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Small-Angle Neutron Scattering and Volumetric Studies of Dilute Solutions of *N,N′*-Dimethylpropyleneurea in Heavy Water[†]

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Small-angle neutron scattering experiments and density measurements were performed on dilute solutions of *N,N′*-dimethylpropyleneurea (DMPU) in heavy water in the mole fraction range 0.005(0.0025)−0.05 at 288.15, 298.15 and 313.15 K. From the experimental results values of the radius of gyration, second osmotic as well as second and third molal volume virial coefficients, and Kirkwood−Buff integrals were calculated. The results led to the conclusions that DMPU has a structure-making effect on water and the pairwise solute−solute interactions exhibit no temperature dependence and are less attractive in DMPU solutions than in *N,N′*-dimethylethyleneurea and tetramethylurea solutions.

1. Introduction

N,N′-Dimethylpropyleneurea (DMPU) represents, similarly to *N,N′*-dimethylethyleneurea (DMEU), a cyclic derivative of tetramethylurea (TMU). Whereas the DMEU molecule contains—instead of the two methyl groups of the TMU molecule—an ethylene group, the DMPU molecule has a propylene group, the middle carbon atom of which lies out of the plane (Figure 1). *N,N′*-Dimethylpropyleneurea is an excellent polar solvent with a wide liquid range (284 K), and it has been suggested as an ideal replacement for the carcinogenic hexamethylphosphotriamide as cosolvent for highly reactive nucleophiles and bases.[1] Since it has an unusually high oxygen donor strength (D_s = 34), high permittivity ($\varepsilon = 36.1$) and a large dipole moment (μ = 4.23 D) many salts are readily soluble in it.[2] DMPU has been widely used in solvation studies of various metal ions.[2,3] The thermodynamic transfer functions for a number of monovalent ions from water have been also determined, and the results were interpreted in terms of the significant difference in the structure between liquid water and DMPU.[4]

The small-angle neutron scattering (SANS) technique offers a possibility to study solute−solute and solute−solvent interactions in dilute aqueous solutions of nonelectrolytes (see, e.g., refs 5 and 6). SANS investigations on dilute aqueous solutions of TMU[7,8] and DMEU[9] revealed that in TMU solutions the pairwise solute−solute attractive interactions become more pronounced with increasing temperature whereas in DMEU solutions they are temperature independent. The findings that the pairwise solute−solute interactions are weaker in DMEU than in TMU solutions have been supported by the results of volumetric studies.[9]

The purpose of this paper is to study the effect of the structural difference between DMEU and DMPU molecules on the intermolecular interactions in their dilute aqueous solutions. To this end small-angle neutron scattering and volumetric studies of the solutions of DMPU in heavy water (D_2O) are carried out in the function of concentration and temperature. The results will be compared with those obtained previously for the TMU−D_2O and DMEU−D_2O systems.

2. Experimental Methods

2.1. Chemicals. *N,N′*-Dimethylpropyleneurea (reported purity ≥99%, absolute) was purchased from Fluka and was used without further purification. In order to increase the contrast for the SANS measurements instead of light water, heavy water (99.82 at. % deuterium content, ISOTOP, Moscow) was used. The solutions were prepared by weighing from DMPU and heavy water.

2.2. Small-Angle Neutron Scattering Measurements. The small angle neutron scattering measurements were carried out on the "Yellow Submarine" instrument at Budapest Neutron Centre.[10] The sample to detector distance and the mean neutron wavelength were 1.3 m and 3.86 Å, respectively. The samples were placed in 2 mm thick quartz cuvettes and then thermostated to ±0.5 K at 288.15, 298.15 and 313.15 K. The scattering experiments covered the scattering vector, q ($q = 4\pi \sin(\theta/2)/\lambda$; θ is the scattering angle, λ is the wavelength), range 0.05−0.45 Å^{-1}. For each sample a mixture for background evaluation has been prepared by mixing of light and heavy water, so that its total scattering cross-section was equal to the incoherent scattering cross-section of the corresponding sample solution.

2.3. Density Measurements. The densities were measured at 288.15, 298.15 and 313.15 K using an Anton-Paar DMA60/602H vibrating-tube densimeter. The temperature of the sample cell was kept constant to ±0.005 K, and the reproducibility of the densities was (1 to 2) × 10^{-5} g/cm^3. Further details on the density measurement are given in the paper on the DMEU−D_2O system.[9]

3. Results

3.1. SANS Measurements. The SANS measurements were carried out on DMPU−D_2O solutions in the DMPU mole fraction range 0.005−0.05. The absolute calibration and background corrections were carried out in the same way as described in ref 9.

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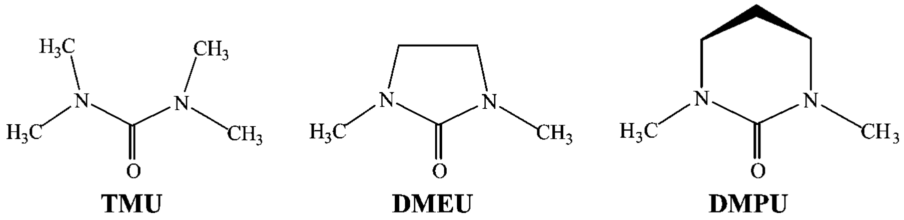

Figure 1. Molecular structure of tetramethylurea (TMU), *N,N'*-dimethylethyleneurea (DMEU) and *N,N'*-dimethylpropyleneurea (DMPU).

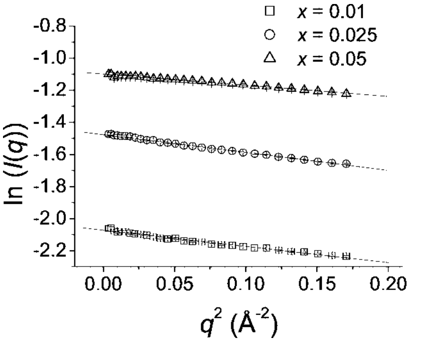

Figure 2. Guinier plots for DMPU$-$D$_2$O solutions at 298.15 K ($I(q)$, coherent scattering intensity; q, scattering vector; x, mole fraction of DMPU).

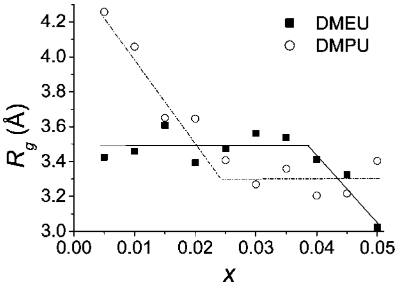

Figure 3. Concentration dependence of the radius of gyration (R_g) in DMPU$-$D$_2$O (present work) and DMEU$-$D$_2$O[9] solutions at 298.15 K (x, mole fraction of the solute).

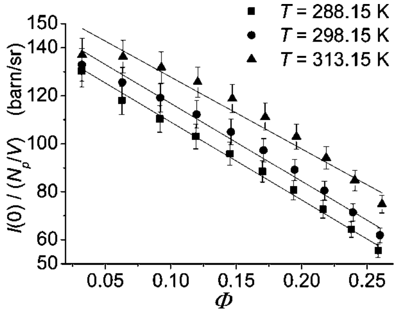

Figure 4. Concentration dependence of the forward scattering intensity per single molecule, $I(0)/(N_p/V)$, of DMPU in D$_2$O measured at different temperatures (Φ, volume fraction of DMPU).

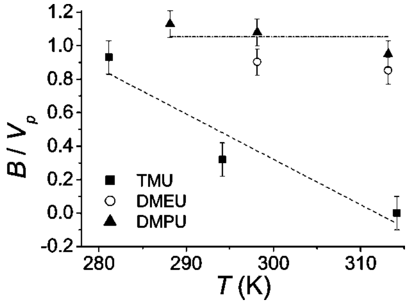

Figure 5. Temperature dependence of the dimensionless second osmotic virial coefficient (B/V_p) for the solutions of DMPU (present work), DMEU[9] and TMU[7] in D$_2$O (the lines are guides to the eye).

The usual way of treating SANS data is to find an appropriate model function which reasonably describes the scattering curves of the system. For DMPU$-$D$_2$O solutions the Guinier model, which was successfully used for DMEU$-$D$_2$O solutions,[9] seemed to be an adequate approach. The details of the data analysis are described elsewhere.[9]

From the Guinier approximation,

$$I(q) = I(0)\exp(-q^2 R_g^{\ 2}/3) \qquad (1)$$

where $I(q)$ is the coherent scattering intensity, the average size of scattering objects (R_g, the average radius of gyration of scattering entities in the solution) and the coherent forward scattering intensity, $I(0)$, can be determined.

For illustration, the Guinier plots for the mole fractions of DMPU $x = 0.01$, 0.025 and 0.05 are shown in Figure 2. The R_g values obtained at 298.15 K are compared with those for *N,N'*-dimethylethyleneurea[9] in Figure 3.

The second osmotic virial coefficient (B) measures the deviation from the ideal behavior due to pairwise solute$-$solute interactions. The relationship between B and g_{ss}^0 (solute$-$solute pair correlation function at infinite dilution) can be given as[5]

$$B = -\frac{1}{2}\int_0^\infty [g_{ss}^0(r) - 1]4\pi r^2\,dr \qquad (2)$$

The dimensionless second osmotic virial coefficient, (B/V_p), can be calculated using the equation[7]

$$I(0) = (N_p/V)(\sum b_i - \rho_s V_p)^2\left(1 - 2\frac{B}{V_p}\Phi\right) \qquad (3)$$

where N_p is the total number of scattering particles, V is the volume of the sample, V_p is the volume of one scattering particle, $\sum b_i$ is the sum of coherent scattering lengths of the nuclei taken over a particle, ρ_s is the coherent scattering length density of the solvent and Φ is the volume fraction of DMPU. The coherent forward scattering intensity per one solute molecule, $I(0)/(N_p/V)$, is plotted as a function of Φ in Figure 4. The experimental data can be well approximated by straight lines over the whole concentration range investigated. The B/V_p values, obtained from the fits to eq 3, are plotted against temperature along with those for TMU[7] and DMEU[9] in Figure 5.

Another approach for characterizing intermolecular interactions in the whole concentration range is provided by the use of Kirkwood$-$Buff integrals (KBIs). They are defined as

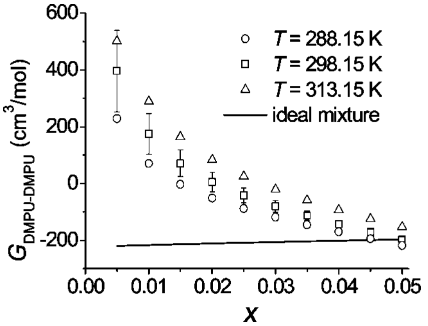

Figure 6. Kirkwood−Buff integrals for DMPU−DMPU interaction ($G_{\text{DMPU-DMPU}}$) in the function of concentration (x, mole fraction of DMPU). The full line refers to the ideal solution at 298.15 K. For clarity the error bars are shown only for the measurements at 298.15 K.

integrals of the partial pair correlation function of the molecules taken over the whole space[11]

$$G_{ij} = \int_0^\infty [g_{ij}(r) - 1]4\pi r^2 \, dr \tag{4}$$

where $g_{ij}(r)$ are the correlation functions between species i and j. G_{ij} gives the tendency of molecule j to cluster around a central molecule i, and therefore they provide information on the solute−solute, solute−solvent and solvent−solvent interactions.

The method of determining KBIs using small-angle X-ray scattering was introduced by Bhatia and Thornton[12] and Nishikawa.[13] The Kirkwood−Buff integrals can be obtained from SANS data as well, using the values of the coherent forward scattering intensity, partial molar volumes of the components and the isothermal compressibility of the solutions following the procedure outlined in refs 6 and 14. The KBIs calculated for the DMPU−DMPU interactions ($G_{\text{DMPU-DMPU}}$) are displayed in the function of concentration and temperature in Figure 6. The KBIs have nonzero values for an ideal mixture,[15] and their values were calculated by using the equations of Shulgin and Ruckenstein.[16]

In Figure 7 the KBIs for DMPU−D_2O solutions are compared with those for DMEU−D_2O solutions calculated from the SANS data of ref 9. The partial molar volumes used in the calculations of KBIs for DMPU−D_2O and DMEU−D_2O solutions were determined from the measured densities (present work and ref 9, respectively). The isothermal compressibility of pure DMPU and DMEU were taken equal to that of TMU,[17] and the values for the mixture were linearly interpolated between this value and that of D_2O.

3.2. Density Measurements. The measurements covered the DMPU mole fraction range 0.0025−0.05. Experimental density values for the DMPU−D_2O solutions at 288.15, 298.15 and 303.15 K are reported in Table 1. The densities of pure DMPU are in satisfactory agreement with those reported in the literature: at 298.15 K 1.05939 g/cm^3 (present work), 1.0596 g/cm^3 (ref 18), 1.0593 g/cm^3 (ref 19) and at 313.15 K 1.04700 g/cm^3 (present work), 1.0467 g/cm^3 (ref 19).

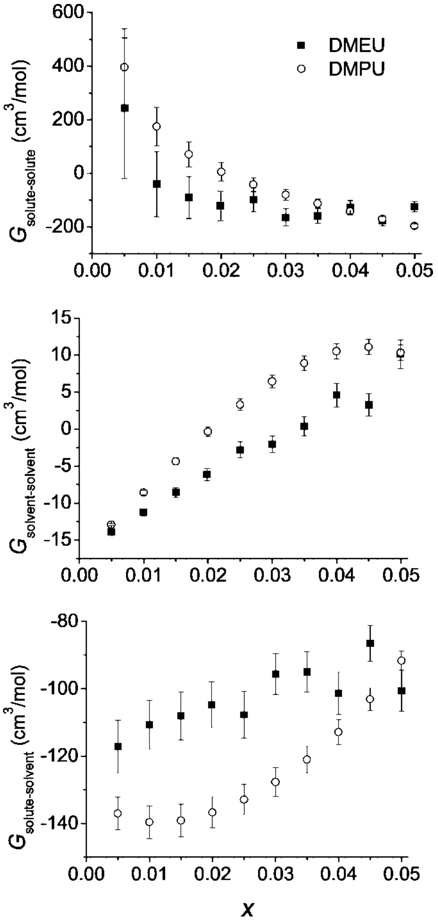

Figure 7. Concentration dependence of the Kirkwood−Buff integrals describing solute−solute ($G_{\text{solute-solute}}$), solvent−solvent ($G_{\text{solvent-solvent}}$), and solute−solvent ($G_{\text{solute-solvent}}$) interactions in DMPU−$D_2O$ and in DMEU−D_2O solutions at 298.15 K (x, mole fraction of the solute).

TABLE 1: Densities of DMPU− Heavy Water Solutions at 288.15, 298.15 and 313.15 K

	ρ, g/cm^3		
concn, mol %	T = 288.15 K	T = 298.15 K	T = 313.15 K
0	1.06785	1.05939	1.04697
0.2501	1.10550	1.10394	1.09926
0.4982	1.10547	1.10373	1.09887
0.7499	1.10554	1.10360	1.09853
1.0004	1.10559	1.10353	1.09826
1.2498	1.10583	1.10354	1.09804
1.4996	1.10601	1.10356	1.09786
2.0005	1.10649	1.10370	1.09757
2.5005	1.10714	1.10398	1.09742
2.9995	1.10780	1.10429	1.09733
3.4992	1.10851	1.10465	1.09728
3.9986	1.10922	1.10503	1.09727
4.4997	1.10996	1.10543	1.09729
4.9976	1.11064	1.10584	1.09735

From the densities of the dilute solutions the partial molar volumes of the solute at infinite dilution ($\bar{V}^\infty$) and the coefficients (V_{xx},V_{xxx}) in the expansion of the excess volume (V^E),

$$V^E = V_{xx}m^2 + V_{xxx}m^3 + ... \tag{5}$$

were evaluated by fitting the function

$$V(m) - V_w^0 = \bar{V}^\infty m + V_{xx}m^2 + V_{xxx}m^3 + ... \tag{6}$$

against the aquamolality (m).[20] The aquamolality is defined by the number of moles of solute per 55.51 mol of water (heavy water), $V(m)$ is the volume of the solution containing 55.51 moles of heavy water, V_w^0 is the volume of 55.51 mol of heavy water. The excess volume of the solution per 55.51 mol of heavy water (V^E) is defined by[20]

$$V^E = V(m) - V_w^0 - \bar{V}^\infty m \tag{7}$$

The coefficients V_{xx} and V_{xxx} (they are called molal volume second and third virial coefficients, respectively) represent the contribution of pair and triplet solute aggregates to the excess volume, respectively.[21] The quantity $V(m) - V_w^0$ was computed

TABLE 2: The Partial Molar Volumes of DMPU, DMEU and TMU at Infinite Dilution ($\bar{V}^{\infty}$) and the Molal Volume Second and Third Virial Coefficients (V_{xx} and V_{xxx}) with Their Standard Deviations for Mixtures with D_2O

T, K	$\bar{V}^{\infty}$, cm^3/mol	V_{xx},[a] cm^3(55.51M_w)/mol^2	V_{xxx}, cm^3(55.51M_w)^2/mol^3
DMPU−D_2O			
288.15	116.97 ± 0.072	−1.837 ± 0.078	0.268 ± 0.019
298.15	118.14 ± 0.060	−1.596 ± 0.068	0.229 ± 0.017
313.15	119.87 ± 0.054	−1.327 ± 0.058	0.188 ± 0.014
DMEU−D_2O[9]			
298.15	104.90 ± 0.072	−0.765 ± 0.051	0.0754 ± 0.0086
313.15	106.66 ± 0.072	−0.678 ± 0.051	0.0667 ± 0.0086
TMU−D_2O[24]			
298.15	110.56 ± 0.083	−1.222 ± 0.076	0.168 ± 0.017

[a] 55.51M_w is the mass of 55.51 mol of heavy water.

from the densities at m (Table 1). The method has been successfully applied to aqueous solutions of polyols,[20] alcohols and diols,[22] 3-methylpyridine[23] and DMEU.[9]

The values obtained for $\bar{V}^{\infty}$, V_{xx}, V_{xxx} at different temperatures along with those for the TMU−D_2O and DMEU−D_2O systems, taken from ref 9, are given in Table 2. Statistical analysis of the variances of the fits showed that the experimental data cannot be adequately described by using only the second virial coefficient (V_{xx}); including the third virial coefficient (V_{xxx}) is required.

4. Discussion

In the analysis of SANS data we have applied the procedure outlined in ref 5 and successfully used for aqueous solutions of DMEU.[9] The Guinier approximation (eq 1) appears to describe well the DMPU−D_2O system as can be seen in Figure 2. The concentration dependencies of the R_g values for DMPU−D_2O and DMEU−D_2O systems at 298.15 K (Figure 3) exhibit a significant difference (the R_g for 288.15 and 313.15 K show the same tendency). The R_g of DMEU scatters around an average value of 3.5 Å in the mole fraction range $x < 0.04$, and at higher concentrations it decreases sharply toward 3 Å. In contrast, the R_g of DMPU decreases with increasing concentration until it reaches a value of about 3.3 Å at $x \cong 0.025$. This behavior suggests that the pairs of DMPU molecules are falling apart with increasing DMPU concentration until they reach an average R_g value corresponding to that of the monomer. The pair of DMEU molecules assumed to be present in the low-concentration range[9] seems to be more stable than that of DMPU molecules. This may arise from the fact that the DMEU molecule has a planar ring[25] whereas in the case of DMPU molecule the middle carbon atom lies out of the plane[3] (see Figure 1). The rather surprising observation that the stable contact pairs of DMPU (DMEU) molecules gradually break up into monomers with increasing concentration may be a consequence of triplet solute−solute interactions. One would expect that further increase in concentration, beyond the concentration range covered by the present study, would lead to the formation of aggregates consisting of more than two solute molecules. The presence of stable solute pairs in aqueous solutions of the cyclic derivatives of tetramethylurea (DMEU, DMPU) is corroborated by the findings of a recent ab initio study of the intermolecular interactions between DMEU and water molecules.[26]

By fitting the experimental coherent forward scattering intensities to eq 3 the dimensionless second osmotic virial coefficients (B/V_p) for DMPU were found to be +1.13 ± 0.08, +1.08 ± 0.08 and +0.95 ± 0.08 at 288.15, 298.15 and 313.15 K, respectively. In sharp contrast with TMU−D_2O solutions,[5] but in good agreement with DMEU−D_2O solutions,[9] the B/V_p values in the DMPU−D_2O solutions do not change with temperature within the experimental uncertainties (Figure 5). This suggests that the pairwise interaction between DMPU molecules is not of the hydrophobic type, i.e., it does not become more attractive at higher temperatures.[27] The B/V_p values for DMPU are more positive than those for DMEU (+0.90 ± 0.08 and +0.85 ± 0.08 at 298.15 and 313.15 K, respectively)[9] which suggests that the pairwise solute−solute interactions are less attractive in DMPU−D_2O than in DMEU−D_2O solutions. In both systems the attractive part of the interaction between solute molecules plays a significant role since the B/V_p values are less positive than that for a hard sphere (+4).[5]

The concentration and temperature dependence of the Kirkwood−Buff integrals describing the DMPU−DMPU interactions in the solution ($G_{\mathrm{DMPU-DMPU}}$) are shown in Figure 6. The integrals increase with rising temperature and decrease with increasing DMPU concentration. In the low concentration range ($x < 0.02$) the KBIs have positive values indicating attractive solute−solute interactions, and then they become negative. This seems to be in good accord with the observed behavior of R_g (Figure 3) which indicates that above $x \cong 0.025$ the DMPU−DMPU pairs fall apart.

The Kirkwood−Buff integrals characterizing solute−solute, solvent−solvent and solute−solvent interactions at 298.15 K are displayed for the DMPU−D_2O and DMEU−D_2O solutions in Figure 7. $G_{\mathrm{solute-solute}}$ decreases with increasing concentration in the case of DMPU−D_2O solutions whereas—if one neglects the data point at $x = 0.0025$—it remains nearly constant in the case of DMEU−D_2O solutions. In both systems the addition of solute molecules to the solutions is accompanied by a slight increase in the solvent−solvent aggregation tendency ($G_{\mathrm{solvent-solvent}}$). The solute−solvent interactions ($G_{\mathrm{solute-solvent}}$), especially for the DMPU−D_2O solution, become more attractive with increasing concentration. This finding is consistent with the gradual breaking up of the pairs of the solute molecules.

The analysis of volumetric data can complete the information about the intermolecular interactions in the solutions of DMEU and DMPU in heavy water derived from SANS. It can be seen from Table 2 that the partial molar volume of the solute at infinite dilution ($\bar{V}^{\infty}$) in DMPU−D_2O solution is larger by 13.2 cm^3/mol than that in DMEU−D_2O solution at 298.15 K, which reflects the difference between the molar volumes of the pure liquids (13.1 cm^3/mol). It is interesting to note that the molar volume difference is 3 cm^3/mol larger than that one would expect from the contribution of a CH_2 group to the van der Waals volume of the solute molecule (10.2 cm^3/mol);[28] it indicates that the introduction of a CH_2 group into the ring demands more space.

The molal volume second and third virial coefficients, V_{xx} and V_{xxx}, provide information on the volume change due to pair and triplet solute−solute interactions, respectively.[20,21] Table 2 shows that triplet interactions cannot be neglected even in these dilute solutions; their contribution to the excess volume, at $m = 1$, is ∼10% in TMU−, DMEU− and DMPU−D_2O solutions. Wurzburger et al.[20] have shown that, if the sign of V_{xx} is negative, the solute has a structure-making effect on water, i.e. the water molecules are more structured in the cospheres than in the bulk. Since the value of V_{xx} is found to be significantly more negative for DMPU−D_2O than for DMEU−D_2O and TMU−D_2O solutions (Table 2), the DMPU molecule has a more pronounced structure-making effect than DMEU and TMU molecules. This is not unexpected since the DMPU molecule contains one more CH_2 group than the DMEU molecule.

5. Conclusions

The intermolecular interactions in dilute solutions of *N*,*N*′-dimethylpropyleneurea were studied by small-angle neutron scattering and density measurements. The concentration dependence of the radius of gyration values suggests that the DMPU−DMPU solute pairs, present in the low concentration range, are less stable than the DMEU−DMEU pairs. The osmotic second virial coefficient of DMPU, similarly to that of DMEU, does not exhibit any temperature dependence. This indicates that in contrast with the aqueous solutions of TMU the interaction between DMPU molecules is not of the hydrophobic type. The Kirkwood−Buff integrals corroborate the above conclusions. The molal volume second virial coefficients obtained from the high precision density measurements show that the DMPU molecule has a more pronounced structure-making effect on water than the DMEU molecule.

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References and Notes

(1) Stroka, J.; Herfort, I.; Schneider, H *J. Solution Chem.* **1990**, *19*, 743.

(2) Lundberg, D.; Ullström, A. S.; D'Angelo, P.; Warminska, D.; Persson, I. *Inorg. Chem. Acta* **2007**, *360*, 2744.

(3) D'Angelo, P.; Chillemi, G.; Barone, V.; Mancini, G.; Sanna, N; Persson, I. *J. Phys. Chem. B* **2005**, *109*, 9178.

(4) Smirnov, P.; Weng, L.; Persson, I. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5248.

(5) Jancsó, G.; Cser, L.; Grósz, T.; Ostanevich, Yu. M *Pure Appl. Chem.* **1994**, *66*, 515.

(6) Almásy, L.; Jancsó, G.; Cser, L. *Appl. Phys. A: Mater. Sci. Process.* **2002**, *74*, S1376.

(7) Bezzabotnov, V. Yu.; Cser, L.; Grósz, T.; Jancsó, G.; Ostanevich, Yu. M *J. Phys. Chem.* **1992**, *96*, 976.

(8) Almásy, L.; Len, A.; Székely, N. K.; Pleštil, J. *Fluid Phase Equilib.* **2007**, *257*, 114.

(9) Székely, N. K.; Almásy, L.; Jancsó, G. *J. Mol. Liq.* **2007**, *136*, 184.

(10) Rosta, L. *Appl. Phys. A: Mater. Sci. Process.* **2002**, *74*, S52.

(11) Kirkwood, J. G.; Buff, F. P. *J. Chem. Phys.* **1951**, *19*, 774.

(12) Bhatia, A. B.; Thornton, T. E. *Phys. Rev. B* **1970**, *2*, 3004.

(13) Nishikawa, K. *Chem. Phys. Lett.* **1986**, *132*, 50.

(14) Almásy, L.; Jancsó, G. *J. Mol. Liq.* **2004**, *113*, 61.

(15) Matteoli, E. *J. Phys. Chem. B* **1997**, *101*, 9800.

(16) Shulgin, I.; Ruckenstein, E. *J. Phys. Chem. B* **1999**, *103*, 2496.

(17) Marcus, Y.; Hefter, G. T *J. Mol. Liq.* **1997**, *73/74*, 61.

(18) Rosenfarb, J.; Huffman, H. L., Jr.; Caruso, J. A *J. Chem. Eng. Data* **1976**, *21*, 150.

(19) Kneisl, P.; Zondlo, J. W. *J. Chem. Eng. Data* **1987**, *32*, 11.

(20) Wurzburger, S.; Sartorio, R.; Guarino, G.; Nisi, M. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2279.

(21) Franks, F. *J. Chem. Soc., Faraday Trans. 1* **1983**, *73*, 830.

(22) Wurzburger, S.; Sartorio, R.; Elia, V.; Cascella, C. *J. Chem. Soc., Faraday Trans. 1* **1990**, *86*, 3891.

(23) Jancsó, G. *J. Solution Chem.* **2006**, *35*, 991.

(24) Jakli, Gy.; Van Hook, W. A *J. Chem. Eng. Data* **1996**, *41*, 249.

(25) Otero, J. C.; Marcos, J. I.; López-Cantarero, E.; Chacón, A. *Chem. Phys.* **1991**, *157*, 201.

(26) Bende A.; Almásy L. *Chem. Phys.* **2008**, *354*, 202.

(27) Franks, F.; Desnoyers, J. E. *Water Sci. Rev.* **1985**, *1*, 171.

(28) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

JP808471P