

Volume-related interaction parameters for dilute solutions of 1,3-dimethylpropyleneurea 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 1,3-dimethylpropyleneurea (DMPU) in normal (H₂O) and heavy (D₂O) water in the aquamolality range from 0.04 to 1.0 at 278.15, 288.15, 298.15, 308.15, 313.15 and 318.15 K. The excess partial molar volumes of DMPU ($\bar{V}^{E,\infty}$) and volume second virial coefficients (ν_{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 H₂O to D₂O, values of $\bar{V}^{E,\infty}$ and ν_{xx} become more negative, suggesting that the hydration sphere around a DMPU molecule is more structured in the specified cases. Comparing the obtained results with earlier those for the analogues of DMPU such as acyclic 1,1,3,3-tetramethylurea (TMU) and cyclic 1,3-dimethylpropyleneurea (DMEU) corroborates the previously made conclusion that the DMPU molecule, being a stronger hydrated, has a more pronounced structure-making effect on water (H₂O or D₂O) than the TMU or DMEU molecule.

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1. Introduction

1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone known as an acronym DMPU (1,3-dimethylpropyleneurea) represents, similar to 1,3-dimethyl-2-imidazolidinone or DMEU (1,3-dimethylethyleneneurea), a cyclic derivative of 1,1,3,3-tetramethylurea (TMU). In the DMPU molecule, two *N,N'*-trans-sited (relative to >C=O) methyl groups are replaced by a propylene group between nitrogen atoms (see Fig. 1). Herewith, unlike the planar (within a ring) DMEU molecule [1], the middle carbon atom of the DMPU one lies out the plane [2]. Liquid DMPU, being an ideally replacing solvent for the carcinogenic hexamethylphosphoric triamide [3,4], has larger polarity with a molecular dipole moment μ (in Cm) of *ca.* 14.11×10^{-30} at 298.15 K [5] as compared to $\mu \approx 13.64 \times 10^{-30}$ for DMEU [5] and $\mu \approx 11.57 \times 10^{-30}$ for TMU [6,7]. At the same time the static dielectric constant ϵ of DMPU, being almost half as much again ϵ for TMU (36.12 [5] and 23.06 [6], respectively), is lesser than that of DMEU ($\epsilon \approx 37.60$ [5]).¹

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¹ The oxygen donor strength D_s and the Gutmann's electron donor number DN for DMPU are estimated to be *ca.* 34 [8] and 42.8 [3], respectively (for TMU: $DN \approx 29.6$ [6]). Unfortunately, such data for DMEU are absent.

Such differences in the molecular and physical properties of the media compared must manifest oneself in the ability of DMPU, DMEU and TMU molecules to be built differently into the initial structure of water. Since TMU and DMEU are the predominantly hydrophobic-hydrating or structure-making solutes and configuration effects play a perceptible role during their hydration [9–17], we would expect a similar behavior for DMPU dissolved in water, too, although both “nonpolar” (cyclic and acyclic) and carbonyl groups of the molecules under comparison interact in a fairly different ways with the surrounding water molecules.

In view of this, we have focused here our attention on volume or packing changes induced by the pairwise interaction of solute DMPU molecules in the aqueous medium. As was shown earlier [11,15,16,18–20], if such changes are examined in H₂O and D₂O simultaneously, the solvent H/D isotope effects in the corresponding thermodynamic (volumetric) properties give indispensable information for a better understanding of the matter in question. Noteworthy is also that the partial molar volumes of the solute at infinite dilution \bar{V}^∞ and the molal volume second virial coefficients ν_{xx} for DMPU–DMPU interactions can be obtained using the excess molar volumes V^E of dilute aqueous (H₂O or D₂O) solutions [11,16,19–21].

At present, we are aware only two studies describing the results of determination of \bar{V}^∞ with using the concentration-dependent values of V^E for solutions of DMPU in heavy [20] and normal [22] water at some temperatures. However, it should be taken

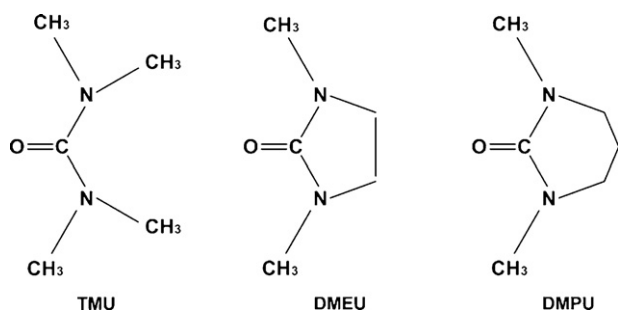


Fig. 1. Molecular structure of 1,1,3,3-tetramethylurea (TMU), 1,3-dimethylethyleneurea (DMEU) and 1,3-dimethylpropyleneurea (DMPU).

into account that the substitution of H₂O by D₂O in an aqueous non-electrolyte solution results in a rather small change in V^E [15,16,19,23–28]. 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.

Thus, the principal objective of this work is to obtain new information on the packing changes in H/D isotopically distinguishable aqueous solutions of DMPU at 278.15, 288.15, 298.15, 308.15, 313.15, and 318.15 K and at $p \sim 0.1$ MPa. In the present paper we report also detailed results on the D₂O–H₂O solvent isotope effects (hereinafter, IEs) on both \bar{V}^∞ and ν_{xx} evaluated with using the virial expansion of V^E , discussing them in comparison with like effects obtained previously [15,16] for solutions of TMU and DMEU in H₂O and D₂O.

2. Experimental

DMPU (C₆H₁₂N₂O; CAS [7226-23-5]) was purchased from Fluka with purity better than 99.0% as checked by GLC and water (H₂O) content less than 0.03 wt.%. The solute specimen was additionally purified using a thermally activated 0.3-nm molecular sieves (under N₂-gas atmosphere) for two days with following vacuum distillation at ca. 340 K and $p \sim 2$ mmHg [29]. The distillate had the refraction index being 1.4877 at 298.15 K (the data reported in literature are 1.4874 [3], 1.4881 [5] and 1.4873 [22]). GLC-analysis showed that final purity of DMPU was $\geq 99.9\%$; 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 light-proof vacuum desiccator over P₂O₅. Water of natural isotope composition was twice distilled to reach the electric conductivity $\kappa \approx 1.3 \times 10^{-6}$ S cm⁻¹. Heavy water (Izotop Co., St. Petersburg; $\kappa \approx 1.0 \times 10^{-6}$ S cm⁻¹) with natural water ¹⁸O-content and deuterium content being 99.95 ± 0.02 at.% D was used as such; the H₂O content of heavy water was taken into account in the calculation of the molar mass of D₂O.

The isotopically distinguishable aqueous solutions of DMPU 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. 0.04 to ca. 1.0 which correspond to DMPU final mole fractions x_2 up to ca. 1.8×10^{-2} (c_{aqm} is defined by the number of moles of the solute per 55.51 moles of H₂O or D₂O). The use of aquamolality scale is necessary in order to allow the proper comparison of the volumetric characteristics at finite concentrations in the presence of equal numbers of H₂O and D₂O molecules [15,19]. The error in the c_{aqm} value was estimated to be less than 2×10^{-5} mol(55.51 M_w)⁻¹ where M_w is the molar mass of normal or heavy water.

Densities of solutions ρ_s were measured (at the above-enumerated six temperatures) using an Anton Paar DMA 4500 vibrating-tube hermetically sealed 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 [30] 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 DMPU at each of the temperatures employed are given in Table 1 together with those found in the literature. As follows from the table, our $\rho(T)$ and $\alpha_p(T)$ values, being systematically lower for ρ and higher for α_p (excepting $T = 318.15$ K) than those obtained by Lemos and Maestre [22], are in sufficiently good agreement with results reported by authors [3,5,20,31,32] in the temperature range below 298.15 K. Noteworthy is also the fact of comparability between results obtained by Székely and Jancsó [20] and ours at all temperatures given in the table.

As regards the literature data on density of pure D₂O, we have found the following results related to completely deuterated (i.e., with 100 at.% D) heavy water, in g cm⁻³: 1.10582 [27], 1.10562 [33], 1.10565 [35], 1.10565 [36] at $T = 278.15$ K; 1.10595 [27], 1.10587 [33], 1.10586 [34], 1.10587 [35], 1.10591 [36] at $T = 288.15$ K; 1.10451 [27], 1.10445 [33], 1.10445 [34], 1.10449 [35], 1.10450 [36] at $T = 298.15$ K; 1.10174 [27], 1.10173 [33], 1.10172 [34], 1.10175 [35], 1.10179 [36] at $T = 308.15$ K; 1.09996 [33], 1.09999 [35] at $T = 313.15$ K; 1.09781 [27], 1.09794 [33], 1.09794 [34], 1.09799 [35], 1.09797 [36] at $T = 318.15$ K.

Densities for binary solutions of DMPU in H₂O and D₂O are summarized in Tables A.1 and A.2 (see in Appendix A), together with the smoothed V_ϕ values calculated using the third-power polynomial expansion

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

and the formula expressing the volume of a binary solution V_s in the aquamolality scale [34]

$$V_s(c_{aqm}) = \frac{55.51 M_w + M c_{aqm}}{\rho_s} = V_w^\circ \left(\equiv \frac{55.51 M_w}{\rho_w} \right) + V_\phi c_{aqm} \quad (2)$$

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

In Table A.3 (see in Appendix A), the comparison of data on $\rho_s(x_2)$ from existing sources with ours at the same solute contents is presented. We are inclined to believe that some scattering in the quantities compared may be explained by differences in the quality of the solution components, and in details of the experimental procedure as well.

According to inferences [19,21], the excess volume of the solution per 55.51 mol of water isotopologue $V_s^E(c_{aqm})$ is given by the expression

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

On the other hand, at rather low concentrations the excess volume defined in Eq. (3) can be expressed as a virial expansion in the solute aquamolality [21,37]

$$V_s^E(c_{aqm}) = \nu_{xx} c_{aqm} + \nu_{xxx} c_{aqm}^2 + \dots \quad (4)$$

Here, according to the McMillan–Mayer theory of solutions [38], the coefficients ν_{xx} and ν_{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 [19,20].

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

T (K)	ρ (g cm ⁻³)		10 ⁴ α_p (K ⁻¹) ^a	
	This work	Literature	This work	Literature
278.15	1.07618	1.074705 ^b	0.777 ± 0.005	0.71 ± 0.02 ^b
288.15	1.06781	1.066833 ^b , 1.06785 ^c	0.783 ± 0.005	0.74 ± 0.02 ^b , 0.79 ± 0.05 ^c
298.15	1.05946	1.059220 ^b , 1.05939 ^c , 1.0600 ^d , 1.0596 ^e , 1.05930 ^f , 1.05953 ^g	0.788 ± 0.005	0.76 ± 0.02 ^b , 0.79 ± 0.05 ^c , 0.79 ± 0.02 ^f
308.15	1.05112	1.050707 ^b , 1.0512 ^e , 1.05094 ^f	0.793 ± 0.005	0.79 ± 0.02 ^b , 0.79 ± 0.02 ^f
313.15	1.04695	1.04697 ^c , 1.04676 ^f	0.796 ± 0.005	0.79 ± 0.05 ^c , 0.80 ± 0.02 ^f
318.15	1.04278	1.042529 ^b , 1.0428 ^e , 1.04259 ^f	0.798 ± 0.005	0.81 ± 0.02 ^b , 0.80 ± 0.02 ^f

^a Calculated by differentiating the equation $\ln \rho = a_0 + a_1(T - T') + a_2(T - T')^2$ relative to $(T - T')$ where T is the average-weighted temperature.

^b Ref. [22].

^c Ref. [20].

^d Ref. [3].

^e Ref. [5].

^f Ref. [31].

^g Ref. [32].

From Eqs. (3) and (4) one obtains

$$V_s(c_{\text{aqm}}) - V_w^\circ = \bar{V}^\infty c_{\text{aqm}} + \nu_{\text{xx}} c_{\text{aqm}}^2 + \nu_{\text{xxx}} c_{\text{aqm}}^3 + \dots \quad (5)$$

By fitting the function $V_s(c_{\text{aqm}}) - V_w^\circ$ against c_{aqm} using the method of least-squares, the \bar{V}^∞ and ν_{xx} values have been computed and collected in Table 3. The given approach was successfully applied earlier to H/D isotopically distinguishable aqueous solutions of DMEU, TMU (see Table 4) and 3-methylpyridine [19] as well as separately to solutions of polyols [21], alcohols and diols [39] in H₂O and solutions of DMPU [20] in D₂O. In the latter case, the data (obtained at three temperatures only) are found to be systematically lower than ours (Table 3), namely, by ~ 0.4 cm³ mol⁻¹ for \bar{V}^∞ and by a third of total for ν_{xx} , on the average. Herewith, based on the *F*-test [40], statistical analysis showed that the contribution of triplet-solute aggregates (term ν_{xxx}) to $V_s^\infty(c_{\text{aqm}})$ in the case of aqueous DMPU should be taken into account, too, when the experimental data are described adequately by Eq. (5) (see Table 3).

4. Discussion

The \bar{V}^∞ values in Table 4 reflect the solute-solvent interactions [11,19]; therefore, it can be expected to provide information on the structure-making or structure-breaking effects of DMPU on water. However, since the intrinsic volume of the non-hydrated solute molecule is not known, it is not possible to obtain direct information on the nature of such interactions. Here it is instructive to compare the volume change undergone by both the water and DMPU molecules in the liquid phase due to the hydration process of DMPU in H₂O with that in D₂O.

It can be seen from data of Table 4 that the $\bar{V}^\infty(\text{in D}_2\text{O}) - \bar{V}^\infty(\text{in H}_2\text{O})$ difference has the negative sign and amounts to $-(0.63 \pm 0.05)$ cm³ mol⁻¹ at $T = 278.15$ K, whereas the molar volume V_w for pure D₂O is 0.098 cm³ mol⁻¹ larger than $V_w(\text{H}_2\text{O})$ at the same temperature [33]. This means that DMPU appears to occupy a larger volume in normal water than in heavy one, notwithstanding that the intrinsic volume of the non-hydrated solute is the same in both cases. Hence the effect of a DMPU molecule on the initial structure of aqueous surroundings is more pronounced in D₂O than in H₂O, in harmony with the generally accepted view that at a given temperature the effect of both structure-making and structure-breaking solutes on heavy water is slightly greater than the corresponding effect on normal water [25,41,42]. At the same time, although \bar{V}^∞ increases with rising temperature in both (H₂O + DMPU) and (D₂O + DMPU) solutions, the IE on this quantity decreases sharply in magnitude as the temperature increases, crossing a “hypothetical zero” at $T = (324 \pm 1)$ K (according to the linear approximation).

A similar temperature-dependent behavior of $\delta\bar{V}^\infty$ (D₂O–H₂O) was observed earlier for DMEU [15], TMU [16,18] and some other predominantly hydrophobic-hydrated solutes such as *N,N*-dimethylformamide [26], *N,N*-dimethylacetamide [27], and *n*-tetraalkylammonium (Et₄N⁺–Pen₄N⁺) salts as well [43]. It should be noted also that the specified volume-isotope changes in infinitely dilute aqueous solutions of TMU and its cyclic derivatives are directly connected with the corresponding enthalpy-isotope those $\delta\Delta_{\text{sol}}H^\infty$ (D₂O–H₂O) [13–17] due to the structure-depend nature of both thermodynamic (packing- and energy-related) dissolution or hydration characteristics [44,45]. Unfortunately, published data on $\Delta_{\text{sol}}H^\infty$ for DMPU in D₂O, which could confirm or reject the given assumption, are still lacking. However, as it was shown recently by Korolev and co-authors [29], the negative and large (in magnitude) $\Delta_{\text{sol}}H^\infty$ values accompanied by a positive $(\partial\Delta_{\text{sol}}H^\infty/\partial T)_p$ slope for DMPU in H₂O are indicative (by analogy with aqueous DMEU and TMU [13,17]) of a predominantly hydrophobic hydration of the solute. Herewith, if one takes account of the fact that the standard molar enthalpies of vaporization, $\Delta_{\text{vap}}H^\circ/\text{kJ mol}^{-1}$, change in a consequence [31,46]: DMPU (~ 67.2) > DMEU (~ 60.1) > TMU (~ 54.3) at 298.15 K, the molecules of DMPU are to be hydrated stronger than those of DMEU or TMU.

The following interesting item is that the \bar{V}^∞ value in both solvents compared is smaller than the molar volume of pure liquid DMPU (see Table 3). This difference ($\bar{V}^\infty - V$), referred to as the excess partial molar volume of the solute $\bar{V}^{E,\infty}$, increases in magnitude when the protiated system is replaced by deuterated one but becomes decreasingly negative when the temperature is rising (see Fig. 2). It means that the mean molar expansibility of pure DMPU, $E_p = (\partial V/\partial T)_p = 0.0954 \pm 0.0010$ cm³ mol⁻¹ K⁻¹, is smaller than the limiting partial molar expansibilities \bar{E}_p^∞ for this solute in H₂O and D₂O that have been found to be 0.1078 ± 0.0011 and 0.1215 ± 0.0002 cm³ mol⁻¹ K⁻¹, respectively. Perhaps the most noteworthy in Fig. 2 is the fact that the $\bar{V}^{E,\infty}$ values for DMPU are smallest in magnitude, compared to those for DMEU and TMU, in both H₂O and D₂O; herewith, as seen in the figure, the considered quantities are differently varying with temperature. It is interesting also that the values of $\delta\bar{V}^{E,\infty}$ (D₂O–H₂O) for DMPU are virtually comparable with those for TMU and amounts to about half of the corresponding IE for DMEU over all the temperature range studied (see in Fig. 3).

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 some other (dipole-dipole and/or van der Waals) interactions between solute and solvent molecules are involved, marking \bar{V}^∞ lower than V [47]. Taking account of the fact that a hydrophobic hydration and solute-solvent hydrogen bonding are the steric-dependent effects, the revealed volume-isotope changes upon dissolution of DMPU

Table 2
Parameters b_j of Eq. (1) for H/D isotopically distinguishable aqueous solutions of DMPU at different temperatures (the fitting standard error is given in the parenthesis)^a

T/K	H ₂ O + DMPU					D ₂ O + DMPU				
	b_0	$10^3 b_1$	$10^3 b_2$	$10^3 b_3$	$10^6 \sigma_b$	b_0	$10^3 b_1$	$10^3 b_2$	$10^3 b_3$	$10^6 \sigma_b$
278.15	0.999962 (2.2 × 10 ⁻⁶)	1.1591 (2.4 × 10 ⁻³)	1.704 (6.0 × 10 ⁻²)	-0.877 (4.1 × 10 ⁻²)	3.08	1.105592 (2.1 × 10 ⁻⁶)	-0.0448 (2.3 × 10 ⁻³)	3.485 (5.7 × 10 ⁻²)	-1.238 (4.0 × 10 ⁻²)	2.69
288.15	0.999099 (1.8 × 10 ⁻⁶)	1.0601 (1.9 × 10 ⁻³)	1.381 (4.9 × 10 ⁻²)	-0.674 (3.3 × 10 ⁻²)	2.53	1.105848 (1.9 × 10 ⁻⁶)	-1.3745 (2.2 × 10 ⁻³)	3.071 (5.4 × 10 ⁻²)	-1.051 (3.7 × 10 ⁻²)	2.58
298.15	0.997047 (1.6 × 10 ⁻⁶)	0.9758 (1.7 × 10 ⁻³)	1.130 (4.3 × 10 ⁻²)	-0.528 (2.9 × 10 ⁻²)	2.20	1.104428 (2.0 × 10 ⁻⁶)	-2.5491 (2.2 × 10 ⁻³)	2.837 (5.6 × 10 ⁻²)	-0.893 (3.8 × 10 ⁻²)	2.67
308.15	0.994033 (2.1 × 10 ⁻⁶)	0.9027 (2.2 × 10 ⁻³)	1.020 (5.7 × 10 ⁻²)	-0.461 (3.9 × 10 ⁻²)	2.92	1.101719 (2.0 × 10 ⁻⁶)	-3.5586 (2.2 × 10 ⁻³)	2.713 (5.6 × 10 ⁻²)	-0.803 (3.8 × 10 ⁻²)	2.65
313.15	0.992216 (2.1 × 10 ⁻⁶)	0.8655 (2.3 × 10 ⁻³)	0.976 (5.8 × 10 ⁻²)	-0.424 (3.9 × 10 ⁻²)	2.95	1.099927 (1.9 × 10 ⁻⁶)	-3.9938 (2.2 × 10 ⁻³)	2.679 (5.5 × 10 ⁻²)	-0.786 (3.7 × 10 ⁻²)	2.40
318.15	0.990216 (2.1 × 10 ⁻⁶)	0.8354 (2.3 × 10 ⁻³)	0.914 (5.9 × 10 ⁻²)	-0.385 (4.0 × 10 ⁻²)	3.02	1.097920 (2.3 × 10 ⁻⁶)	-4.4341 (2.6 × 10 ⁻³)	2.646 (6.4 × 10 ⁻²)	-0.748 (4.4 × 10 ⁻²)	3.06

^a Units: $b_0, g\text{ cm}^{-3}$; $b_1, g(55.51 M_w)\text{ mol}^{-1}\text{ cm}^{-3}$; $b_2, g(55.51 M_w)^2\text{ mol}^{-2}\text{ cm}^{-3}$; $b_3, g(55.51 M_w)^3\text{ mol}^{-3}\text{ cm}^{-3}$.

^b The standard deviation for least-squares representation of ρ_s .

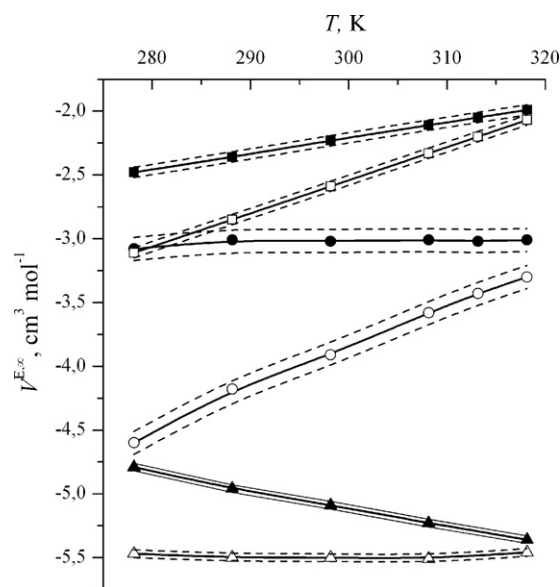


Fig. 2. The temperature dependences of the excess limiting partial molar volumes ($\bar{V}^{E,\infty}$) in normal (solid symbols) and heavy (open symbols) water for DMPU (\blacksquare, \square), DMEU (\bullet, \circ) and TMU ($\blacktriangle, \triangle$). The dashed lines limit the half-width of the confidence interval for quantities considered.

(Table 3 and Figs. 2 and 3) are directly related to both structural peculiarities of this solute and differences in the interaction properties of H₂O and D₂O, including the more pronounced ability of heavy water molecules to form hydrogen-bonded aggregates with a solute molecule [18,48,49]. As we mentioned above (in Section 1), it manifests oneself in the ability of DMPU, DMEU and TMU molecules to be built differently into the initial structure of each of solvents compared. So, a free C–N rotation in C–N(CH₃)₂ groups is feasible in a TMU molecule, but such a rotation is not allowed in the DMEU and DMPU molecules because of a cyclization [50]. On the other hand, a DMEU molecule has a planar ring [1] whereas in the case of a DMPU molecule the middle carbon atom (within a ring) lies out of the plane [2]. This suggests that the steric incompatibility effects may be bigger in the case of hydration of the DMPU and seemingly TMU molecules.

Indeed, considering the distinction between \bar{V}^∞ and the van der Waals volume V_{vdw} of the solute molecules,² we have found that the “decyclization” of a hydrated DMEU molecule, to form TMU, and the introduction of a CH₂ group into its ring, to form DMPU, result in the same structure-packing effect: the “excluded space” becomes more by ca. 3.6 cm³ mol⁻¹ in normal water and by ca. 4.1 cm³ mol⁻¹ in heavy water than that one would expect from the comparison of the V_{vdw} quantities for these solutes. A similar conclusion was made recently by Székely and Jancsó [20] at comparing the volume effects induced by hydration the DMEU and DMPU in the D₂O medium.

As can be seen from Table 3, the sign of v_{xx} is negative for both (H₂O + DMPU) and (D₂O + DMPU) solutions; however, its absolute values are systematically larger in the latter case. According to relationship between v_{xx} and the overlap of hydration co-spheres of the solute pairs discussed thoroughly by Würzburger et al. [21], the negative sign at v_{xx} and $\delta v_{xx}(D_2O-H_2O)$ shows that the water molecules, occupying larger volumes in the co-sphere than in the bulk, are more structured in the former case. It corroborates the above findings that the solute considered has a structure-making effect on the aqueous surroundings. Herewith, comparing data of

² Calculated using the approach [51], the V_{vdw} values are equal ca. 69.8, 63.3 and 72.9 cm³ mol⁻¹ for TMU, DMEU and DMPU, respectively. Data on \bar{V}^∞ at 298.15 K was taken from Table 3 and Refs. [15,16].

Table 3
The molar volumes (V) of DMPU and its partial molar volumes at infinite dilution (\bar{V}^∞) in H_2O and D_2O as well as the volume-related second and third virial coefficients (ν_{xx} and ν_{xxx}) for solutions compared, with their 95%-confidence interval half-widths ($\pm\xi$), at different temperatures (T , K).

T	V^a	\bar{V}^∞ ^a	ν_{xx} ^b	ν_{xxx} ^c	σ ^d
$H_2O + DMPU$					
278.15	119.101	116.62 \pm 0.03	-3.16 \pm 0.09	0.89 \pm 0.07	0.00321
288.15	120.035	117.68 \pm 0.03	-2.71 \pm 0.08	0.69 \pm 0.06	0.00252
298.15	120.981	118.75 \pm 0.03	-2.36 \pm 0.07	0.54 \pm 0.06	0.00228
308.15	121.941	119.83 \pm 0.03	-2.17 \pm 0.10	0.46 \pm 0.08	0.00322
313.15	122.426	120.39 \pm 0.04	-2.09 \pm 0.11	0.42 \pm 0.08	0.00328
318.15	122.916	120.93 \pm 0.03	-1.99 \pm 0.10	0.38 \pm 0.08	0.00321
$D_2O + DMPU$					
278.15	119.101	115.99 \pm 0.04	-3.29 \pm 0.11	1.00 \pm 0.08	0.00308
288.15	120.035	117.18 \pm 0.03	-2.78 \pm 0.08	0.83 \pm 0.05	0.00249
298.15	120.981	118.39 \pm 0.03	-2.42 \pm 0.08	0.69 \pm 0.06	0.00252
308.15	121.941	119.61 \pm 0.02	-2.21 \pm 0.07	0.60 \pm 0.05	0.00235
313.15	122.426	120.23 \pm 0.02	-2.12 \pm 0.07	0.58 \pm 0.05	0.00235
318.15	122.916	120.85 \pm 0.03	-2.04 \pm 0.09	0.54 \pm 0.06	0.00292

^a In $cm^3 mol^{-1}$.

^b In $cm^3 (55.51 M_w) mol^{-2}$, where 55.51 M_w is the mass of 55.51 mol of normal or heavy water.

^c In $cm^3 (55.51 M_w)^2 mol^{-3}$ (see also Footnote b).

^d Standard deviation of the fit, in $cm^3 (55.51 M_w)^{-1}$ (see also Footnote b).

Tables 3 and 4, one can conclude that the DMPU molecule has a more pronounced structure-making effect than TMU and DMEU molecules in each of water isotopologues considered. On the one hand, this is not unexpected since the DMPU molecule contains one more CH_2 group than the DMEU molecule. On the other hand, the given fact is arguable because the TMU molecule exhibits as a whole the higher hydrophobicity compared to that of the DMPU molecule [20].

At the same time, as we mentioned already above, the change in the enthalpy of solute hydration, $\Delta_{hydr}H^\circ$, caused by a substitution of DMEU or TMU for DMPU points to the pronounced strengthening (by 9–14 $kJ mol^{-1}$) of the solute hydration [13,17,29], correlating with data on ν_{xx} (Tables 3 and 4). Since the energy spent to destroy the "net" solute structure increases appreciably on going from TMU to DMEU and further to DMPU, it is clear that such a difference in $\Delta_{hydr}H^\circ$ is defined not only by the solute hydrophobicity, but also by the nature of its association with the surrounding aqueous medium through hydrogen-bonding, and dipole-dipole interactions as well. Indeed, this solute order is in harmony with that expected from the magnitudes of the electron density on the carbonyl oxygen and the dipole moment of a molecule (see in Section 1).

Also, in harmony with the above observation, the results of small-angle neutron scattering (SANS) experiments [9,11,20] indicate that the pairwise solute–solute interactions in H/D isotopically distinguishable aqueous solutions of DMPU are less attractive than in the similar solutions of DMEU and, especially, TMU. It seems to be quite logical if one takes account of the fact that the effects of hydrophobic interaction (occurring between solute molecules in the concentration-depend solution range) and hydrophobic hydration (relating to solute–solvent and solvent–solvent interactions in the infinite- or high-diluted solution) are substantially distinguishable in nature [48,52].

Finally, Table 3 shows that the volume-related triplet contributions to the solute–solute interactions (ν_{xxx}) in both ($H_2O + DMPU$) and ($D_2O + DMPU$) solutions are rather significant, exceeding the corresponding values for aqueous TMU [16] twice and more. Herewith, unlike data on $\delta\nu_{xx}(D_2O-H_2O)$, the IEs on ν_{xxx} are not ignorable. But such a surprisingly different behaviors of ν_{xxx} is not yet subject to a reasonable explanation.

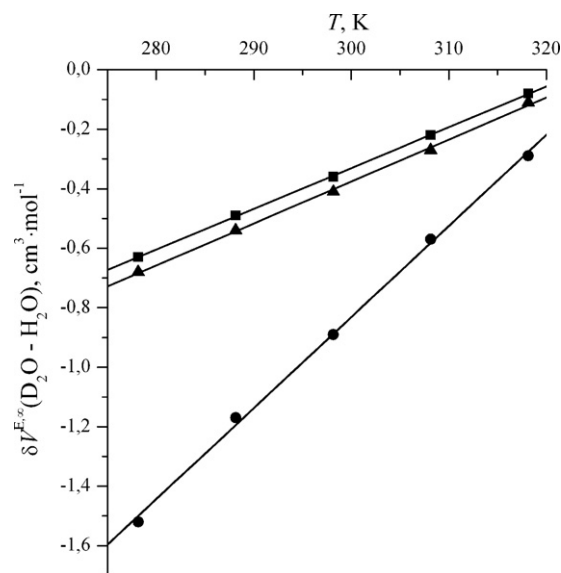


Fig. 3. The temperature dependences of the H/D solvent isotope effects on the excess limiting partial molar volume ($\bar{V}^{E,\infty}$) for aqueous DMPU (■), DMEU (●) and TMU (▲). The values of half-width of the confidence interval for the volume property in question do not exceed $\pm 0.13 cm^3 mol^{-1}$ at worst (Table 3) in the present work and Refs. [15,16].

Table 4
The volume-related second virial coefficients (ν_{xx} , $cm^3 (55.51 M_w) mol^{-2}$) for H/D isotopically distinguishable aqueous solutions of DMEU [15] and TMU [16] at different temperatures.

System	278.15 K	288.15 K	298.15 K	308.15 K	318.15 K
$H_2O + DMEU$	-1.79 \pm 0.20	-1.61 \pm 0.19	-1.38 \pm 0.18	-1.20 \pm 0.17	-0.94 \pm 0.16
$D_2O + DMEU$	-2.28 \pm 0.13	-2.07 \pm 0.15	-1.70 \pm 0.19(-0.77 \pm 0.05) ^a	-1.54 \pm 0.16	-1.23 \pm 0.07
$H_2O \rightarrow D_2O$	-0.49 \pm 0.24	-0.46 \pm 0.24	-0.32 \pm 0.26	-0.34 \pm 0.23	-0.29 \pm 0.18
$H_2O + TMU$	-2.26 \pm 0.05	-1.80 \pm 0.05	-1.51 \pm 0.03	-1.21 \pm 0.03	-0.88 \pm 0.05
$D_2O + TMU$	-2.32 \pm 0.04	-1.85 \pm 0.04	-1.56 \pm 0.03(-1.22 \pm 0.08) ^a	-1.27 \pm 0.05	-0.97 \pm 0.03
$H_2O \rightarrow D_2O$	-0.06 \pm 0.07	-0.05 \pm 0.06	-0.05 \pm 0.04	-0.06 \pm 0.06	-0.09 \pm 0.06

^a Ref. [11].

Table A.1

Experimental densities ρ_s of DMPU solutions in normal water (H₂O) and smoothed apparent molar volumes V_ϕ of the solute at the studied aquamolalities c_{aqm} and temperatures T .^a

c_{aqm}	$T=278.15\text{ K}$		$T=288.15\text{ K}$		$T=298.15\text{ K}$		$T=308.15\text{ K}$		$T=313.15\text{ K}$		$T=318.15\text{ K}$	
	ρ_s	V_ϕ	ρ_s	V_ϕ	ρ_s	V_ϕ	ρ_s	V_ϕ	ρ_s	V_ϕ	ρ_s	V_ϕ
0.00000	0.999965 ^b	–	0.999101 ^b	–	0.997047 ^b	–	0.994035 ^b	–	0.992219 ^b	–	0.990216 ^b	–
0.03864	1.00041	116.47	0.99951	117.57	0.99743	118.65	0.99438	119.73	0.99255	120.31	0.99054	120.85
0.07586	1.00085	116.36	0.99991	117.47	0.99779	118.57	0.99472	119.65	0.99288	120.24	0.99086	120.77
0.1037	1.00118	116.28	1.00021	117.40	0.99807	118.50	0.99498	119.59	0.99312	120.18	0.99109	120.72
0.1575	1.00183	116.12	1.00080	117.27	0.99861	118.39	0.99548	119.48	0.99360	120.07	0.99155	120.62
0.2215	1.00260	115.95	1.00151	117.11	0.99926	118.25	0.99608	119.36	0.99418	119.95	0.99211	120.49
0.2812	1.00334	115.79	1.00217	116.97	0.99987	118.13	0.99664	119.24	0.99472	119.84	0.99263	120.40
0.4070	1.00490	115.47	1.00360	116.69	1.00117	117.88	0.99784	119.01	0.99587	119.61	0.99374	120.18
0.5303	1.00646	115.18	1.00501	116.44	1.00246	117.65	0.99904	118.79	0.99702	119.41	0.99485	119.98
0.6771	1.00832	114.88	1.00670	116.16	1.00401	117.39	1.00047	118.56	0.99839	119.17	0.99617	119.75
0.8298	1.01025	114.60	1.00846	115.90	1.00562	117.15	1.00196	118.33	0.99983	118.95	0.99756	119.53
0.9878	1.01223	114.36	1.01027	115.67	1.00728	116.93	1.00350	118.12	1.00131	118.74	0.99899	119.32

^a Units: ρ_s , g cm⁻³; V_ϕ , cm³ 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. [30].

Table A.2

Experimental densities ρ_s of DMPU solutions in heavy water (D₂O) and smoothed apparent molar volumes V_ϕ of the solute at the studied aquamolalities c_{aqm} and temperatures T .^a

c_{aqm}	$T=278.15\text{ K}$		$T=288.15\text{ K}$		$T=298.15\text{ K}$		$T=308.15\text{ K}$		$T=313.15\text{ K}$		$T=318.15\text{ K}$	
	ρ_s	V_ϕ	ρ_s	V_ϕ	ρ_s	V_ϕ	ρ_s	V_ϕ	ρ_s	V_ϕ	ρ_s	V_ϕ
0.00000	1.10559 ^b	–	1.10585 ^b	–	1.10443 ^b	–	1.10172 ^b	–	1.09993 ^b	–	1.09792 ^b	–
0.05395	1.10560	115.80	1.10578	117.02	1.10430	118.26	1.10153	119.49	1.09972	120.09	1.09769	120.73
0.07516	1.10561	115.73	1.10576	116.96	1.10425	118.21	1.10147	119.44	1.09964	120.05	1.09760	120.69
0.1092	1.10563	115.63	1.10573	116.87	1.10418	118.13	1.10136	119.37	1.09952	119.98	1.09747	120.62
0.1478	1.10566	115.52	1.10571	116.78	1.10411	118.05	1.10125	119.30	1.09939	119.91	1.09732	120.55
0.1994	1.10572	115.37	1.10569	116.65	1.10403	117.94	1.10111	119.20	1.09923	119.81	1.09713	120.46
0.2964	1.10585	115.10	1.10568	116.43	1.10390	117.74	1.10088	119.02	1.09896	119.64	1.09682	120.29
0.4525	1.10617	114.71	1.10576	116.10	1.10377	117.44	1.10059	118.75	1.09860	119.38	1.09639	120.04
0.5906	1.10653	114.39	1.10589	115.83	1.10373	117.21	1.10040	118.53	1.09834	119.17	1.09607	119.83
0.7016	1.10685	114.17	1.10603	115.65	1.10373	117.04	1.10028	118.37	1.09817	119.02	1.09585	119.68
0.8471	1.10731	113.92	1.10625	115.43	1.10376	116.84	1.10016	118.19	1.09799	118.84	1.09561	119.51
0.9670	1.10769	113.74	1.10644	115.29	1.10381	116.70	1.10009	118.06	1.09786	118.72	1.09543	119.39

^a Units: ρ_s , g cm⁻³; V_ϕ , cm³ mol⁻¹; c_{aqm} , mol (M_w 55.51 mol)⁻¹ where M_w is the molar mass of heavy (deuterated) water.

^b Other data on ρ (g cm⁻³) for heavy water with the deuterium content being 100 at.% D are presented in Section 3.

5. Concluding remarks

Thus, we have corroborated the previous findings [20] that the DMPU molecule has a more pronounced structure-making effect, being hydrated as a whole stronger, than DMEU or TMU molecules. Like the latter cases, the hydration (of a predominantly hydrophobic type) is enhanced in heavy water. Herewith the values of the excess limiting partial molar volume or volumetric effect of dissolution [44] for DMPU in both normal and heavy water are found to be smallest in magnitude, compared to those for DMEU and TMU, whereas the D₂O–H₂O solvent isotope effects in this quantity for DMPU and TMU are virtually comparable with each other, amounting to about half of the corresponding isotope effect for DMEU. It

may be seen primarily as the result of a different abilities of the compared molecules to be built into the initial structure of water with forming hydrogen and other bonds. Also, it is estimated that the volume-related triplet contributions to the solute–solute interactions in dilute aqueous solutions of DMPU are rather significant, exceeding the similar values for aqueous TMU twice and more. However, to understand this behavior clearly, further detailed studies are needed.

Appendix A.

See Appendix Tables A.1–A.3.

Table A.3

Comparison of our densities ρ_s (g cm⁻³) with those from other sources for solutions of DMPU in H₂O and D₂O at 298.15 K.

x_2 , m.f.	H ₂ O + DMPU			D ₂ O + DMPU		
	This work	Ref. [22] ^a	Deviation	This work ^b	Ref. [20] ^c	Deviation ^d
0.0025	0.99843	0.99842	0.00001	1.10413	1.10394	0.00019 (0.00005)
0.0050	0.99985	0.99985	0.00000	1.10392	1.10373	0.00019 (0.00005)
0.0075	1.00130	1.00131	–0.00001	1.10379	1.10360	0.00019 (0.00005)
0.0100	1.00278	1.00280	–0.00002	1.10373	1.10353	0.00020 (0.00006)
0.0125	1.00428	1.00430	–0.00002	1.10373	1.10354	0.00019 (0.00005)
0.0150	1.00578	1.00579	–0.00001	1.10376	1.10356	0.00020 (0.00006)
0.0175	1.00729	1.00727	0.00002	–	–	–

^a Calculated with using the coefficients of equation (Redlich–Kister type) reported by authors.

^b Estimated using Eq. (1) and parameters of Table 2.

^c D₂O: 99.82 at.% deuterium content.

^d In parenthesis, a deviation corrected to 99.95 at.% D is presented using the Kell's reference data [33].

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