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Small-angle neutron scattering and volumetric studies of dilute solutions of N,N' -dimethylethyleneurea in heavy water

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Abstract

Small-angle neutron scattering experiments and density measurements were carried out on dilute solutions of N,N' -dimethylethyleneurea (DMEU) in heavy water in the aquamolality ranges 0.28–2.92 and 0.28–4.17, respectively, at 298.15 and 313.15 K. The results obtained for DMEU, the cyclic analogue of tetramethylurea (TMU), were compared with those reported for TMU solutions in the literature. Whereas in the aqueous solution of TMU the hydrophobic interaction increases with increasing temperature, the second osmotic virial coefficient obtained from the concentration dependence of the forward scattering intensities in the DMEU solution is temperature independent. In contrast with the TMU solution, the radius of gyration in the DMEU solution appears to be constant below the aquamolality of about 2. The molal volume second virial coefficient (V_{xx}), calculated from the densities of the solutions, is negative, which indicates that DMEU has a structure-making effect on water. In the TMU solution the value of V_{xx} was found to be more negative, which suggests that the water molecules are more structured in the hydration sphere of TMU than in that of DMEU molecule. The results of both the SANS and the volumetric studies on dilute solutions of DMEU lead to the conclusion that the pair-wise solute–solute interactions are weaker in DMEU than in TMU solutions.

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Keywords: N,N' -dimethylethyleneurea; SANS; Density; Binary mixtures

1. Introduction

Small-angle neutron scattering (SANS) is a well-known experimental method for investigating the properties of solutions containing rather large neutron–optical inhomogeneities, e.g., macromolecules, colloid particles, aggregates of small molecules. However, it has been demonstrated that SANS studies can provide information about solute–solute and solute–solvent interactions in aqueous solutions of non-electrolytes even in the case of small molecules [1,2]. Thus, for example, the concentration and temperature dependence of the second osmotic virial coefficient obtained from the SANS investigation of the aqueous solutions of tetramethylurea (TMU) indicated significant hydrophobic interactions between TMU molecules which become more attractive at higher temperatures [3]. The Kirkwood–Buff integrals obtained from SANS measurements on aqueous solutions of pyridine [4] and 3-methylpyridine [5] showed the presence of strong attractive interactions between

the solute molecules occurring already at very small concentrations that leads to the aggregation of solute molecules.

From the excess molar volumes of dilute aqueous solutions, determined by high precision density measurements, the partial molar volume of the solute at infinite dilution and the molal volume second virial coefficient can be obtained [6]. These provide information on the structure-making or structure-breaking effects of the solute on water and on the volume change produced by the pair-wise interaction of solute molecules [6,7].

N,N' -dimethylethyleneurea (1,3-dimethyl-2-imidazolidinone; DMEU) represents the cyclic analogue of TMU; it contains – instead of two methyl groups – an ethylene group and thus has a ring structure (see Fig. 1).

The structure and properties of aqueous TMU solutions, as well as the intermolecular interactions in the solutions, were widely studied by different experimental and theoretical techniques: various physico-chemical methods (see references in [8]), density [9], NMR spectroscopy [10,11], piezometry [10], small-angle X-ray scattering [10], positron annihilation [12], ultrasonic velocity [12], vapor pressure osmometry [13], quasi-elastic neutron scattering, neutron spin echo [8,14], small-

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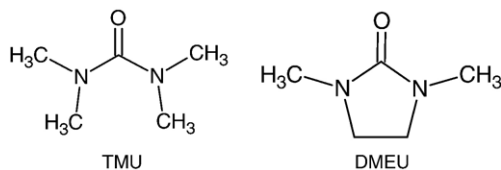


Fig. 1. Molecular structure of tetramethylurea (TMU) and *N,N'*-dimethylethyleneurea (DMEU).

angle neutron scattering [3,35], wide-angle neutron scattering [15], free energy simulation of the hydration of TMU [16], ab initio studies of water-TMU interactions [17], Monte Carlo simulation [18] and molecular dynamics simulation [19–21].

In contrast to the TMU solutions, the properties of the aqueous solutions of DMEU were much less investigated. Density measurements showed that there is a maximum at the DMEU mole fraction of about 0.35 [22]; from viscosity measurements it was found that the hydrodynamic volume of the DMEU molecule in the aqueous solution is much larger than its van der Waals volume [22]. Infrared investigation of the C=O stretching band of the DMEU molecule indicated a significant solute-solvent interaction in the solution [23].

The purpose of this paper is to study the effect of the structural difference between TMU and DMEU molecules on the intermolecular interactions in their aqueous solutions. Small-angle neutron scattering and volumetric studies of the solutions of DMEU in heavy water (D₂O) are carried out in the function of concentration and temperature. The comparison of the results with those obtained previously for the TMU — D₂O system can be expected to provide information on the differences in the intermolecular interactions in the solutions.

2. Experimental

2.1. Chemicals

N,N'-dimethylethyleneurea (reported purity $\geq 99.5\%$, absolute, stored over molecular sieve) was purchased from Aldrich and was used without further purification. In order to increase the contrast for the SANS measurements instead of light water heavy water (99.40 at.% deuterium content, ISOTOP, Moscow) was used. The solutions were prepared by weighing from DMEU and heavy water and they covered the aquamolality range $m=0.28$ – 4.17 (aquamolality is defined by the number of moles of solute per 55.51 mol of solvent). The same solutions have been used for both the SANS and the density measurements.

2.2. Small-angle neutron scattering measurements

The small-angle neutron scattering measurements were performed on the “Yellow Submarine” instrument at Budapest Neutron Centre [24]. Sample to detector distance of 1.3 m and the mean neutron wavelength of 3.86 Å were used. The samples were placed in 2 mm thick quartz cells, which were thermostatted to ± 0.5 K at 298.15 and 313.15 K. Scattering of a 1 mm thick light water sample and scattering from empty cell were also measured for calibration. For each sample a

background mixture 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 298.15 and 313.15 K using an Anton–Paar DMA60/602H vibrating-tube densimeter. The temperature of the sample cell was kept constant, using a circulating water bath, to ± 0.005 K. The temperature of the sample chamber was monitored with a thermistor which was calibrated against a 100 Ω Leeds and Northrup 4160 four-terminal platinum-resistance thermometer. The densimeter was calibrated with water and dry air. Each measurement was repeated at least twice and the reproducibility of the densities was $(1 \text{ to } 2) \times 10^{-5} \text{ g/cm}^3$.

3. Results

3.1. SANS measurements

The SANS measurements were carried out on DMEU–D₂O solutions in the aquamolality range 0.28–2.92 (DMEU mole fraction range 0.005–0.05). The scattering curves from the samples were corrected for sample transmission and scattering from empty quartz cell. The intensities were brought to absolute values with the scattering of a 1 mm thick light water sample. The same procedure has been followed for the background solutions. The background values were then subtracted from the scattering intensities of the samples, giving the coherent scattering cross-section.

For systems consisting of uniform particles in a homogeneous medium, the following approximation is used for the modelling of small-angle neutron scattering data [3]

$$I(q) \equiv d\Sigma(q)/d\Omega = (N_p/V)(\Sigma b_i - \rho_s V_p)^2 P(q)S(q) \quad (1)$$

where $I(q)$ is the coherent scattering intensity, q is the scattering vector ($q=4\pi\sin(\theta/2)/\lambda$; θ is the scattering angle, λ is the wavelength), $d\Sigma(q)/d\Omega$ is the coherent scattering cross-section of the sample normalized to unit sample volume (cm^{-1}), 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, Σb_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, $P(q)$ is the form factor of the scattering particle and $S(q)$ is the interparticle structure factor, which contains information on the spatial distribution of the scattering particles.

For determination of the average sizes of scattering objects, the Guinier approximation is frequently used

$$I(q) = I(0)\exp(-q^2 R_g^2/3) \quad (2)$$

where $I(0)$ is the coherent forward scattering intensity. By fitting the experimental data to Eq. (2) $I(0)$ and R_g , the average radius of gyration of molecules and molecular associates in the solution, can be determined.

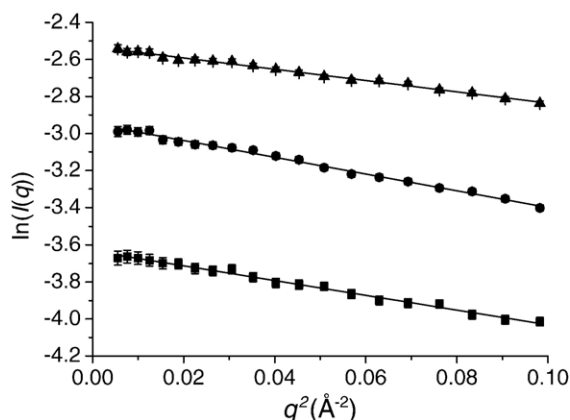


Fig. 2. Guinier plots for $m=0.56$ (■), 1.72 (●) and 2.92 (▲) DMEU–D₂O solutions at 298.15 K (m : aquamolality).

For illustration, the Guinier plots for the aquamolality $m=0.56$, 1.72 and 2.92 are shown in Fig. 2. The scattering curves were fitted with this model in the range $q < 0.3 \text{ Å}^{-1}$ in order to fulfill the Guinier criterion ($q_{\text{max}} R_g < 1.3$). The R_g values obtained are plotted against DMEU concentration in Fig. 3.

The second osmotic virial coefficient (B) measures the deviation from the ideal behavior due to pair-wise solute–solute interactions. For spherical objects the relationship between B and g_{ss}^0 (solute–solute pair correlation function at infinite dilution) can be given as [1]

$$B = -\frac{1}{2} \int_0^\infty [g_{ss}^0(r) - 1] 4\pi r^2 dr \quad (3)$$

Considering the DMEU molecules as primary scattering particles, the dimensionless second osmotic virial coefficient, (B/V_p), can be calculated using the equation

$$I(0) = (N_p/V) (\Sigma b_i - \rho_s V_p)^2 \left(1 - 2 \frac{B}{V_p} \Phi \right) \quad (4)$$

where Φ is the volume fraction of DMEU [3].

The coherent forward scattering intensity per one solute molecule obtained from the Guinier fits (Eq. (2)), is plotted in the function of Φ in Fig. 4.

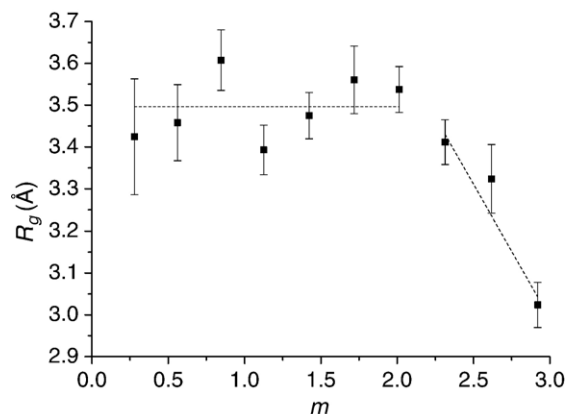


Fig. 3. Concentration (m : aquamolality) dependence of the radius of gyration (R_g) in DMEU–D₂O solution at 298.15 K.

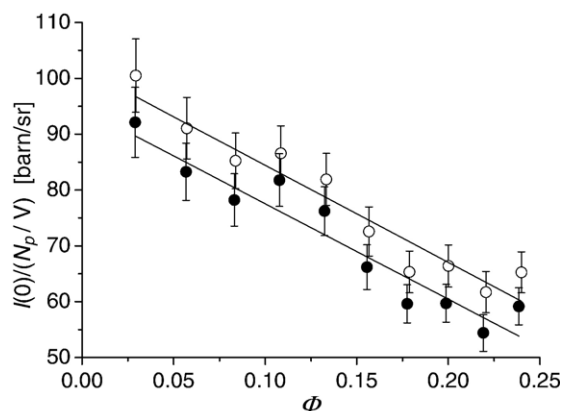


Fig. 4. Concentration dependence (Φ : volume fraction of DMEU) of the forward scattering intensity per single molecule ($I(0)/(N_p/V)$) of DMEU in D₂O measured at 298.15 K (●) and 313.15 K (○).

3.2. Density measurements

Experimental density values for the DMEU–D₂O solutions at 298.15 and 303.15 K are given in Table 1. The densities of pure DMEU were found to be 1.05763 and 1.04476 g/cm^3 at 298.15 and 303.15 K, respectively. At 298.15 K the agreement between the present density value and those reported in the literature (1.0519 g/cm^3 [25] and 1.0516 [26]) is rather poor and may be due to the higher purity of the DMEU sample used in the present work.

The excess property of a solution is the difference between the value that the property takes for the real solution and the value it would have for the ideal solution (in this case the reference state for the solvent is the molar volume of the pure liquid, whereas that for the solute is the partial molar volume of the solute at infinite dilution). The excess volume of the solution per 55.51 mol of heavy water, V^E , is therefore given by [6]

$$V^E = V(m) - V_w^0 - \bar{V}^\infty m \quad (5)$$

where, $V(m)$ is the volume of the solution containing 55.51 mol of heavy water and m moles of the solute; V_w^0 is the volume of 55.51 mol of heavy water and \bar{V}^∞ is the partial molar volume of the solute at infinite dilution; m is the aquamolality. The volumes $V(m)$ and V_w^0 have been calculated from the densities

Table 1

Densities of DMEU — heavy water solutions at 298.15 and 313.15 K

m	ρ ($T=298.15 \text{ K}$) g/cm^3	ρ ($T=313.15 \text{ K}$) g/cm^3
0	1.10382	1.09935
0.2791	1.10355	1.09868
0.5605	1.10313	1.09788
1.1333	1.10300	1.09696
1.7166	1.10320	1.09642
2.3129	1.10361	1.09611
2.9228	1.10408	1.09591
3.5531	1.10461	1.09580
4.1740	1.10510	1.09570

m is the aquamolality (number of moles of solute per 55.51 mol of heavy water).

Table 2

The partial molar volumes of DMEU and TMU at infinite dilution (\bar{V}^∞) and the molal volume second and third virial coefficients (V_{xx} and V_{xxx}) with their standard deviations for mixtures with D₂O (σ^2 is the variance of fit)

T/K	\bar{V}^∞ cm ³ /mol	V_{xx}^a cm ³ (55.51M _w)/ mol ²	V_{xxx} cm ³ (55.51M _w) ² / mol ³	σ^2 cm ⁶ / (55.51 M _w) ²
<i>DMEU – D₂O</i>				
298.15	104.32±0.10	−0.325±0.030		0.0322
	104.90±0.072	−0.765±0.051	0.0754±0.0086	0.00271
313.15	106.15±0.091	−0.288±0.026		0.0257
	106.66±0.072	−0.678±0.051	0.0667±0.0086	0.00272
<i>TMU – D₂O</i> [9]				
298.15	109.82±0.096	−0.461±0.038		0.0542
	110.56±0.083	−1.222±0.076	0.168±0.017	0.0092

^a 55.51M_w is the mass of 55.51 mol of heavy water.

of the solution ($\rho(m)$) and that of pure heavy water (ρ_w), respectively

$$V(m) = (55.51M_w + Mm)/\rho(m) \quad (6)$$

$$V_w^0 = 55.51M_w/\rho_w \quad (7)$$

where M_w and M are the molar masses of heavy water and DMEU, respectively.

At low concentrations the excess volume defined in Eq. (5) can be expressed as a virial expansion in the solute aquamolality [27]

$$V^E = V_{xx}m^2 + V_{xxx}m^3 + \dots \quad (8)$$

where the coefficients V_{xx} and V_{xxx} (they are called also molal volume second and third virial coefficients, respectively) represent the contribution of pair and triplet solute aggregates to the excess volume, respectively. From Eqs. (5) and (8) one obtains

$$V(m) - V_w^0 = \bar{V}^\infty m + V_{xx}m^2 + V_{xxx}m^3 + \dots \quad (9)$$

By fitting the function $V(m) - V_w^0$ against m using the method of least-squares, \bar{V}^∞ , V_{xx} and V_{xxx} can be determined. The obtained values for \bar{V}^∞ , V_{xx} , their standard deviations as well as the variances of fits (residual sum of squares/($n-2$); n is the number of experimental data points) are reported in Table 2. To decide whether the third virial coefficient (V_{xxx}) in Eq. (9) is required to represent the experimental data, the F test was employed [28]. At both temperatures it was found that V_{xxx} is statistically significant, therefore the experimental data cannot be adequately described by using only the second virial coefficient (V_{xx}).

4. Discussion

For the analysis of the SANS experimental data we have applied the procedure outlined in [3] and successfully used for aqueous solutions of tetramethylurea. The basic assumption of the analysis was that the solvent can be treated as a

homogeneous medium, and the coherent scattering is caused by the solute molecules floating in the medium. Since the size of DMEU molecule is quite small, the scattering curves display a rather featureless shape. The Guinier approximation (Eq. (2)) appears to describe well our system; the scattering intensities in Guinier representation give proper straight lines as can be seen in Fig. 2. The R_g values obtained for 298.15 K are plotted against DMEU concentration in Fig. 3 (the R_g values from the 313.15 K measurements show the same tendency, but they are higher by 0.19 ± 0.05 Å than those found at 298.15 K). As can be seen from the figure at dilute concentrations, $m < 2$, R_g scatters around an average value of 3.5 Å, while at higher concentrations it decreases sharply towards 3 Å.

The trends seen in Fig. 3 can be interpreted in the following way. At small concentrations there is a weak association between the solute molecules, giving a radius of gyration of 3.5 Å, which may correspond to a pair of DMEU molecules. This is not surprising if one considers that the DMEU molecule has a planar ring [29] and a rather high dipole moment (4.09 D [25]). Above $m \approx 2$, the observed decrease in the Guinier radius is possibly due to the increase of the interparticle interactions.

Next we address the behaviour of the coherent forward scattering intensity. Fig. 4 shows that the concentration dependence of the forward scattering intensity can be well approximated by a straight line over the whole concentration range investigated. By fitting the experimental data to Eq. (4) the dimensionless second osmotic virial coefficients (B/V_p) were found to be 0.90 ± 0.08 and 0.85 ± 0.08 at 298.15 and 313.15 K, respectively. In sharp contrast with TMU – D₂O solutions [3], the B/V_p values in the DMEU–D₂O solutions do not change with temperature within the experimental uncertainties (Fig. 5). This suggests that the pair-wise interaction between DMEU molecules is not of the hydrophobic type, i.e., it does not become more attractive at higher temperatures [30]. For a hard sphere Eq. (3) gives a value of +4 for B/V_p (see e.g. [1]). The B/V_p values (+0.90 and +0.85) are less positive than that for a hard sphere which indicates the presence of significant attractive solute–solute interactions in the DMEU–D₂O solutions. It can be seen from the B/V_p values that the magnitude of

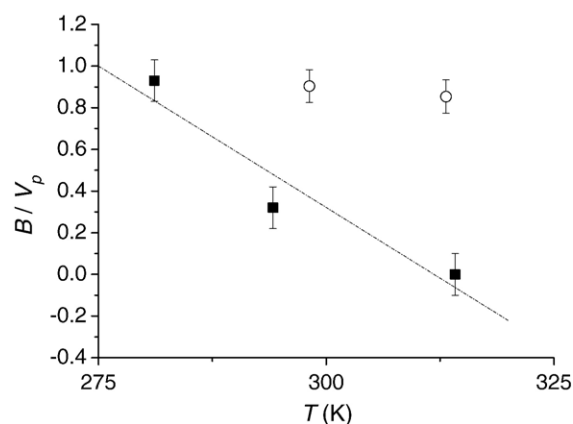


Fig. 5. Temperature dependence of the dimensionless second osmotic virial coefficient (B/V_p) for the solutions of TMU (■) and of DMEU (○) in D₂O (the line on this plot is just guide to the eye).

the DMEU–DMEU interaction at 298.15–313.15 K is about the same as that of the TMU–TMU interaction at 281 K. The observation that the attractive solute–solute interactions are more pronounced in TMU–D₂O than in DMEU–D₂O solutions is also born out by the values of the molal volume second virial coefficients (V_{xx}) given in Table 2.

It may be noted in passing that in the case of the aqueous solution of TMU there is an excellent agreement between the second osmotic virial coefficient values (B/V_p) of 0.32 (at 294.15 K) and 0.305 (at 298.15 K) obtained from SANS [3] and vapor pressure osmometer [13] studies, respectively. This strongly supports our previous conclusion [3] that one has to use the partial molar volume of the solute in Eq. (1) to calculate “the volume occupied by the solute in the solution” in the evaluation of SANS experimental data.

The surprisingly different behaviour of the two analogue molecules in aqueous solution as seen by neutron scattering can be more deeply understood by analyzing the volumetric data.

The partial molar volume of the solute at infinite dilution (\bar{V}^∞) in DMEU–D₂O solution reflects the solute–solvent interactions, therefore it can be expected, in principle, to provide information on the structure-making or structure-breaking effects of DMEU 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 solute–solvent interactions.

It is instructive to consider the influence of the van der Waals volume of the solute molecules on the \bar{V}^∞ values in the aqueous solutions of alkylureas. The \bar{V}^∞ values in aqueous TMU–H₂O and tert-butylurea (TBU)–H₂O solutions are the same: 109.48 ± 0.12 and 109.48 ± 0.03 at 288.15 K, 110.47 ± 0.10 and 110.38 ± 0.02 cm³/mol at 298.15 K, respectively. (The values for TMU were calculated using the density data given in [9], whereas those for TBU were taken from Table 1 of [6]). Since the van der Waals volumes of TMU and TBU molecules calculated from group contributions [31] are the same (75.0 and 74.7 cm³/mol) one can conclude that the tert-butyl group behaves like the four methyl groups as far as its effect on the water structure is concerned. The 10% difference between the van der Waals volumes of TMU and DMEU (75.0 and 68.2 cm³/mol) is reflected, in part, by their \bar{V}^∞ values in D₂O solutions (at 298.15 K 110.56 and 104.90 cm³/mol, respectively, see Table 2). The change in the limiting partial molal volume which results from the replacement of two –CH₃ by two –CH₂– groups can be estimated from the group contributions of –CH₃ and –CH₂– in aqueous solutions (18.1 and 15.9 cm³/mol, respectively [32]); the value of 4.4 cm³/mol is in satisfactory agreement with those obtained from the experimental density data (4.65 cm³/mol in H₂O [9,22] and 5.76 cm³/mol in D₂O).

The molal volume second virial coefficient, V_{xx} , in Eq. (8) provides information on the volume change produced by the pair-wise interaction of solute molecules [6,27]. The relationship between V_{xx} and the overlap of hydration cospheres of the solute pairs has been thoroughly discussed by Wurzbürger et al. [6]. It was shown that if the water molecules occupy larger volumes in the cosphere than in the bulk, i.e. water molecules

are more structured in the cospheres than in the bulk, the sign of V_{xx} is negative, and the solute has a structure-making effect on water. As can be seen from Table 2, the V_{xx} values are negative at both temperatures, consequently DMEU molecules have a structure-making effect on water. From the density data on TMU–D₂O ($m=0.19$ – 3.51) at 298.15 K [9] the values for the molal volume virial coefficients were calculated by using Eqs. (6)–(9) and are given in Table 2. (It should be noted that since the equation used in [9] to fit the experimental density data does not have the proper limiting behaviour with concentration, the original data were used in Eq. (9) to obtain V_{xx} and V_{xxx} .) In harmony with the conclusions from SANS investigations [3] and molecular dynamics simulation [21] the negative sign of V_{xx} indicates a structure-making effect, i.e. an increased overall structure in the hydration shell of TMU molecule. The value for V_{xx} is more negative in TMU–D₂O than in DMEU–D₂O solutions (see Table 2) which suggests a more significant structure-making effect of the TMU molecule on the water structure. The stronger interaction of the TMU molecule with water is also reflected by the larger shift of the C=O stretching vibration toward lower frequencies when the molecule passes from the pure liquid state to the solution phase; (66.0 and 43.3 cm^{−1} for TMU and DMEU, respectively) [23].

The fact that the experimental density data for the solutions of both DMEU and TMU in D₂O, even in the dilute region, cannot be adequately described by taking into account only the second virial coefficient (see Table 2) shows that triplet contributions to the solute–solute interactions (V_{xxx}) cannot be neglected; e.g. in DMEU–D₂O solutions at $m=1$ triplet effects contribute ~10% to the excess volume, V^E . On the other hand, for the dilute aqueous solutions of DMEU ($m=0.01$ – 2.3) [22] and TBU ($m=0$ – 0.6) [6], only one parameter, V_{xx} , was sufficient to represent the density data. It is interesting to note that the volumetric virial coefficients of alkylureas in aqueous solutions follow the observation for amino acid amines in water, namely, the more apolar the solute the more negative is the coefficient [33]. At 298.15 K the corresponding V_{xx} values are -0.711 ± 0.025 (in H₂O) and -0.765 ± 0.051 (in D₂O) for DMEU, -0.82 ± 0.05 (in H₂O) for TBU, and -1.01 ± 0.08 (in H₂O) and -1.222 ± 0.076 cm³(55.51 M_w)/mol² (in D₂O) for TMU (the dipole moments of DMEU, TBU and TMU are 4.09 [25], 4.25 [34] and 3.37 [25], respectively).

5. Conclusions

The present SANS experimental results indicate an attractive interaction between the DMEU solute molecules in D₂O solutions, which can be quantitatively characterized by the second osmotic virial coefficient, calculated from the forward scattering intensity. Measurements performed at 298.15 and 313.15 K resulted practically in the same B/V_p values within the experimental precision, which is in marked contrast with the behaviour of aqueous TMU solution [1]. Such behaviour may suggest that the attractive interaction between DMEU molecules is not of the hydrophobic type.

The observed behaviour of the radius of gyration shows that pronounced solute–solute aggregation (possibly pair formation)

occurs at lower concentrations ($m < 2$). The average size of the aggregates, as given by the radius of gyration, is rather small, so that aggregates consisting of more than two solute molecules may be present only in a very low proportion and cannot be identified from the present data.

The molal volume second virial coefficients obtained from high precision density measurements suggest that DMEU molecules, similarly to TMU molecules, have a structure-making effect on the water structure. It was found that this effect is more pronounced in the TMU–D₂O solutions and is accompanied by a stronger pair-wise solute–solute interaction.

Acknowledgments

This paper is dedicated to Professor László Cser on the occasion of his 70th birthday. We are grateful to him for the knowledge we had learnt from him in the field of neutron scattering. We are indebted to Ms Anna Szuja for help in carrying out the density measurements.

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