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Volume-related interaction parameters for dilute solutions of tetramethylurea in normal and heavy water between 278.15 K and 318.15 K

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ABSTRACT

Density measurements were carried out on dilute solutions of tetramethylurea (TMU) in normal and heavy water in the aquamolality ranges 0.058–1.74 and 0.052–1.72, respectively, at 278.15 K, 288.15 K, 298.15 K, 308.15 K, and 318.15 K. The excess partial molar volumes of TMU ($\bar{V}^{\mathrm{E},\infty}$) and volume second virial coefficient (v_{xx}), calculated from the densities of the H/D isotopically distinguishable solutions, are negative, which indicate that the solute has a predominantly structure-making effect on aqueous surroundings. With decreasing temperature and on going from protiated solvent to deuterated one the values of $\bar{V}^{\mathrm{E},\infty}$ and v_{xx} become more negative, suggesting that the hydration sphere around a TMU molecule is more structured in the specified cases. The obtained results were discussed allowing for enthalpic and some other characteristics of TMU solutions in normal and heavy water.

1. Introduction

Due to their practical and theoretical significance, the structural and thermodynamic properties of the tetramethylurea (TMU) aqueous solutions attract remarkable and continuing interest. Studying such systems should contribute to an understanding of various biochemical processes including the protein denaturation and synthesis of pharmaceuticals [1–3]. Interest in aqueous solutions of TMU also stems from the structure transformations of the solvent in the course of both hydration and intermolecular interactions associated with the competition between the contributions of the hydrophilic and hydrophobic parts of the solute molecule and their joint action on the surroundings [4–19].

Some of these problems are avoided if thermodynamic properties of the aqueous TMU are examined in H_2O and D_2O, and solvent isotope effects in such properties then give useful information on both the structure-related differences between normal and heavy water and the interactions between the solute and H/D isotopically distinguishable solvents compared [4,9,13,15,18–22]. Herewith it have been shown that the partial molar volumes of the solute at infinite dilution $\bar{V}^{\infty}$ and the molal volume second virial coefficients v_{xx} for TMU–TMU interactions can be obtained using the excess molar volumes V^{E} of dilute aqueous (H_2O or D_2O) solutions [15,19,23]. It can provide information on differences in the structure-making or structure-breaking effects of the solute on water H/D isotopologues and in volume or “packing” change produced by the pair-wise interaction of solute molecules as well [15,24].

Meanwhile, we are aware only one study [9] describing the results of determination of the apparent molar volumes V_{ϕ} (including $V_{\phi}^{\infty} \equiv \bar{V}^{\infty}$) of TMU as a function of concentration in heavy water at three temperatures (288.15 K, 298.15 K and 313.15 K). Other such investigations [4,20] have been carried out only at 298.15 K. Also, it should be taken into account that the substitution of H_2O by D_2O in an aqueous non-electrolyte solution results in a rather small change in V^{E} [24–32]. Therefore, it is important to use a solute of the same quality and high purity in the preparation of H/D isotopically distinguishable aqueous solutions, and to carry out the density measurements under the same conditions.

The purpose of this paper is to study the effect of H/D isotopic substitution (in a solvent molecule) on the packing-related changes in dilute aqueous solutions of TMU at temperatures from 278.15 K to 318.15 K (with a step of 10 K) and at and $p \cong 0.1$ MPa. The solvent isotope effect will be discussed in terms of the differences in both $\bar{V}^{\infty}$ and v_{xx} evaluated with using the virial expansion of V^{E}. In Section 4, data on enthalpic and some other characteristics of TMU solutions in normal and heavy water will be used to reveal

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Table 1
Densities ρ and cubic expansion coefficients α_p for the pure tetramethylurea at temperatures from 278.15 K to 318.15 K.

T (K)	ρ (g cm^{-3})		$10^3\alpha_p$ (K^{-1})	
	This work	Literature	This work^{a}	Literature
278.15	0.98034	–	0.931 ± 0.005	–
288.15	0.97120	0.971358^{b}	0.942 ± 0.005	0.95 ± 0.01^{b}
298.15	0.96204	0.962519^{b}, 0.96252^{c}, 0.9620^{d} 0.96207^{e}, 0.96194^{f} 0.96192^{g} 0.9619^{h,i,j}, 0.9622^{k} 0.962107^{l}, 0.96301^{m}	0.954 ± 0.005	0.90 ± 0.01^{b}, 0.919^{f} 1.41 ± 0.01^{h}
308.15	0.95284	0.954027^{b}, 0.95304^{f}	0.966 ± 0.005	0.85 ± 0.01^{b}, 0.940^{f}
318.15	0.94362	0.946304^{b}, 0.94402^{f}, 0.9458^{k}	0.979 ± 0.005	0.80 ± 0.01^{b}, 0.962^{f}

[a] Calculated by differentiating the equation $\ln \rho = a_0 + a_1(T - T') + a_2(T - T')^2$ relative to $(T - T')$ at $T' = 298.15$ K.
[b] Ref. [39].
[c] Ref. [3].
[d] Ref. [6].
[e] Ref. [16].
[f] Ref. [33].
[g] Ref. [34].
[h] Ref. [35].
[i] Ref. [40].
[j] Ref. [41].
[k] Ref. [42].
[l] Ref. [43].
[m] Ref. [44].

the specific features of the structural behavior of the solute in the hydrating medium, too.

2. Experimental

TMU (Merck, analytical grade) was initially purified using a drying by 0.4-nm sieves under air-proof conditions for several days; then the sample was distilled at reduced pressure ($p \cong 5$ mmHg) as described previously [33,34]. In all experiments only the middle fraction of TMU was used. HPLC-analysis showed that final purity of TMU was better than 99.9 mol%; the residual water content, determined with a Karl Fisher titration, was below 0.01 wt%. The solute refraction index determined using a Pulfrich refractometer PR2 was 1.44933 ± 0.00003 at 298.15 K (the reliable literature values are 1.4494 [34] and 1.4493 [35]). Before and after experiments, the fresh-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 $\kappa \approx 1.3 \times 10^{-6}$ S cm^{-1}. Heavy water D_2O (Izotop Co., St. Petersburg; $\kappa \approx 1.0 \times 10^{-6}$ S cm^{-1}) with natural ^{18}O-content was used as such. Its deuterium content being 99.90 ± 0.02 at.% D was tested by measuring density and comparing the obtained value with reference one (100 at.% D) [36,37] at each temperature; the H_2O content of the heavy water was taken into account in the calculation of the molar mass of D_2O.

The H/D isotopically distinguishable aqueous solutions of TMU were prepared under air-free conditions by weighing with a precision of 0.1 mg. Their compositions were expressed in the form of aquamolality c_{aqm} ranging from *ca.* 0.05 to 1.75 which correspond to TMU mole fraction range $x_2 \cong 9 \times 10^{-4}$ to 3×10^{-2} (c_{aqm} is defined by the number of moles of the solute per 55.51 moles of H_2O or D_2O). The use of aquamolality scale is necessary in order to allow the proper comparison of the volume properties at finite concentrations in the presence of equal numbers of H_2O and D_2O molecules [24]. The error in the c_{aqm} value was estimated to be less than 2×10^{-5} mol $(55.51M_w)^{-1}$ where M_w is the molar mass of normal or heavy water.

Densities of solutions ρ_s were measured at 278.15 K, 288.15 K, 298.15 K, 308.15 K and 318.15 K using an Anton Paar DMA 4500 vibrating-tube (hermetic) densimeter. The temperature of the measuring cell was kept constant to ±0.005 K at the desired temperature. The densimeter was calibrated with dry air and freshly prepared normal water assumed to be those of the IAPWS Formulation 1995 [38] just prior to each series of ρ_s measurements, which were made at least thrice for each solution. The reproducibility in ρ_s was better than $\pm(1 \times 10^{-5})$ g cm^{-3} and the uncertainty in each of such values did not exceed $\pm(1.5 \times 10^{-5})$ g cm^{-3}.

3. Results

Experimental density ρ and cubic expansion coefficient α_p values of pure TMU at each of the temperatures employed are given in Table 1 together with those found in the literature. As follows from the table, our ρ value at 298.15 K is in sufficiently good agreement with results reported by authors [6,16,33–35,40–43]. Besides, data on ρ at 288.15 K and 308.15 K taken from sources [39,33], respectively, agree rather satisfactory with ours, too. Herewith the quantity considered at 278.15 K is reported here for the first time.

Densities for binary solutions of TMU in H_2O and D_2O are summarized in Tables 1A and 2A (see Appendix A), together with the smoothed V_ϕ values calculated by using the third-power polyno-

Table 2
Parameters b_j of Eq. (1) for H/D isotopically distinguishable aqueous solutions of tetramethylurea at different temperatures^{a}.

T/K	H_2O + TMU					D_2O + TMU				
	b_0	10^3b_1	10^3b_2	10^4b_3	$10^6\sigma$ ^{b}	a_0	10^3b_1	10^3b_2	10^4b_3	$10^6\sigma$ ^{b}
278.15	0.999963	2.5235	1.7925	−4.530	5.09	1.105485	−8.6431	3.2748	−5.991	5.65
288.15	0.999100	1.6568	1.4626	−3.567	4.49	1.105744	−9.8841	2.9319	−5.134	5.83
298.15	0.997046	0.8777	1.2751	−3.085	2.19	1.104345	−10.9757	2.7582	−4.671	4.83
308.15	0.994033	0.2149	1.0684	−2.473	3.18	1.101617	−11.9101	2.5950	−4.054	6.61
318.15	0.990210	−0.3748	0.8090	−1.541	4.10	1.097819	−12.7235	2.4026	−3.307	3.47

[a] Units: b_0, g cm^{-3}; b_1, g $(55.51M_w)$ mol^{-1} cm^{-3}; b_2, g $(55.51M_w)^2$ mol^{-2} cm^{-3}; b_3, g $(55.51M_w)^3$ mol^{-3} cm^{-3}.
[b] The standard deviation for least-squares representation of ρ_s.

mial expansion

$$\rho_s = b_0 + b_1 c_{aqm} + b_2 c_{aqm}^2 + b_3 c_{aqm}^3 \qquad (1)$$

and the formula expressing the volume of a binary solution V_s in the aquamolality scale [45]

$$V_s(c_{aqm}) = \frac{55.51 M_w + M c_{aqm}}{\rho_s} = V_w^o(\equiv 55.51 M_w/\rho_w) + V_\phi c_{aqm} \qquad (2)$$

where M and ρ_w are the molar mass of the solute (TMU) and the density the solvent (normal or heavy water), respectively. The b_j coefficients of Eq. (1) are given in Table 2.

According to inferences [23,24], the excess volume of the solution per 55.51 mol of water isotopologue $V_s^E(c_{aqm})$ is given by the expression

$$V_s^E(c_{aqm}) = V_s(c_{aqm}) - V_w^o - \bar{V}^\infty c_{aqm} \qquad (3)$$

On the other hand, at low concentrations the excess volume defined in Eq. (3) can be expressed as a virial expansion in the solute aquamolality [23,46]

$$V_s^E(c_{aqm}) = \upsilon_{xx} c_{aqm} + \upsilon_{xxx} c_{aqm}^2 + \cdots \qquad (4)$$

Here, according to the McMillan–Mayer theory of solutions [47], the coefficients υ_{xx} and υ_{xxx} being known also as the molal volumetric second- and third-virial coefficients, represent the contribution of pair- and triplet-solute aggregates to the excess volume, respectively [24]. From Eqs. (3) and (4) one obtains

$$V_s(c_{aqm}) - V_w^o = \bar{V}^\infty c_{aqm} + \upsilon_{xx} c_{aqm}^2 + \upsilon_{xxx} c_{aqm}^3 + \cdots \qquad (5)$$

By fitting the function $V_s(c_{aqm}) - V_w^\circ$ against c_{aqm} using the method of least-squares, the $\bar{V}^\infty$, υ_{xx} and υ_{xxx} quantities can be determined. The method has been successfully applied earlier to aqueous (H- or D-substituted) solutions of *N*,*N*′-dimethylethyleneurea [15], *N*,*N*′-dimethylpropyleneurea [19], polyols [23], 3-methylpyridine [24] and alcohols and diols [48].

The obtained values of $\bar{V}^\infty$, υ_{xx} and υ_{xxx} as well as their 95%-confidence interval half-widths [49] are given in Table 3. Herewith, based on the *F* test [49], statistical analysis showed that the experimental data on $V_s^E(c_{aqm})$ cannot be adequately described by using only the second virial coefficient (υ_{xx}); including the third-virial coefficient (υ_{xxx}) is required.

Comparison of the present $\bar{V}^\infty$ values (Table 3) at some temperatures can be made with results existing in literature for both the isotopically distinguishable systems compared [4,9] and the (H_2O + TMU) one only [5,18,41,50]. The values reported by Philip et al. [4], $\bar{V}^\infty$ (H_2O) = 115.30 ± 0.05 cm^3 mol^{-1} and $\bar{V}^\infty$ (D_2O) = 115.58 ± 0.05 cm^3 mol^{-1} at T = 298.15 K, are in rather good agreement with our own, as a whole. However, unlike data [4], we have revealed that the D_2O–H_2O solvent isotope effect (IE or δ) on $\bar{V}^\infty$ is negative in sign, being *ca.* −0.4 cm^3 mol^{-1} (see Table 3). The results presented by Jákli and Van Hook [9] at 288.15 K, 298.15 K and 313 K testify also that the considered IEs are negative and decreasing in magnitude as the temperature is rising. Meanwhile, in authors' opinion [9], it is inappropriate to quantitatively interpret their approximated parameters as $\bar{V}^\infty$ and $\delta\bar{V}^\infty$ (D_2O–H_2O) values. As regards data on $\bar{V}^\infty$ (H_2O) taken from works [5,18,41,50], they are systematically higher (by 0.7 cm^3 mol^{-1}, on the average) than ours due to using the calculation procedure employed commonly for estimating $\bar{V}^\infty$ of aqueous electrolytes. So, if to use Eqs. (1) and (2) for the adequate fitting of the recent density (or V_ϕ) results [18], one can obtain the following values of $\bar{V}^\infty$ (cm^3 mol^{-1}), υ_{xx} (cm^3(55.51M_w) mol^{-2}) and υ_{xxx} (cm^3(55.51M_w)^2 mol^{-3}), respectively: 114.18 ± 0.05, −2.70 ± 0.15, 0.73 ± 0.09 (278.15 K); 115.28 ± 0.06, −2.49 ± 0.17, 0.71 ± 0.10 (288.15 K); 115.98 ± 0.03, −1.77 ± 0.08, 0.46 ± 0.05 (298.15 K) and 117.01 ± 0.04, −1.55 ± 0.12, 0.42 ± 0.07 (308.15 K).

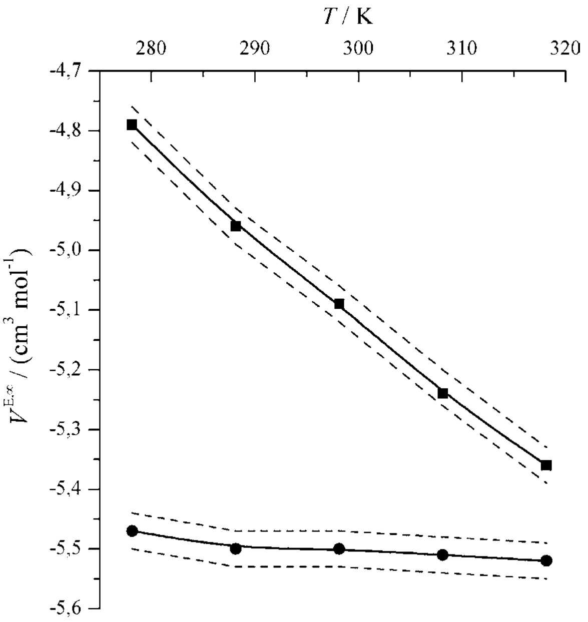

Fig. 1. The temperature dependences of the partial excess limiting molar volumes of TMU ($\bar{V}^{E,\infty}$) in normal (■) and heavy water (●). In the present figure as well as in below-located figures, the dashed lines limit the half-width of the confidence interval (±ζ [49]) for quantities considered.

4. Discussion

As it have been mentioned in Section 1, the volumetric measurements are helpful in developing a comprehensive picture of both hydration and intermolecular interactions. This is particularly true when partial and excess molar volumes are combined with the corresponding IEs because these volume effects are dominated by changes in the interparticle interactions (H compared to D) in binary isotopically distinguishable systems. Most of these changes concern a difference between the librational and hindered-translational motions as well as "volumes" of molecules in the liquid phases of H_2O and D_2O [9,51–53]. A decrease in the zero-point vibrational energy of water molecules caused by their deuteration brings about the formation of D-bonds in an aqueous medium that are stronger but more susceptible to destruction under the influence of a solute and temperature, compared with the similar protium bonds [52,53]. These circumstances indicate that a hydrophilic-type (via H- or D-bonding) interaction, along with a hydrophobic-type one, play substantial roles in the volume changes caused by the H/D isotope substitution in an aqueous medium.

Considering the results presented in Table 3 and Fig. 1 from this point of view led us to the inference that $\bar{V}^\infty$ in both solvents compared is smaller than the molar volume of pure liquid TMU. This difference referred to as the excess partial molar volume of the solute, $\bar{V}^{E,\infty}(= \bar{V}^\infty - V)$, increases in magnitude when (H_2O + TMU) is replaced by (D_2O + TMU). However, in the former case $\bar{V}^{E,\infty}$ changes monotonically from −4.8 cm^3 mol^{-1} at 278.15 K to −5.4 cm^3 mol^{-1} at 318.15 K, whereas in the latter case this quantity is independent (within the limits of approximating error) of temperature, being *ca.* −5.5 cm^3 mol^{-1}. That is, the molar expansibility $E_p = (\partial V/\partial T)_p = \alpha_p V$ (Tables 1 and 3) of pure TMU is virtually temperature-indistinguishable with its limiting partial molar expansibility $\bar{E}_p^\infty$ in D_2O (see Fig. 2). It is interesting that like similarity in expansibilities under comparison have been found previously [32] for the cyclic analogue of TMU, 1,3-dimethyl-2-imidazolidinone (DMI), dissolved in H_2O. In the case of (D_2O + DMI), on the contrary, the $\bar{V}^{E,\infty}$ value becomes decreasingly negative as the temperature increases.

Table 3

The partial molar volumes of TMU at infinite dilution ($\bar{V}^{\infty}$) in H_2O and D_2O and the volume-related second and third-virial coefficients (υ_{xx} and υ_{xxx}) for mixtures compared, with their 95%-confidence interval half-widths ($\pm\,\xi$), at different temperatures.

T (K)	$\bar{V}^{\infty\,a}$ ($cm^3\,mol^{-1}$)	$\upsilon_{xx}{}^{b}$ ($cm^3(55.51M_w)\,mol^{-2}$)	$\upsilon_{xxx}{}^{b}$ ($cm^3(55.51M_w)^2\,mol^{-3}$)	σ^{c} ($cm^3\,(55.51M_w)^{-1}$)
H_2O + TMU				
278.15	113.70 ± 0.03	−2.26 ± 0.05	0.43 ± 0.02	0.00460
288.15	114.65 ± 0.03	−1.80 ± 0.05	0.33 ± 0.02	0.00459
298.15	115.66 ± 0.02	−1.51 ± 0.03	0.28 ± 0.02	0.00329
308.15	116.68 ± 0.02	−1.21 ± 0.03	0.22 ± 0.02	0.00330
318.15	117.74 ± 0.03	−0.88 ± 0.05	0.14 ± 0.02	0.00496
D_2O + TMU				
278.15	113.02 ± 0.02	−2.32 ± 0.04	0.42 ± 0.02	0.00390
288.15	114.11 ± 0.02	−1.85 ± 0.04	0.34 ± 0.02	0.00376
298.15	115.25 ± 0.02	−1.56 ± 0.03	0.30 ± 0.02	0.00286
308.15	116.40 ± 0.03	−1.27 ± 0.05	0.24 ± 0.02	0.00444
318.15	117.58 ± 0.02	−0.97 ± 0.03	0.16 ± 0.02	0.00286

[a] Molar volume of the pure TMU, V ($cm^3\,mol^{-1}$), are 118.493 (278.15 K), 119.608 (288.15 K), 120.747 (298.15 K), 121.912 (308.15 K), and 123.104 (318.15 K).

[b] $55.51M_w$ is the mass of 55.51 mol of normal or heavy water.

[c] Standard deviation of the fit.

It is obvious that the revealed packing changes upon dissolution of TMU are directly related to both structural peculiarities of the solute and differences in the above-mentioned properties of solvents H_2O and D_2O, including the more pronounced ability of heavy water molecules to form hydrogen-bonded aggregates (hydration complexes) with a TMU molecule [13,51]. As a consequence, it manifests oneself in the ability of the latter to be built differently into the initial structure of each of solvents compared. One of the possible reasons for arising H/D isotope distinctions in $\bar{V}^{E,\infty}$ (T) is also the "isotope shift" between regions of anomalous changes in the density or molar volume of H_2O (near 277.134 K) and D_2O (near 284.335 K) on the temperature scale [37,52,53]. At the same time the surprisingly different temperature-dependent behavior of both $\bar{V}^{E,\infty}$ (Fig. 1) and $\bar{E}_p^{\infty}$ (Fig. 2) for TMU in normal and heavy water is not yet subject to a reasonable explanation.

It should be noted here that a negative sign at the $\bar{V}^{E,\infty}$ value is characteristic for systems where both H(D)-bonding and van der Waals forces between solute and solvent molecules are involved, marking $\bar{V}^{\infty}$ lower than V [54]. However, since the intrinsic volume of the non-hydrated solute molecule is not known, the difference quantities $\bar{V}^{E,\infty}$ cannot provide direct information on the structure-packing changes due to interparticle solute–solvent interactions in aqueous solutions compared.[1] Such information can be partly extracted from temperature dependences of $\bar{E}_p^{\infty}$, according to thermodynamic relation firstly proposed by Hepler [56]

$$\left(\frac{\partial\bar{c}_p^{\infty}}{\partial p}\right)_T = -T\left(\frac{\partial^2\bar{V}^{\infty}}{\partial T^2}\right)_p \tag{6}$$

where $\bar{c}_p^{\infty}(T)$ is the partial molar heat capacity of a solute. In our case, $(\partial^2\bar{V}^{\infty}\partial T^2)_p = (\partial\bar{E}_p^{\infty}/\partial T)_p$ is positive, being $(3.0 \pm 0.3) \times 10^{-4}\,cm^3\,mol^{-1}\,K^{-1}$ on the average, and according to the common classification of solutes [56,57] TMU would be a structure-making solute.

This fact would be in accordance with view based on the recent calorimetric experiments [13,51] that in this molecule the effects of four hydrophobic ($-CH_3$) groups on water structure in the diluted solutions are predominant in relation to the effects of the hydrophilic ($-C{=}O$) moiety. Particularly, the results [51] showed that $\bar{c}_p^{\infty}$ and standard heat capacities of TMU dissolution $\Delta_{sol}c_p^{\infty}$ being 454 and 219 (±5) J $mol^{-1}\,K^{-1}$ for (H_2O + TMU) and 483 and 248 (±5) J $mol^{-1}\,K^{-1}$ for (D_2O + TMU), respectively, at 298.15 K are positive and large as observed usually for hydrophobic-hydrated solutes [58,59] and become more positive at replacement of H_2O with D_2O. At the same time, unlike the above-specified data on $\delta c_p^{\infty}(\delta\Delta_{sol}c_p^{\infty})$, we have not found the similar positive IE on $(\partial\bar{E}_p^{\infty}/\partial T)_p$, probably, due to the overlapping errors.

As can be seen from Table 3, the sign of υ_{xx} is negative for both (H_2O + TMU) and (D_2O + TMU) solutions; however, its absolute values are systematically larger in the latter case. According to relationship between υ_{xx} and the overlap of hydration co-spheres of the solute pairs discussed thoroughly by Würzburger et al. [23], the negative sign at υ_{xx} and $\delta\upsilon_{xx}(D_2O–H_2O)$ shows that the water molecules, occupying larger volumes in the co-sphere than in the bulk, are more structured in the former case. That is, the solute has a structure-making effect on the aqueous surroundings. Herewith the positive sign of both the molal enthalpic

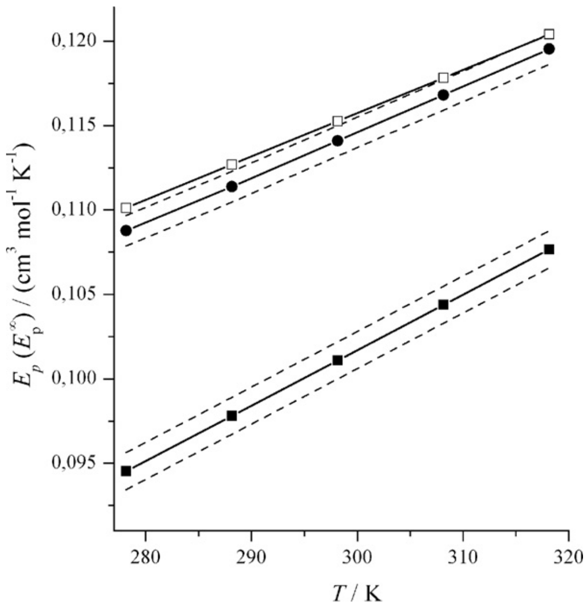

Fig. 2. The temperature dependences of the molar expansibility of TMU (E_p, □) and its partial molar expansibilities at infinite dilution ($\bar{E}_p^{\infty}$) in normal (■) and heavy water (●).

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[1] Assuming that $\bar{V}^{\infty}$ consists of the van der Waals "molecular" volume of TMU, $N_A\upsilon_w = 69.8\,cm^3\,mol^{-1}$ (where N_A is the Avogadro number) [55], plus a varying volume of empty space near the solute molecules, one can conclude only that these interactions in the deuterium-substituted aqueous medium are accompanied by the formation of more densely packed structure that surrounds a TMU molecule, probably due to a strengthening of hydrogen-bonding. It is confirmed by the fact that IE on the enthalpy of TMU hydration [51] is roughly equal to IE on the average energy of water–water hydrogen bond being *ca.* −1.0 kJ mol^{-1} at 298.15 K [52]. Herewith the majority molecules of TMU are di-hydrogen-bonded in H_2O or D_2O, according to the results of an IR-study [12].

second virial coefficients h_{xx} and the corresponding IE measures up to the same situation. Indeed, as it have been reported previously [13], h_{xx} makes up $2060 \pm 50\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for (H_2O + TMU) and $2300 \pm 120\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for (D_2O + TMU) at 298.15 K. In harmony with this observation, the results of small-angle neutron scattering (SANS) experiments [7] and molecular dynamics simulation [60] indicate that the pair-wise interaction between TMU molecules in the H/D isotopically distinguishable aqueous media is of the hydrophobic type, too.

Table 3 shows also that the volume-related triplet contributions to the solute–solute interactions (v_{xxx}) cannot be neglected even in the dilute region under study. Suffice it to say that in both (H_2O + TMU) and (D_2O + TMU) solutions at $c_{aqm} = 1$ triplet effects contribute more than 15% to V^E (see Eq. (4) and Table 3). However, unlike data on $\delta v_{xx}(D_2O{-}H_2O)$, the corresponding values of IEs on v_{xxx} are ignorable.

Our results support the view [23] that a qualitative relationship between the signs of v_{xx} and h_{xx} may be valid only if applied to a predominantly hydrophobic or hydrophilic solute molecule. On the other hand, taking into account the structure-depend nature of both packing- related and energy-related hydration characteristics [25,32,61], we can suggest that there is an obvious interrelation between the volumetric ($\delta\bar{V}^{\infty}$) and enthalpic ($\delta\Delta_{\mathrm{hydr}}H^{\infty}$) IEs of TMU dissolution (hydration) in the aqueous medium. Naturally, the "structural pattern" of such interrelation on going from one temperature to another will appreciably varies.

As it can see from Fig. 3, the correlation dependence between $\delta\Delta_{\mathrm{hydr}}H^{\infty}$ ($D_2O{-}H_2O$) [51] and $\delta\bar{V}^{\infty}$ ($D_2O{-}H_2O$) for TMU in water at $T = (278.15{-}318.15)$ K is a linear function that can be regarded as an argument in favor of the belief that these IEs are thermodynamically related. The given relationship convincingly demonstrates that both the volume and enthalpy changes are manifested to a large extent at low temperatures, *i.e.*, when the aqueous structure packing that surrounds a TMU molecule is the most pronounced mainly due to the solute structure-making effect (hydrophobic hydration type). With increasing temperature, IEs on $\bar{V}^{\infty}$ and $\Delta_{\mathrm{hydr}}H^{\infty}$ decrease abruptly in magnitude, crossing linearly a "hypothetical zero" in the closely spaced temperature regions, within 330 ± 3 K and 340 ± 4 K, respectively (from results of fitting). Hence, in the case of $\delta\bar{V}^{\infty}$ ($D_2O{-}H_2O$) = 0, the corresponding enthalpy-isotope effect does not reverse sign remaining to be slightly negative (see in Fig. 3).

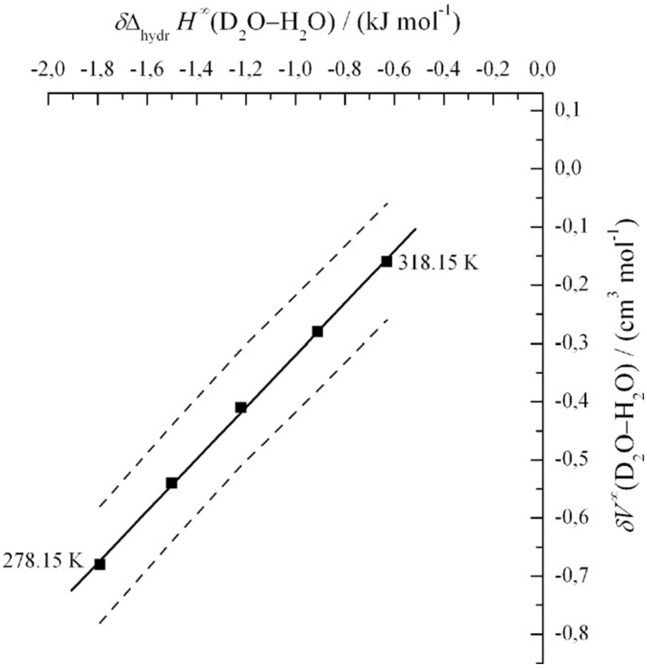

Fig. 3. The correlation between the temperature-depend changes in $D_2O{-}H_2O$ solvent isotope effects on the standard molar volume ($\delta\bar{V}^{\infty}$) and enthalpy ($\delta\Delta_{\mathrm{hydr}}H^{\infty}$) [51] effects of TMU hydration in water.

On the one hand, this situation is in agreement with the previous conclusion [51] that, at the observed sign-inversion temperatures, TMU has probably the same structural effects on H_2O and D_2O that manifested for the volume or enthalpy IEs by mutual compensation of its hydrophobic and hydrophilic parts. It can be connected with the faster thermal predestruction of the hydrogen-bonding spatial network (due to the faster volume expansion) of heavy water compared to that of H_2O. On the other hand, it is evidence that the enthalpy hydration effect in the case of (D_2O + TMU) should be considered providing for the additional contribution caused presumably by a stronger solute–solvent interaction due to configurational differences in the molecular packings of H/D isotopically distinguishable systems compared at $\delta\bar{V}^{\infty} = 0$.

However, these inferences should be particularized by using the more informative experimental and theoretical approaches.

Appendix A.

See Tables 1A and 2A.

Table 1A

Experimental densities ρ_s of TMU solutions in normal water (H_2O) and smoothed apparent molar volumes V_{ϕ} of the solute at the studied aquamolalities c_{aqm} and temperatures T [a].

c_{aqm}	T = 278.15 K		T = 288.15 K		T = 298.15 K		T = 308.15 K		T = 318.15 K	
	ρ_s	V_{ϕ}	ρ_s	V_{ϕ}	ρ_s	V_{ϕ}	ρ_s	V_{ϕ}	ρ_s	V_{ϕ}
0.000000	0.999965[b]	–	0.999101[b]	–	0.997047[b]	–	0.994035[b]	–	0.990216[b]	–
0.057643	1.00012	113.55	0.99920	114.54	0.99710	115.57	0.99405	116.61	0.99019	117.74
0.088271	1.00020	113.48	0.99926	114.48	0.99713	115.53	0.99406	116.57	0.99018	117.71
0.13094	1.00032	113.39	0.99934	114.41	0.99718	115.47	0.99408	116.52	0.99017	117.67
0.14335	1.00035	113.36	0.99936	114.39	0.99720	115.45	0.99408	116.51	0.99017	117.66
0.27635	1.00079	113.10	0.99966	114.17	0.99738	115.26	0.99417	116.36	0.99017	117.54
0.41590	1.00129	112.83	1.00002	113.96	0.99761	115.08	0.99429	116.21	0.99018	117.41
0.58821	1.00197	112.52	1.00050	113.71	0.99794	114.87	0.99448	116.04	0.99024	117.28
0.75921	1.00272	112.24	1.00105	113.48	0.99831	114.68	0.99470	115.89	0.99033	117.15
0.97864	1.00373	111.91	1.00179	113.21	0.99884	114.46	0.99504	115.71	0.99047	117.00
1.1038	1.00432	111.74	1.00223	113.08	0.99915	114.35	0.99524	115.62	0.99057	116.93
1.3398	1.00547	111.45	1.00308	112.84	0.99977	114.15	0.99564	115.46	0.99079	116.80
1.3481	1.00551	111.44	1.00312	112.83	0.99979	114.15	0.99566	115.46	0.99080	116.79
1.6776	1.00710	111.12	1.00431	112.57	1.00065	113.94	0.99623	115.28	0.99113	116.65
1.7449	1.00742	111.06	1.00455	112.52	1.00082	113.90	0.99635	115.25	0.99120	116.63

[a] Units: ρ_s, g cm^{-3}; V_{ϕ}, cm^3 mol^{-1}; c_{aqm}, mol (M_w 55.51 mol)$^{-1}$ where M_w is the molar mass of normal (protiated) water.

[b] Taken from Ref. [38].

Table 2A
Experimental densities ρ_s of TMU solutions in heavy water (D_2O) and smoothed apparent molar volumes V_ϕ of the solute at the studied aquamolalities c_{aqm} and temperatures T[a].

c_{aqm}	T = 278.15 K		T = 288.15 K		T = 298.15 K		T = 308.15 K		T = 318.15 K	
	ρ_s	V_ϕ	ρ_s	V_ϕ	ρ_s	V_ϕ	ρ_s	V_ϕ	ρ_s	V_ϕ
0.000000	1.10549[b]	–	1.10575[b]	–	1.10435[b]	–	1.10162[b]	–	1.09782[b]	–
0.051515	1.10505	112.90	1.10524	114.03	1.10379	115.18	1.10101	116.33	1.09717	117.52
0.084044	1.10478	112.82	1.10494	113.97	1.10344	115.13	1.10064	116.29	1.09677	117.49
0.11163	1.10456	112.76	1.10468	113.92	1.10315	115.09	1.10032	116.26	1.09643	117.46
0.15893	1.10419	112.66	1.10424	113.83	1.10267	115.02	1.09978	116.20	1.09585	117.42
0.22437	1.10370	112.52	1.10366	113.72	1.10201	114.92	1.09907	116.13	1.09508	117.36
0.25024	1.10351	112.46	1.10344	113.68	1.10176	114.89	1.09879	116.10	1.09478	117.34
0.33514	1.10293	112.28	1.10274	113.53	1.10096	114.77	1.09790	116.00	1.09381	117.27
0.45471	1.10218	112.05	1.10181	113.34	1.09988	114.61	1.09670	115.88	1.09250	117.17
0.57827	1.10146	111.81	1.10091	113.15	1.09883	114.46	1.09552	115.75	1.09120	117.07
0.59794	1.10137	111.78	1.10078	113.13	1.09867	114.43	1.09534	115.73	1.09100	117.06
0.85682	1.10011	111.33	1.09911	112.77	1.09668	114.14	1.09307	115.49	1.08848	116.87
1.1486	1.09897	110.90	1.09748	112.44	1.09467	113.87	1.09074	115.26	1.08587	116.68
1.4209	1.09809	110.56	1.09614	112.17	1.09297	113.65	1.08877	115.08	1.08364	116.53
1.7242	1.09725	110.25	1.09479	111.93	1.09123	113.47	1.08672	114.91	1.08133	116.38

[a] Units: ρ_s, g cm^{-3}; V_ϕ, cm^3 mol^{-1}; c_{aqm}, mol (M_w 55.51 mol)$^{-1}$ where M_w is the molar mass of heavy (deuterated) water.

[b] Literature data on ρ/(g cm^{-3}) for the completely deuterated (100 at.% D) heavy water [37]: 1.10562 (278.15 K), 1.10587 (288.15 K), 1.10445 (298.15 K), 1.10173 (308.15 K), and 1.09794 (318.15 K).

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