0 \times 10^{-6}$ S cm^{-1}) was used as such. According to results of an additional densimetric analysis, with allowance for $\rho(D_2O)$ reference data [30], the deuterium content in heavy water studied was 99.92 ± 0.02 at%.

The experimental enthalpies of solution $\Delta_{sol}H^m$(DMPU)[2] were measured at T = (278.15, 283.15, 288.15, 298.15 and 313.15) K and atmospheric pressure 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 of (278–333) K. The calorimeter setup and experimental procedure were described in detail recently [31].

3. Results and discussion

One can see in Fig. 2 that, in accord with the calorimetric measurements performed, the $\Delta_{sol}H^m$ values in the high dilution region do not depend virtually (within the experimental error) on *m*. Therefore, the $\Delta_{sol}H^\infty$ values have been calculated as average values $\left|\Delta_{sol}H^m\right|_{av}$ over five measurements, according to the procedure [14,32]. The experimental data on $\Delta_{sol}H^\infty$ for DMPU are listed in Table 1, together with the results reported earlier by one of us (D.V. Batov) with co-authors for (H_2O + DMPU) [28]. It is seen from the data in this table that the agreement between the present $\Delta_{sol}H^\infty$ values and those obtained in the work [28] is very good at 298.15 K but less satisfactory at 313.15 K (in the latter case, the distinction in $\Delta_{sol}H^\infty$ reaches up to 0.5 kJ mol^{-1} or about 2% of the total).

Proceeding from the results presented in Table 1, one may conclude that the dissolution of DMPU in both ordinary and heavy water is accompanied by a considerable heat evolution over the whole temperature range studied. As the temperature rises, the $\Delta_{sol}H^\infty$ value becomes decreasingly negative; on going from (278.15 to 313.15) K, the exothermicity of dissolution of DMPU reduces by *ca.* 4.2 kJ mol^{-1} for the protiated system and by *ca.* 6.7 kJ mol^{-1} for the deuterated system in magnitude. However, a change in the isotope composition of the aqueous medium has as a whole rather slight influence on $\Delta_{sol}H^\infty$, varying this temperature-dependent quantity not more than 3.5% at 278.15 K and 2% at 313.15 K. Since the uncertainty in the $\Delta_{sol}H^\infty$ determination is not more than 0.4% of the total, it will be a good plan to carry out the subsequent discussion of the IEs in question.

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[1] Gutmann's electron donor and acceptor numbers (*DN* and *AN*) for DMPU are estimated to be *ca.* 42.8 and 15.2, respectively [24].

[2] Here *m* is the solution molality [moles of the solute (DMPU) per 1 kg of the solvent (H_2O or D_2O)].

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

T	H_2O + DMPU		D_2O + DMPU	
	$10^2 \times m$[a]	$-\Delta_{sol}H^{\infty}$ [b]	$10^2 \times m$[a]	$-\Delta_{sol}H^{\infty}$ [b]
278.15	1.45–2.48	26.41 ± 0.05	1.28–2.42	27.35 ± 0.06
283.15	1.78–2.73	25.52 ± 0.04	1.37–2.65	26.40 ± 0.03
288.15	1.27–2.74	24.61 ± 0.04	1.26–2.22	25.47 ± 0.06
298.15	1.73–3.30	22.87 ± 0.04 22.80 ± 0.02 [28]	1.49–2.28	23.52 ± 0.03
313.15	1.54–2.65	20.22 ± 0.03 20.72 ± 0.08 [28]	1.70–3.41	20.61 ± 0.07

[a] Concentration (molality) ranges in which the $\Delta_{sol}H^{m}$ values for DMPU were averaged.
[b] Errors represent 95% confidence interval half-width [14,32].

Like the present results, the large and negative $\Delta_{sol}H^{\infty}$ values accompanied by a positive slope $(\partial\Delta_{sol}H^{\infty}/\partial T)_p$ have been also observed previously [15,16,33,34] for aqueous DMEU and TMU whose hydration "behavior" is indicative of a predominantly hydrophobic type [2–4,33–37]. Because the changes in $\Delta_{sol}H^{\infty}$ on substituting H_2O by D_2O are numerically equal to those in $\Delta_{hydr}H^{\circ}$ (these enthalpy characteristics as defined do not contain the contributions from the interaction between the solute molecules) [9,15], the negative $\delta\Delta_{sol}H^{\infty}(H_2O \rightarrow D_2O)$ and positive $\delta(\partial\Delta_{sol}H^{\infty}/\partial T)_p$ values for the deuterium-substituted aqueous medium can be considered as an evidence that this type of DMPU hydration is enhanced in D_2O (see Fig. 3).

One can see in Fig. 3 that a solute dissolution in both ordinary and heavy water becomes decreasingly exothermic on going from TMU to DMPU and further to DMEU. Herewith the transitions **I** and **II** (in Fig. 1) entail the substantial but opposite changes in $\Delta_{sol}H^{\infty}$ (by *ca.* 7.6 and −5.6 kJ mol^{-1}, respectively, at 298.15 K), meaning that the heat loss on going from TMU to DMPU (**III**) is fairly insignificant (being ~2 kJ mol^{-1}). At the same time the corresponding "absolute" IEs change in the order TMU > DMEU > DMPU, amounting to (in kJ mol^{-1}) −1.22, −1.07 and −0.65, respectively, at 298.15 K.[3] It is surprising, if we consider the findings [26] that the DMPU molecule has a more pronounced structure-making effect on a water H- or D-isotopologue than TMU and DMEU molecules. Note that, as a rule, the enhancement of the given effect being directly connected with the hydrophobic hydration phenomenon results in increasing the negative value of $\delta\Delta_{sol}H^{\infty}(H_2O \rightarrow D_2O)$ in magnitude [9–11,13].

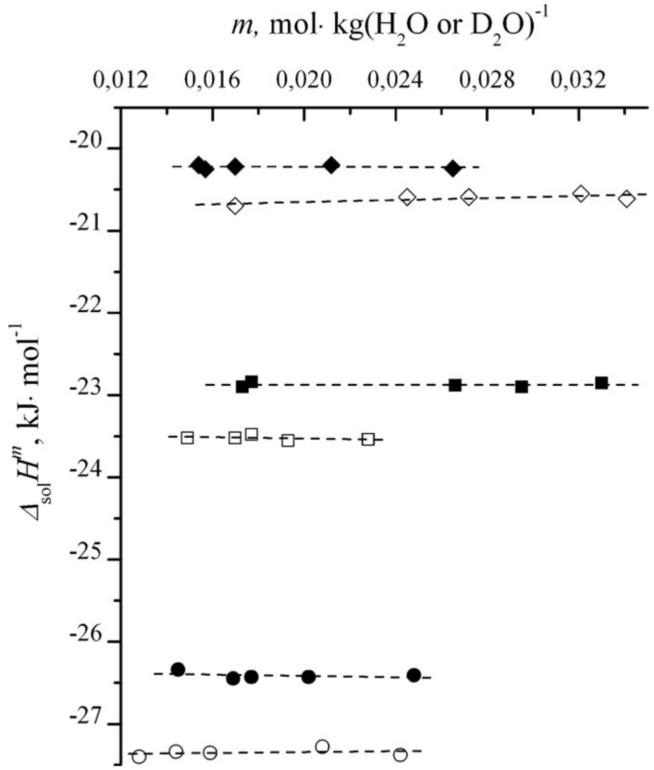

Fig. 2. The concentration-dependent molar enthalpies of DMPU solution in ordinary water (closed symbols) and heavy water (open symbols) against the solution molality at 278.15 K (●; ○), 298.15 K (■; □), and 313.13 K (♦; ◇). The average-weighted values are depicted as the linearly approximated ones (dotted lines).

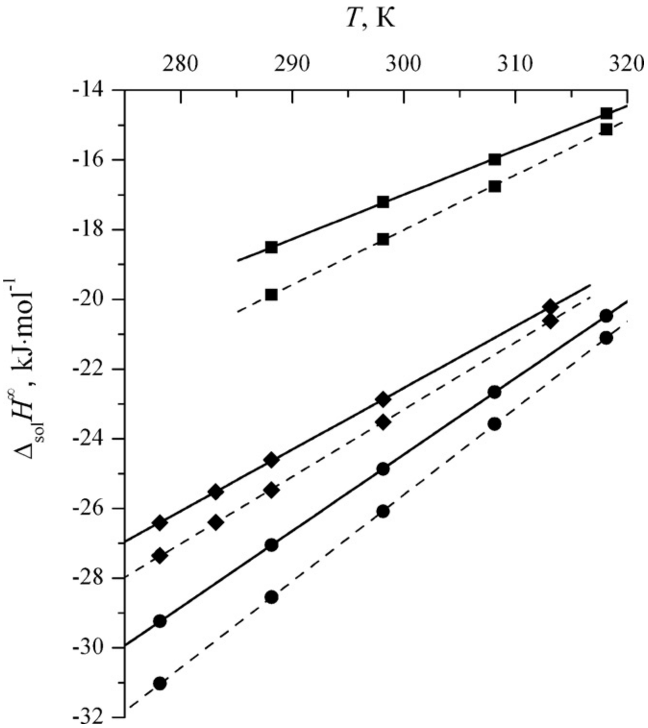

Fig. 3. The standard molar enthalpies of solution of TMU (●), DMEU (■), and DMPU (♦) in ordinary water (solid lines) and heavy water (dashed lines) as a function of temperature. The values of half-width of confidence interval for the enthalpy characteristics in question do not exceed ±0.13 kJ mol^{-1} at worst (see Table 2 in the present work and Refs. [15,16] as well).

Such an unusual behavior of the given IEs may arise from the fact that both hydrophobic hydration and solute–solvent hydrogen bonding are the steric-dependent effects. That is, the revealed enthalpy-isotope changes upon dissolution of DMPU (see in Table 1 and Fig. 3) are directly related to both structural peculiarities of this solute and differences in the interaction properties of H_2O and D_2O, including the more pronounced ability of heavy water molecules to form hydrogen-bonded aggregates (hydration complexes) with a solute molecule [9,38,39]. As a consequence, it manifests itself in the ability of DMPU, DMEU and TMU molecules to be built differ-

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[3] Numerical values are taken from Table 1 and Refs. [15,16]. Comparing $\delta\Delta_{sol}H^{\infty}(H_2O \rightarrow D_2O)$ on a per-unit basis, one may come to a different series: DMEU (0.062) > TMU (0.049) > DMPU (0.029).

ently into the initial structure of each of the solvents compared. So, a free C–N rotation in C–N(CH_3)$_2$ groups is feasible in a “nonplanar” TMU molecule, but such a rotation is not allowed in the DMEU and DMPU molecules because of a cyclization [22]. On the other hand, a DMEU molecule has a planar ring [40] whereas in the case of a DMPU molecule the middle carbon atom (within a ring) lies out of the plane [41]. Herewith the “decyclization” of a hydrated DMEU molecule, to form TMU, and the introduction of a CH_2 group into its ring, to form DMPU, result in the same structure-packing effect [26,42,43]: the “excluded space” becomes more by *ca.* 3 cm^3 mol^{-1} than that one would expect from the comparison of van der Waals volumes of these solutes [44]. This suggests that the steric incompatibility effects may be bigger in the case of hydration of the DMPU and TMU molecules.

To understand this situation more clearly, other energy-related thermodynamic properties, including $\Delta_{\text{hydr}}H^{\circ}$ and heat capacity changes for the solution process, $\Delta_{\text{sol}}c_p^{\infty}$, for DMPU in both solvents compared, must be considered (together with the similar results for aqueous DMEU and TMU) too, as we attempt to do below.

For calculating $\Delta_{\text{sol}}c_p^{\infty}$, the temperature dependences of $\Delta_{\text{sol}}H^{\infty}$ were approximated by the linear equation [6,15]

$$\Delta_{\text{sol}}H^{\infty}(T) = \Delta_{\text{sol}}H^{\infty}(\theta) + \Delta_{\text{sol}}c_p^{\infty}\theta\left(\frac{T}{\theta}-1\right) \qquad (1)$$

where $\Delta_{\text{sol}}H^{\infty}(T)$ and T (current temperature, K) are variables, $\Delta_{\text{sol}}H^{\infty}(\theta)$ and $\Delta_{\text{sol}}c_p^{\infty}$ are the enthalpy and heat capacity parameters at a reference temperature θ = 298.15 K, respectively. The form of the equation assumes that $\Delta_{\text{sol}}c_p^{\infty}$ does not depend on temperature. The results of approximation by Eq. (1) show that $\Delta_{\text{sol}}c_p^{\infty}$ value is (176.6 ± 2) J mol^{-1} K^{-1}, compared to (149 ± 5) J mol^{-1} K^{-1} [28], for (H_2O + DMPU) and (192.8 ± 3) J mol^{-1} K^{-1} for (D_2O + DMPU), respectively, are positive and large as observed usually for hydrophobic-hydrated solutes [3–6,33–36] and become more positive at replacement of H_2O with D_2O. Previously [15,16], the corresponding values for DMEU and TMU in ordinary and heavy water were found to be (127 ± 5) and (157 ± 6) J mol^{-1} K^{-1} and (219.3 ± 1) and (248.4 ± 1) J mol^{-1} K^{-1}, respectively.

Since such a behavior of $\Delta_{\text{sol}}c_p^{\infty}$ reflects primarily the structural changes in the solvent induced by increasing energy fluctuations (due to increasing the number of shorter water – water hydrogen bonds) in the nearest vicinity of nonpolar groups [36], it can be corroborated that the effect of hydrophobic hydration is more pronounced in the deuterated aqueous media. Herewith the acyclic form of the solute (a TMU molecule) is the more hydrophobic one, as it has been emphasized recently by Jancsó and co-workers [21,26], and in our previous works [11,14–16] as well. Seen in this context, the fact that $\Delta_{\text{sol}}c_p^{\infty}(\text{DMPU}) - \Delta_{\text{sol}}c_p^{\infty}(\text{DMEU}) \approx 50$ J mol^{-1} K^{-1} is not unexpected because the DMPU molecule contains one more CH_2 group than the DMEU molecule (Fig. 1). Meanwhile the IE on $\Delta_{\text{sol}}c_p^{\infty}$ for DMPU being *ca.* 15 J mol^{-1} K^{-1} is half as large as $\delta\Delta_{\text{sol}}c_p^{\infty}$ ($H_2O \rightarrow D_2O$; DMEU) ≈ $\delta\Delta_{\text{sol}}c_p^{\infty}$ ($H_2O \rightarrow D_2O$; TMU) ≈ 30 J mol^{-1} K^{-1}.[4]

Using Eq. (1), one can predict also the temperature range in which $\delta\Delta_{\text{sol}}H^{\infty}(H_2O \rightarrow D_2O)$ becomes zero, taking on a positive (by sign) value at higher temperatures. We have found that such an “inversion point” for DMPU, T_{inv} = (338 ± 2) K, lies between the T_{inv} values for solutes DMEU, (334 ± 3) K [15], and TMU, (340 ± 1) K [16]. Taking it into account along with the above-specified IEs on $\Delta_{\text{sol}}c_p^{\infty}$, one can make a proposal that effects of hydrophobic hydration and hydrogen-bonding in heavy water occur against the background of a more pronounced configurational rearrangement caused by a higher rate of the predestruction of its “local” molecular packing under influence of the solute molecules and temperature, compared to a protiated aqueous medium. This explains, to some extent, why IEs on $\Delta_{\text{sol}}H^{\infty}$ decreases in magnitude as the temperature rises. Herewith the “parent” structure of water isotopologues seems to be best suited for incorporating into them a more compact DMEU molecule, creating additional steric hindrances when a DMPU molecule interacts with aqueous surroundings by the predominantly hydrophobic mechanism. In turn, a less pronounced character of change in $\delta\Delta_{\text{sol}}c_p^{\infty}(H_2O \rightarrow D_2O)$ for DMPU may be caused by the additional pre-destroying of water structure and, as a result, strengthening of hydrophilic hydration via C=O···H(D)–O-bonding (as it was found for acyclic methyl-substituted ureas in H_2O and D_2O [45]). Such an inference seems quite reasonable, if one takes account of that the molecular dipole moment and, obviously, proton-accepting ability of DMPU is higher than those of DMEU [15,24–26,29].

However, the quantities considered (*i.e.*, $\Delta_{\text{sol}}H^{\infty}$ and $\Delta_{\text{sol}}c_p^{\infty}$) do not provide complete information on the energy changes in solvent structure induced by the hydration of DMPU, DMEU and TMU molecules. To compare the hydration effects of the three solutes in question (being liquids in a pure state), the energy spent to destroy the structure packing of each of them (*i.e.*, the standard molar enthalpies of vaporization, $\Delta_{\text{vap}}H^{\circ}$) must be taken into account. In view of this, we have estimated the data on $\Delta_{\text{hydr}}H^{\circ}(T)$, using the $\Delta_{\text{vap}}H^{\circ}(T)$ values (in kJ mol^{-1}), which have been calculated from the linear relationships {Eqs. (2)–(4)} based on the corresponding temperature dependences [46,47]

$$\Delta_{\text{vap}}H^{\circ}(\text{DMPU}) = 67.2(\pm 0.9) - 0.087(\pm 0.006) \times (T - \theta) \qquad (2)$$

$$\Delta_{\text{vap}}H^{\circ}(\text{DMEU}) = 60.1(\pm 0.9) - 0.075(\pm 0.006) \times (T - \theta) \qquad (3)$$

$$\Delta_{\text{vap}}H^{\circ}(\text{TMU}) = 54.3(\pm 0.6) - 0.085(\pm 0.007) \times (T - \theta) \qquad (4)$$

Here, θ = 298.15 K. No other data on $\Delta_{\text{vap}}H^{\circ}$ for the cyclic derivatives considered have been found in the literature. As regards this quantity for TMU, the reported results are widely scattered but data of Kozyro et al. [48], Airoldi et al. [49] and Vorob’eva and Miroshnichenko [50], being (53.4 ± 0.5), (51.1 ± 0.7) and (57.1 ± 0.7) kJ mol^{-1}, respectively, at T = 298.15 K, appear to be of rather high accuracy. (Derived recently by Della Gatta et al. [33] from enthalpies of formation in liquid and gaseous states of TMU [42], this quantity is substantially higher: ~66.2 kJ mol^{-1}.)

The results of computing $(\delta)\Delta_{\text{hydr}}H^{\circ}(T)$ using Eqs. (2)–(4) are listed in Table 2, where the $(\delta)\Delta_{\text{tr}}\Delta_{\text{hydr}}H^{\circ}(T)$ values relating to transitions **I**–**III** (Fig. 1) in the H/D isotopically distinguishable aqueous media are also included. It should be noted that Eq. (1) was used here for evaluating the smoothed $\Delta_{\text{sol}}H^{\infty}$ (and, as a consequence, $\Delta_{\text{hydr}}H^{\circ}$) vales at the same five temperatures in the range from (278.15 to 318.15) K.

The analysis of data presented in Table 2 leads us to the following.

Firstly, in all cases considered, the $\Delta_{\text{hydr}}H^{\circ}$ values and the differences in corresponding IEs for solutes compared decrease markedly when temperature is rising. These facts seem to be in accordance with the above tendency to weakening of the hydrophobic hydration with increasing temperature due to breaking of hydrogen bonds and the subsequent destruction of the spatially coordinated (ice-like) structure of the surrounding aqueous medium.

Secondly, the $\Delta_{\text{tr}}\Delta_{\text{hydr}}H^{\circ}(T)$ values caused by a substitution of both DMEU and TMU for DMPU (transitions **II** and **III**) points to the pronounced strengthening of the solute hydration; herewith the specified quantities seem to be temperature-independent (at least, within error limits). Since the energy spent to destroy the “net” solute structure increases appreciably at TMU → DMEU → DMPU replacements {Eqs. (2)–(4)}, it is clear that such a difference in $\Delta_{\text{tr}}\Delta_{\text{hydr}}H^{\circ}$ (being from 9 to 14 kJ mol^{-1}) is defined not only by the solute hydrophobicity, but also by the nature of its association with

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[4] Alternative value reported by authors [45] for the solute TMU is $\delta\Delta_{\text{sol}}c_p^{\infty}$ ($H_2O \rightarrow D_2O$) = (23 ± 2) J mol^{-1} K^{-1}.

Table 2
The smoothed values of enthalpies of hydration ($\Delta_{\rm hydr}H^\circ$, kJ mol^{-1}) for TMU and its cyclic derivatives in the H/D isotopically distinguishable aqueous media at various temperatures[a].

Solutes and solute → solute transitions ($\Delta_{\rm tr}$)	Solvents and solvent isotope effects (δ)	278.15 K	288.15 K	298.15 K	308.15 K	318.15 K
TMU	H_2O	−85.2	−82.2	−79.1	−76.1	−73.1
	D_2O	−87.0	−83.7	−80.3	−77.0	−73.7
	$H_2O \rightarrow D_2O$	−1.79	−1.50	−1.21	−0.92	−0.63
DMEU	H_2O	−81.4	−79.3	−77.3	−75.3	−73.3
	D_2O	−83.0	−80.7	−78.4	−76.1	−73.7
	$H_2O \rightarrow D_2O$	−1.67	−1.37	−1.07	−0.77	−0.47
DMPU	H_2O	−95.3	−92.7	−90.1	−87.4	−84.8
	D_2O	−96.3	−93.5	−90.7	−87.9	−85.1
	$H_2O \rightarrow D_2O$	−0.97	−0.81	−0.65	−0.49	−0.33
TMU → DMEU (**I**)[b]	H_2O	3.8	2.9	1.8	0.8	−0.2
	D_2O	4.0	3.0	1.9	0.9	0
	$H_2O \rightarrow D_2O$	0.13	0.13	0.14	0.15	0.16
DMEU → DMPU (**II**)[b]	H_2O	−14.0	−13.4	−12.8	−12.1	−11.5
	D_2O	−13.3	−12.8	−12.3	−11.8	−11.4
	$H_2O \rightarrow D_2O$	0.70	0.56	0.42	0.28	0.14
TMU → DMPU (**III**)[b]	H_2O	−10.1	−10.5	−10.9	−11.3	−11.7
	D_2O	−9.3	−9.8	−10.4	−10.9	−11.4
	$H_2O \rightarrow D_2O$	0.82	0.69	0.56	0.43	0.30

[a] The uncertainties in $\Delta_{\rm hydr}H^\circ$, including errors of the fitting procedure by Eq. (1), do not exceed ±1.2 kJ mol^{-1}. For estimating $\delta\Delta_{\rm hydr}H^\circ(H_2O \rightarrow D_2O)$, the uncertainties in $\delta\Delta_{\rm sol}H^\infty$ being generally no more than ±0.15 kJ mol^{-1} are taken into account.

[b] See in Fig. 1.

the surrounding aqueous medium through hydrogen-bonding, and dipole–dipole interactions as well. Indeed, this solute order, as it was mentioned already above, is in harmony with that expected from the magnitudes of the electron density on the carbonyl oxygen and the dipole moment of a molecule.

Thirdly, the fact that $\Delta_{\rm hydr}H^\circ$(DMEU) is comparable with $\Delta_{\rm hydr}H^\circ$(TMU) in both H_2O and D_2O (transitions **I**) may also serve as the corroboration that a more polar cyclic molecule is responsible for the higher electron-donating ability. However, if for both solutes compared the $\delta\Delta_{\rm hydr}H^\circ(H_2O \rightarrow D_2O)$ value at 298.15 K is roughly equal to the IE on energy of water – water hydrogen-bonding being about −1.0 kJ mol^{-1} [18,51], for the solute DMPU this quantity is estimated at −0.65 kJ mol^{-1} only. Such a surprisingly different behavior of enthalpy-isotope characteristic of hydration of TMU and its cyclic analogues is not yet subject to a reasonable explanation. To understand this behavior clearly, further detailed studies are needed.

4. Concluding remarks

We have established that the molecules of DMPU are hydrated as a whole stronger than those of DMEU or TMU and predominantly hydrophobic is enhanced in heavy water. The isotope effect on the enthalpy of solution (hydration) for DMEU is found to be significantly smaller than those for DMEU and TMU. It may be seen primarily as the result of the different ability of the compared molecules to be built into the initial structure of water by forming hydrogen bonds.

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