Thermal Expansion and Structure of 1,3-Dimethylurea, Tetramethylurea, and Tetrabutylammonium Bromide Aqueous Solutions Derived from Density Measurements†

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On the basis of density measurements, the determination of apparent and partial molar volumes of the solutes in the title solutions have been carried out previously at and around room temperatures both in H_2O and D_2O solutions as a function of composition. They showed minima at intermediate compositions, and a number of other properties of these solutions also indicated radical structural changes and differences versus composition. On this basis, we have chosen these solutions to analyze also the solvent partial molar volume and its thermal expansibility, which were not involved in the earlier studies, to these structural changes and differences. To obtain reliable thermal expansibility results, the density measurements were extended down to low temperatures. High precision density measurements of the normal water solutions were carried out in wide temperature [(274.15 to 308.15) K] and molality, m [(0.05 to 3 < 6) mol·kg^{-1}], ranges at closely spaced temperature intervals. From the measured densities, both the solute and the solvent partial molar volumes and their thermal expansibilities were calculated. The results are analyzed in terms of the cage model of the hydrophobic effect, and they are correlated to the solvent excess enthalpy and entropy and to their $H_2O + D_2O$ isotope effects. Although all the title solutions show dominant "interstitial" solution character, their structure is determined by a variety of structural equilibriums, depending mainly on the polar/apolar balance of the "mixed" solute molecules, on their H-bond donor/acceptor ability, and on the solute/solvent ratio.

Introduction

Due to their practical and theoretical significance, the structure of the 1,3-dimethylurea (DMU), tetramethylurea (TMU), and tetrabutylammonium bromide (TBuAmBr) aqueous solutions attracts remarkable and continuing interest. The alkyl-ureas are effective conformational perturbants; therefore, the study of the structure of their solutions should contribute to an understanding of the denaturation process.[1,2] Solutions of the tetraalkylammonium halides are model systems studying hydrophobic effects.[3,4]

In previous years, our laboratory has participated in a comprehensive program to study their molecular structure and the structural changes with temperature and composition using various experimental techniques. This series of polar organic molecules was chosen to compare the structural transformations of the solvent in the course of hydration and hydration interactions associated with the competition between the contributions of the hydrophilic and (increasingly) hydrophobic parts of these solute molecules.

Our previous thermodynamic investigations included vapor pressure and $H_2O + D_2O$ vapor pressure isotope effect (VPIE) measurements on DMU,[5,6] TMU,[5,7] and TBuAmBr[8] solutions over wide temperature and composition ranges and apparent ($V_{2,\Phi}$) and partial molar volume ($\bar{V}_2$) determinations of the solutes (2) DMU,[5,9] TMU,[5,9] and TBuAmBr,[8] at and around room temperatures, both in H_2O and D_2O solutions. The adiabatic compressibility (β) of the TMU[10] and TBuAmBr[11] in normal water solutions has also been determined, combined with positron annihilation measurements. The $V_{2,\Phi}$ and $\bar{V}_2$ results showed minima at intermediate compositions, $m(\bar{V}_{2,\min})$, and the extreme of the other determined properties of these solutions also indicated radical structural differences and changes versus composition.

To obtain further structural information on the title solutions, we determined the solute (2) and solvent (1) partial molar volumes ($\bar{V}_2$, $\bar{V}_1$) and their thermal expansibilities ($\bar{V}_{2,E}$, $\bar{V}_{1,E}$) from high precision density measurements extended down to low temperatures.

The large majority of the apparent and partial molar volume investigations has been carried out at or around room temperatures as a function of the concentration, and thermal expansion studies have not often been involved to elucidate structural changes in aqueous solutions.

Hepler[12] has demonstrated on the H_2O/D_2O behavior that the $(\partial^2V/\partial T^2)_P$ derivative gives a basis for the distinction between "structure making" and "structure breaking", because though the relation $(\partial C_P/\partial P)_T = -T(\partial^2 V/\partial T^2)_P$, it is related to the heat capacity (C_P) of the water. On this basis, structure-breaking solutes should have negative $(\partial^2V/\partial T^2)_P$ and structure-making solutes positive $(\partial^2V/\partial T^2)_P$ derivatives. Apelblat and Manzurola used this concept to analyze their $(\partial^2V_{2,\Phi}/\partial T^2)_P$ results, obtained for NaCl,[13] KCl,[13] NaBr,[14] and LiCl[15] aqueous solutions. They concluded that the behavior of the obtained $-T(\partial^2V_{2,\Phi}/\partial T^2)_P$ results correspond to the moderately different structure-breaking influences of these solutes on the solvent structure, although new structural information here could not be deduced.

Determining the second and higher order (temperature and/or pressure) derivatives of the Gibbs energy, which controls structural equilibria in aqueous solutions, apparently the most

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comprehensive study so far has been carried out by Koga et al.[16,17] From results obtained for 2-butoxyethanol and some other polar organic solutions, they succeeded to distinguish up to three regions with significantly different solute−solvent interactions in the temperature−mole fraction fields. They pointed out that the higher order the derivative, the more detailed the information it contains, and the transitions between the differing structural regions are accompanied by anomalies in the third derivatives of the Gibbs energy.

Experimental Section

Materials. Laboratory distilled water was treated with basic potassium permanganate and twice redistilled using an all-glass apparatus. 1,3-Dimethylurea (Merck, analytical grade) was recrystallized from ethanol and dried under vacuum at $T = (330 \text{ to } 340)$ K to constant mass. Tetramethylurea (Merck, analytical grade) was freshly distilled under vacuum. Stock ("mother") solutions were prepared gravimetrically. Due to the increasing $m(V_{2,\mathrm{min}})$ compositions of the TBuAmBr, TMU, and DMU series, the composition of their "mother" solutions was adjusted to $m = (3, 4, \text{and } 6)$ mol·kg^{-1}, respectively, and 10 to 12 "daughter" solutions were diluted by mass. Prior to the density measurements, the diluted samples were degassed by freezing−pumping−thawing cycles to remove dissolved air to increase accuracy and to prevent formation of bubbles in the sample cell during measurement.

Density Measurements. Densities were measured using an Anton-Paar vibrating tube densimeter of the type DMA 60/602 H. The calibration constant was determined daily using the known densities of air and H_2O. A detailed discussion regarding the accuracy of the calibration and of the obtainable density data is given in ref 18.

The temperature of the (external) sample cell was kept constant at the different experimental temperatures to < ± 0.01 K. The density measurement of the solution samples was repeated at least twice with renewed sample in the cell, in each case with several (6 to 10) readings of the vibration frequency, until the reproducibility of the densities of the individual samples was within six-figure precision. The temperature of the sample chamber was monitored with a thermistor, which has been calibrated to $T < \pm 0.01$ K uncertainty against a Pt resistance thermometer coupled with a thermostatted Leeds and Northrup G-1 Mueller bridge.

Results

Densities. The experimental density results (listed in the Appendix) could be fitted to eq 1 within experimental uncertainties, where ρ_m and ρ_o are the densities of solution and pure solvent, respectively.

$$(\rho_m - \rho_o)/m = P_1 + P_2 m^{1/2} + P_3 m + P_4 m^{3/2} + P_5 m^2 \tag{1}$$

To calculate ρ_o versus temperature, Kell's equation[19] was used. Giving the ρ_m results in this form, instead of the usual $(\rho_m - \rho_o)$ form, has the advantage that it undergoes much smaller relative changes versus molality. The parameters of the fits are reported in Table 1, together with the standard deviations.

Apparent and Partial Molar Volumes. Apparent molar volumes were calculated from the measured densities using eq 2.[20]

$$V_{2,\Phi} = (M/\rho) - [10^3(\rho - \rho_0)/(m\rho\rho_0)] \tag{2}$$

where M is the molar mass of the solute and ρ and ρ_0 are the densities of solution and pure solvent, respectively. In the calculation for the molar mass of DMU, TMU, and TBuAmBr, (88.109, 116.16, and 322.371) g·mol^{-1} were used, respectively.

The $V_{2,\Phi}$(TBuAmBr) results could be fitted within experimental uncertainty (≤ ± (0.1 to 0.2) cm^3·mol^{-1}) to an equation of the form

$$\mathrm{V}_{2,\Phi} = A_1 + A_2 m^{1/2} + A_3 m^2 + A_4 m^{3/2} + A_5 m^2 \tag{3}$$

while for those of the $V_{2,\Phi}$(DMU) and $V_{2,\Phi}$(TMU) results, a four-constant fit proved adequate.

The solute partial molar volumes, $\bar{V}_2$(DMU) and $\bar{V}_2$(TMU), were calculated from the equation[17]

$$\bar{V}_2 = V_\Phi + m\left(\frac{\partial V_\Phi}{\partial m}\right)_P = A_1 + \frac{3}{2}A_2 m^{1/2} + 2A_3 m + \frac{5}{2}A_4 m^{3/2} \tag{4}$$

and $\bar{V}_2$(TBuAmBr) from

$$\bar{V}_2 = V_\Phi + \frac{1}{2}m^{1/2}\left(\frac{\partial V_\Phi}{\partial m^{1/2}}\right)_P = A_1 + \frac{3}{2}A_2 m^{1/2} + 2A_3 m + \frac{5}{2}A_4 m^{3/2} + 3A_5 m^2 \tag{5}$$

The solvent partial molar volumes, $\bar{V}_1$(DMU) and $\bar{V}_1$(TMU), were calculated from

$$\bar{V}_1 = \frac{M_{H_2O}}{\rho_{H_2O}} + m\left(\frac{\partial V_\Phi}{\partial m}\right)_P = \frac{M_{H_2O}}{\rho_{H_2O}} + \frac{1}{2}A_2 m^{1/2} + A_3 m + \frac{3}{2}A_4 m^{3/2} \tag{6}$$

and for $\bar{V}_1$(TBuAmBr) from

$$\bar{V}_1 = \frac{M_{H_2O}}{\rho_{H_2O}} - \frac{m^{3/2}}{2x55.508}(A_2 + 2A_3 m^{1/2} + 3A_4 m + 4A_5 m^{3/2}) \tag{7}$$

The temperature and composition behavior of the $\bar{V}_2$ and $\bar{V}_1$ results are shown in Figures 1a,b, 2a,b and 3a,b.

Partial Molar Expansibilities. The $\bar{V}_2$ and $\bar{V}_1$ versus m results were transposed (converted) to $\bar{V}$ vs T/K − 273.15 ones and fitted to three-constant polynomials, except for the $\bar{V}_1$(TMU) results, where four-constant fits were necessary. For the solvent, we could calculate excess partial molar expansibilities, $\bar{V}^E_{1,E} = \bar{V}_{1,E} - V^*_{1,E}$, because the accurate reference, $V^*_{1,E} = (\partial V^*_{H_2O}/\partial \mathrm{T})_p$, could be obtained from Kell's density data.[19]

The composition and temperature behavior of $\bar{V}_{2,E}$ and $\bar{V}^E_{1,E}$ are shown in Figures 1c,d, 2c,d, and 3c,d.

Discussion

Solute Partial Molar Volumes, $\bar{V}_2$. A widely accepted interpretation of the composition and temperature behavior of $V_{2,\Phi}$ and $\bar{V}_2$ of polar organic solutes, given by Wen and Saito,[3] was based on their measurements on the tetraalkylammonium homologues (R_4AmBr). The initial negative slopes and the minimum values at intermediate compositions, $m(\bar{V}_{2,\mathrm{min}})$, were rationalized with an "interstitial" solution process, in which the alkyl chains are hidden in a complete or partial solvent cage. The minimum becomes more pronounced and shifts to lower concentrations with increasing hydrophobic character of the solute molecule and with decreasing temperature. The process results in a structural rearrangement and stabilization of the solvent clusters surrounding the hydrophobic (part of the) molecule (hydrophobic hydration sphere).

Table 1. Least-Squares Parameters of Equation 1[a]

T/K − 273.15	P_1 / $g\cdot cm^{-3}\cdot kg\cdot mol^{-1}$	P_2 / $g\cdot cm^{-3}\cdot kg^{3/2}\cdot mol^{-3/2}$	P_3 / $g\cdot cm^{-3}\cdot kg^{2}\cdot mol^{-2}$	P_4 / $g\cdot cm^{-3}\cdot kg^{5/2}\cdot mol^{-5/2}$	P_5 / $g\cdot cm^{-3}\cdot kg^{3}\cdot mol^{-3}$	SD
Dimethylurea						
1	$8.914\cdot10^{-3}$	$1.305\cdot10^{-3}$	$-4.300\cdot10^{-4}$	$-1.061\cdot10^{-4}$	-	$3.0\cdot10^{-5}$
2	$8.609\cdot10^{-3}$	$1.675\cdot10^{-3}$	$-6.989\cdot10^{-4}$	$-4.031\cdot10^{-4}$	-	$3.0\cdot10^{-5}$
3	$8.251\cdot10^{-3}$	$2.416\cdot10^{-3}$	$-1.130\cdot10^{-3}$	$1.066\cdot10^{-4}$	-	$3.0\cdot10^{-5}$
4	$8.394\cdot10^{-3}$	$2.036\cdot10^{-3}$	$-1.079\cdot10^{-3}$	$6.380\cdot10^{-5}$	-	$3.0\cdot10^{-5}$
5	$8.548\cdot10^{-3}$	$1.365\cdot10^{-3}$	$-5.492\cdot10^{-4}$	$-5.607\cdot10^{-5}$	-	$4.0\cdot10^{-5}$
6	$8.593\cdot10^{-3}$	$1.136\cdot10^{-3}$	$-4.495\cdot10^{-4}$	$-6.670\cdot10^{-5}$	-	$3.0\cdot10^{-5}$
7	$8.568\cdot10^{-3}$	$1.099\cdot10^{-3}$	$-4.677\cdot10^{-4}$	$-5.668\cdot10^{-5}$	-	$3.0\cdot10^{-5}$
8	$8.518\cdot10^{-3}$	$9.470\cdot10^{-4}$	$-3.329\cdot10^{-4}$	$-8.735\cdot10^{-5}$	-	$4.0\cdot10^{-5}$
9	$8.438\cdot10^{-3}$	$9.401\cdot10^{-4}$	$-3.413\cdot10^{-4}$	$-8.374\cdot10^{-5}$	-	$4.0\cdot10^{-5}$
10	$8.386\cdot10^{-3}$	$9.325\cdot10^{-4}$	$-3.486\cdot10^{-4}$	$-8.011\cdot10^{-5}$	-	$4.0\cdot10^{-5}$
15	$8.366\cdot10^{-3}$	$3.779\cdot10^{-4}$	$-7.885\cdot10^{-5}$	$-1.204\cdot10^{-4}$	-	$3.0\cdot10^{-5}$
25	$8.019\cdot10^{-3}$	$2.062\cdot10^{-4}$	$-9.911\cdot10^{-5}$	$-9.624\cdot10^{-5}$	-	$3.0\cdot10^{-5}$
35	$7.611\cdot10^{-3}$	$3.472\cdot10^{-4}$	$-3.098\cdot10^{-4}$	$-3.564\cdot10^{-5}$	-	$3.0\cdot10^{-5}$
Tetramethylurea						
1	$2.065\cdot10^{-3}$	$1.906\cdot10^{-3}$	$6.223\cdot10^{-4}$	$-4.803\cdot10^{-4}$	-	$4.0\cdot10^{-5}$
2	$1.693\cdot10^{-3}$	$2.461\cdot10^{-3}$	$1.933\cdot10^{-4}$	$-3.743\cdot10^{-4}$	-	$2.0\cdot10^{-5}$
3	$1.825\cdot10^{-3}$	$1.790\cdot10^{-3}$	$7.216\cdot10^{-4}$	$-5.057\cdot10^{-4}$	-	$4.0\cdot10^{-5}$
4	$1.551\cdot10^{-3}$	$2.059\cdot10^{-3}$	$5.814\cdot10^{-4}$	$-4.833\cdot10^{-4}$	-	$4.0\cdot10^{-5}$
5	$1.572\cdot10^{-3}$	$1.915\cdot10^{-3}$	$5.560\cdot10^{-4}$	$-4.527\cdot10^{-4}$	-	$4.0\cdot10^{-5}$
6	$1.387\cdot10^{-3}$	$2.122\cdot10^{-3}$	$3.500\cdot10^{-4}$	$-3.914\cdot10^{-4}$	-	$3.0\cdot10^{-5}$
7	$1.232\cdot10^{-3}$	$2.318\cdot10^{-3}$	$1.622\cdot10^{-4}$	$-3.410\cdot10^{-4}$	-	$3.0\cdot10^{-5}$
8	$1.103\cdot10^{-3}$	$2.314\cdot10^{-3}$	$1.762\cdot10^{-4}$	$-3.444\cdot10^{-4}$	-	$3.0\cdot10^{-5}$
9	$1.138\cdot10^{-3}$	$2.004\cdot10^{-3}$	$4.235\cdot10^{-4}$	$-4.110\cdot10^{-4}$	-	$5.0\cdot10^{-5}$
10	$1.082\cdot10^{-3}$	$1.901\cdot10^{-3}$	$4.540\cdot10^{-4}$	$-4.073\cdot10^{-4}$	-	$4.0\cdot10^{-5}$
15	$5.647\cdot10^{-4}$	$1.975\cdot10^{-3}$	$3.405\cdot10^{-4}$	$-3.652\cdot10^{-4}$	-	$4.0\cdot10^{-5}$
25	$3.321\cdot10^{-4}$	$8.944\cdot10^{-4}$	$8.633\cdot10^{-4}$	$-4.357\cdot10^{-4}$	-	$4.0\cdot10^{-5}$
35	$-3.745\cdot10^{-4}$	$1.041\cdot10^{-3}$	$5.285\cdot10^{-4}$	$-3.115\cdot10^{-4}$	-	$3.0\cdot10^{-5}$
Tetrabutylammonium bromide						
3	$2.799\cdot10^{-2}$	$-4.017\cdot10^{-3}$	$1.591\cdot10^{-2}$	$-1.475\cdot10^{-2}$	$2.596\cdot10^{-3}$	$4.0\cdot10^{-5}$
4	$2.765\cdot10^{-2}$	$-4.497\cdot10^{-3}$	$1.870\cdot10^{-2}$	$-1.938\cdot10^{-2}$	$4.755\cdot10^{-3}$	$1.3\cdot10^{-4}$
5	$2.724\cdot10^{-2}$	$-3.617\cdot10^{-3}$	$1.702\cdot10^{-2}$	$-1.827\cdot10^{-2}$	$4.527\cdot10^{-3}$	$1.2\cdot10^{-4}$
6	$2.681\cdot10^{-2}$	$-2.589\cdot10^{-3}$	$1.508\cdot10^{-2}$	$-1.701\cdot10^{-2}$	$4.267\cdot10^{-3}$	$1.2\cdot10^{-4}$
7	$2.636\cdot10^{-2}$	$-1.799\cdot10^{-3}$	$1.359\cdot10^{-2}$	$-1.601\cdot10^{-2}$	$4.062\cdot10^{-3}$	$1.3\cdot10^{-4}$
8	$2.608\cdot10^{-2}$	$-1.501\cdot10^{-3}$	$1.258\cdot10^{-2}$	$-1.513\cdot10^{-2}$	$3.842\cdot10^{-3}$	$1.1\cdot10^{-4}$
9	$2.599\cdot10^{-2}$	$-1.937\cdot10^{-3}$	$1.286\cdot10^{-2}$	$-1.524\cdot10^{-2}$	$3.876\cdot10^{-3}$	$1.2\cdot10^{-4}$
10	$2.567\cdot10^{-2}$	$-1.043\cdot10^{-3}$	$1.103\cdot10^{-2}$	$-1.404\cdot10^{-2}$	$3.628\cdot10^{-3}$	$1.2\cdot10^{-4}$
15	$2.577\cdot10^{-2}$	$-7.780\cdot10^{-3}$	$2.284\cdot10^{-2}$	$-2.298\cdot10^{-2}$	$6.041\cdot10^{-3}$	$5.0\cdot10^{-5}$
20	$2.466\cdot10^{-2}$	$-7.068\cdot10^{-3}$	$2.020\cdot10^{-2}$	$-2.085\cdot10^{-2}$	$5.579\cdot10^{-3}$	$4.0\cdot10^{-5}$
25	$2.317\cdot10^{-2}$	$-4.540\cdot10^{-3}$	$1.477\cdot10^{-2}$	$-1.680\cdot10^{-2}$	$4.635\cdot10^{-3}$	$4.0\cdot10^{-5}$
30	$2.200\cdot10^{-2}$	$-3.461\cdot10^{-3}$	$1.226\cdot10^{-2}$	$-1.492\cdot10^{-2}$	$4.223\cdot10^{-3}$	$4.0\cdot10^{-5}$
35	$2.124\cdot10^{-2}$	$-2.532\cdot10^{-3}$	$8.949\cdot10^{-3}$	$-1.214\cdot10^{-2}$	$3.557\cdot10^{-3}$	$4.0\cdot10^{-5}$

[a] $\rho_{H_2O}/(g\cdot cm^{-3})$ (T/K − 273.15):[19] 0.999902 (1); 0.999943 (2); 0.999967 (3); 0.999975 (4); 0.999967 (5); 0.999943 (6); 0.999905 (7); 0.999850 (8); 0.999784 (9); 0.999703 (10); 0.999103 (15); 0.998207 (20); 0.997048 (25); 0.99565 (30); 0.994035 (35).

Similarly to the R_4AmBr series, the $m(\bar{V}_{2,\min})$ occurs at lower molality with the increasing hydrophobic content of our solutes, i.e., $m(\bar{V}_{2,\min}) = (\approx 4.0, \approx 2.5, \text{and} \approx 0.8)\ \text{mol}\cdot\text{kg}^{-1}$ (at $T = 298.15$ K) for DMU, TMU, and TBuAmBr, respectively (Figures 1a to 3a).

We conclude that below the $m(\bar{V}_{2,\min})$ compositions ("water-rich" region) "bulk" water and completely hydrated solute species are at equilibrium, while above the $m(\bar{V}_{2,\min})$ compositions, completely and partially hydrated solute species are at equilibrium. Accordingly, $m(\bar{V}_{2,\min})$ is the consequence of the structural rearrangement of the solution where all the solvent water becomes under the influence of the solute.

Solute Partial Molar Expansibility, $\bar{V}_{2,E}$. Up to the $m(\bar{V}_{2,\min})$ compositions of the different solutes, the magnitudes of the $\bar{V}_{2,E}$ results seem to be proportional to the sizes of the organic (hydrophobic) parts of the molecules, i.e., $(\bar{V}_{2,E})\text{DMU} \le (\bar{V}_{2,E})\text{TMU} \le (\bar{V}_{2,E})\text{TBuAmBr}$ (Figures 1c to 3c).

Within a solution system, the magnitude of $\bar{V}_{2,E}$ corresponds to the caging effect; i.e., it increases with the difference of $\bar{V}_2^{\infty} - \bar{V}_2$ ($\bar{V}_2^{\infty} = \bar{V}_2$ at infinite dilution) and with decreasing temperature. Consequently, it has its maximal value at the composition of $m(\bar{V}_{2,\min})$, when all the solvent (bulk) water becomes under the influence of the solute. Only the $\bar{V}_{2,E}$(DMU) results at $T \le 288.15$ K and $m \le 2.5\ \text{mol}\cdot\text{kg}^{-1}$ represent exceptions, presumably due to a "substitutional" (hydrophilic) hydration competition (details are discussed later).

In contrast to the $\bar{V}_{2,E}$ behaviors in the "water-rich" region, above the $m(\bar{V}_{2,\min})$ compositions neither the temperature dependence nor the composition dependence of the $\bar{V}_{2,E}$ results of the three solutions show similarity. The reason for their significant difference should be related to their different hydration species and to the different equilibria with increasing compositions. Their rationalization will be attempted through the solvent properties, $\bar{V}_1^E$ and $\bar{V}_{1,E}^E$.

Solvent Excess Partial Molar Volumes, $\bar{V}_1^E$. Additional structural information might be expected first of all from the $\bar{V}_1^E$ (and $\bar{V}_{1,E}^E$) results, which neither in our earlier investigations nor by others were considered. To analyze the temperature and concentration behavior of $\bar{V}_1^E$ (and $\bar{V}_{1,E}^E$) of the title solutions, we prefere to correlate these to the solvent excess

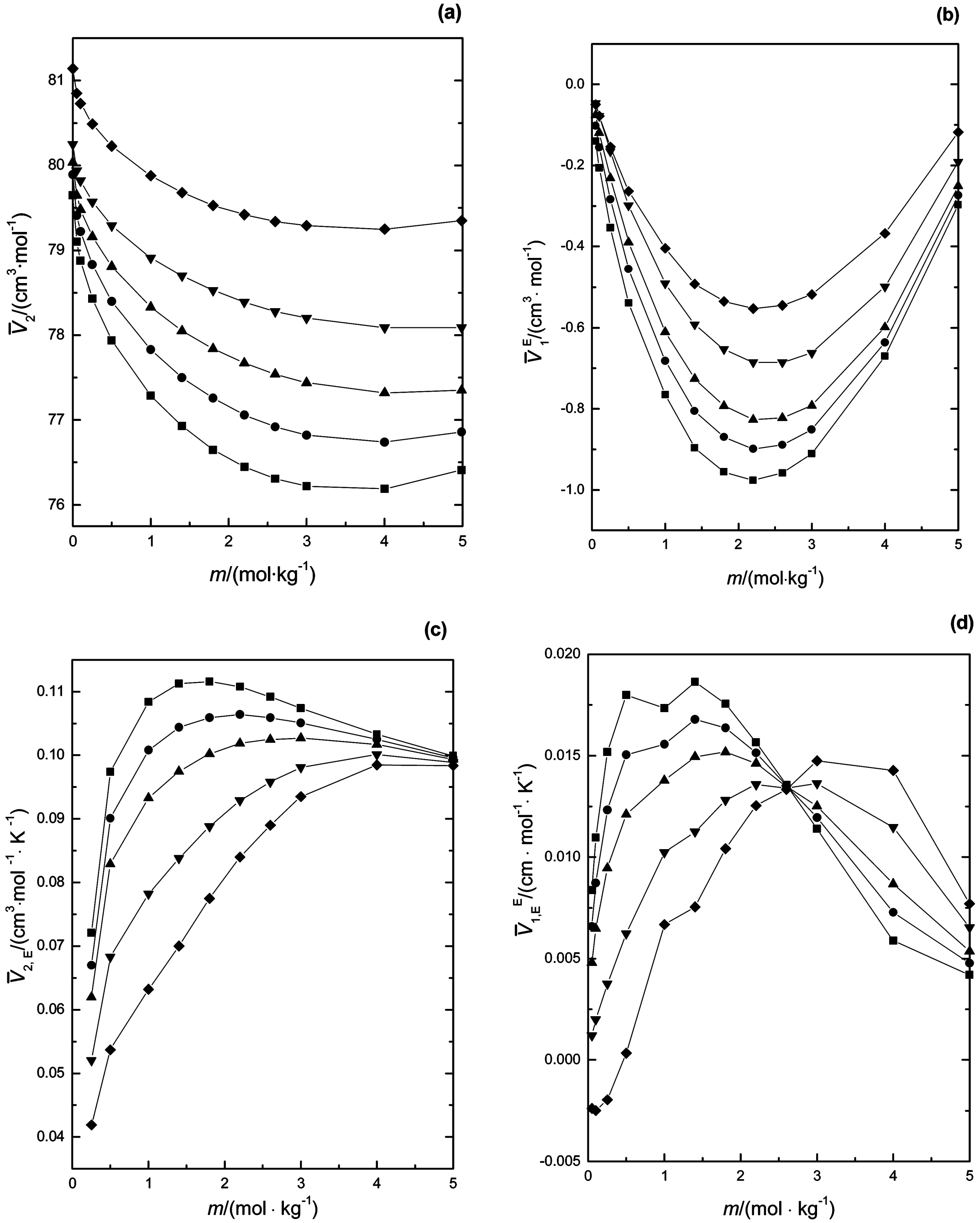

Figure 1. Solute and solvent excess partial molar volumes ($\bar{V}_2$, $\bar{V}_1^E$) and their expansibilities ($\bar{V}_{2,E}$, $\bar{V}_{1,E}^E$) in 1,3-dimethylurea solutions. Results: ■, 278.15 K; ●, 283.15 K; ▲, 288.15 K; ▼, 298.15 K; and ♦, 308.15 K. Lines for $\bar{V}_2$ and $\bar{V}_1^E$ from eqs 4 and 6, respectively. Lines for $\bar{V}_{2,E}$ and $\bar{V}_{1,E}^E$ are arbitrary ones, only to show tendencies.

enthalpy (ΔH_1^E) and entropy ($T\Delta S_1^E$), obtained from H_2O + D_2O vapor pressure isotope effect studies.[5-8]

The most significant difference among the $\bar{V}_1^E$ behaviors of the three solutions seems to be that while $\bar{V}_1^E$(DMU) and $\bar{V}_1^E$(TMU) show an expected minima with increasing composition, $\bar{V}_1^E$(TBuAmBr) shows a maxima (Figures 1b to 3b). Similarly to the $\bar{V}_2$ results, for the space-economy of the interstitial solution process, one should expect an increasingly negative $\bar{V}_1^E$ trend with increasing hydrophobicity of the solutes. Only the $\bar{V}_1^E$(DMU) and $\bar{V}_1^E$(TMU) results correspond to this expectation, showing up to -1.0 (~6 %) and -1.5 (~10 %) cm^3·mol^{-1} deviations from $V_{H_2O}^*$, while the positive $\bar{V}_1^E$(TBuAmBr) result indicates a different solution mechanism.

A reasonable rationalization of the different solution mechanism seems to be that the small CH_3 groups can be incorporated into the tetrahedral associated ("icelike") void solvent structure, without its significant reorganization or rearrangement. The structural enhancement ("structure-making") effect with the DMU and TMU solutions therefore arises mainly from the stabilization (lifetime enhancement) of the "original" tetrahedral structuredness of the solvent water.

In contrast to the interstitial solution mechanism of the smaller alkyl groups, the caging of the large C_4H_9 alkyl chains requires significant structural reorganization of the solvent,

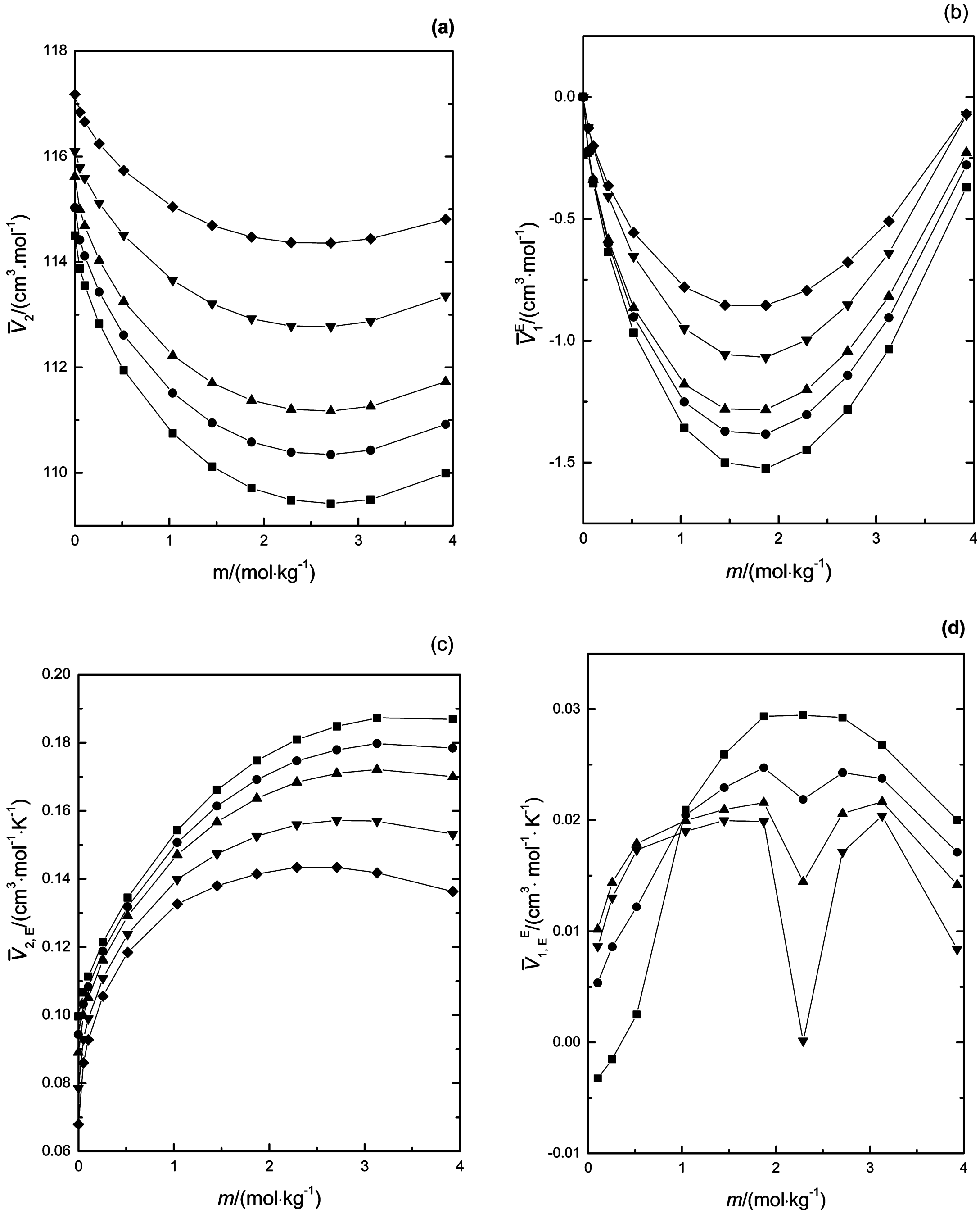

Figure 2. Solute and solvent excess partial molar volumes ($\bar{V}_2$, $\bar{V}_1^E$) and their expansibilities ($\bar{V}_{2,E}$, $\bar{V}_{1,E}^E$) in tetramethylurea solutions. Results: ■, 278.15 K; ●, 283.15 K; ▲, 288.15 K; ▼, 298.15 K; and ◆, 308.15 K. Lines for $\bar{V}_2$ and $\bar{V}_1^E$ from eqs 4 and 6, respectively. Lines for $\bar{V}_{2,E}$ and $\bar{V}_{1,E}^E$ are arbitrary ones, only to show tendencies.

becoming a "clathrate-hydrate-like" arrangement with increasing composition.

The $\bar{V}_1^E$(TBuAmBr) results show maxima at $m = \approx 0.9$ $\mathrm{mol{\cdot}kg^{-1}}$ composition, and the isotherms intersect at $m = \approx 1.7$ $\mathrm{mol{\cdot}kg^{-1}}$, indicating two significant structural rearrangements of the solution at these compositions (Figure 3b). Correlating these extreme to those of the solvent excess enthalpy and entropy,[8] a quite reliable analysis of the solution structure in the three composition region can be established.

a. m (0 to ~ 0.9) mol·kg^{-1}. Up to $m = \approx 0.9$ $\mathrm{mol{\cdot}kg^{-1}}$ ($= m(\bar{V}_{2,\min})$) composition, bulk water and fully hydrated solute molecules are in equilibrium. At $m = \approx 0.9$ $\mathrm{mol{\cdot}kg^{-1}}$ composition the hydration process is completed, corresponding to a hydration number (n) of ≈ 60. Because the hydrated water is tetra- and/or polyhedral hydrogen bonded, it is less dense than the pure water, and since the caging process is stronger at lower temperatures, $\bar{V}_1^E$ increases with decreasing temperature.

b. m (0.9 to ~ 1.7) mol·kg^{-1}. In this composition range the hydration spheres overlap (interact), and a new equilibrium takes place between fully and partially hydrated solute species. At $m = \approx 1.7$ $\mathrm{mol{\cdot}kg^{-1}}$, the hydration spheres will be "shared" between the neighboring solute molecules, and the solution structure, in time average, should resemble that of the "host−guest" arrangement of the solid TBuAmBr clathrate hydrate.[21] The stoichiometry of its polyhedral clathrate hydrate corresponds to 1:33 solute/solvent ratio, i.e.,

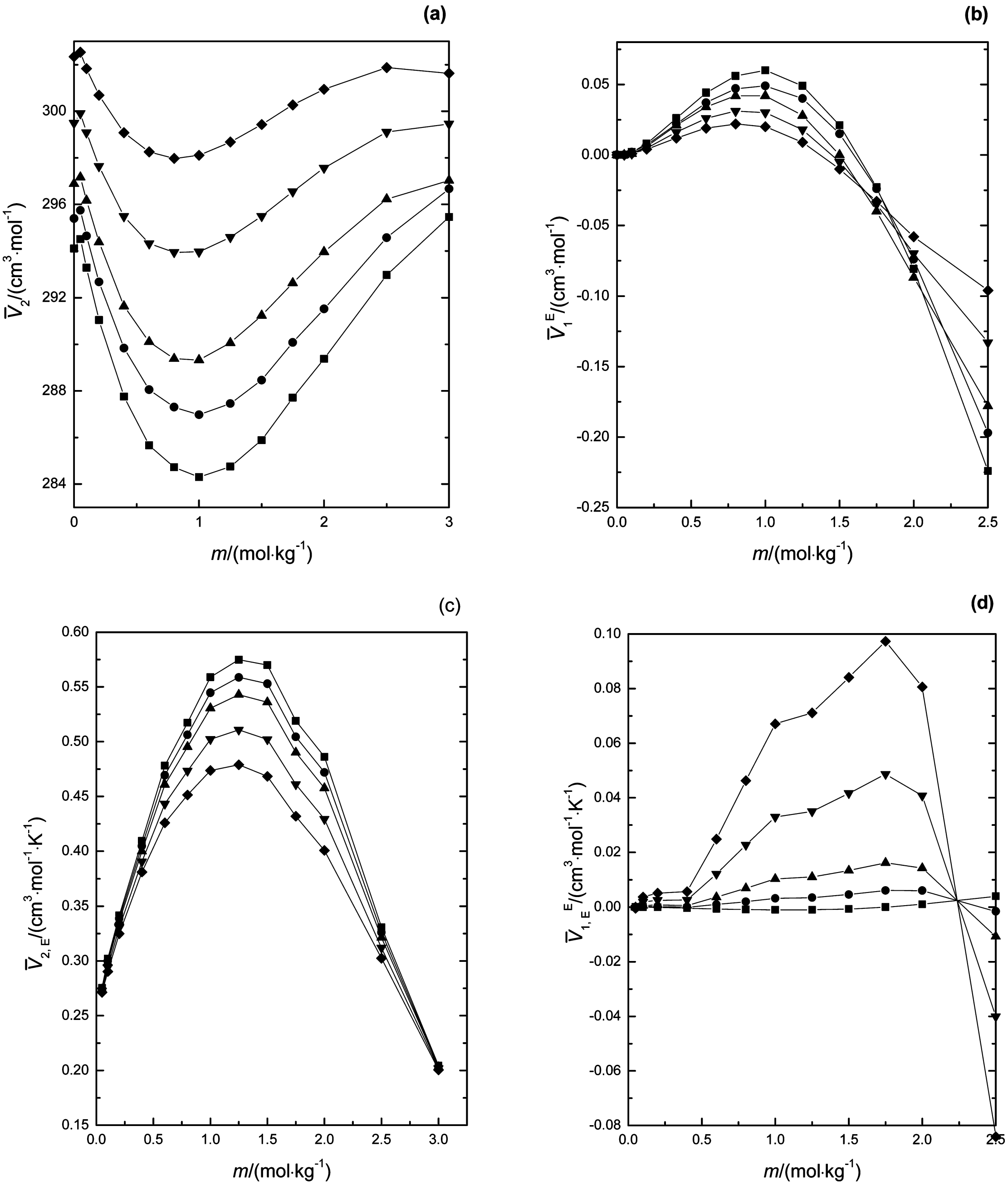

Figure 3. Solute and solvent excess partial molar volumes ($\bar{V}_2$, $\bar{V}_1^E$) and their expansibilities ($\bar{V}_{2,E}$, $\bar{V}_{1,E}^E$) in tetrabutylammonium bromide solutions. Results: ■, 278.15 K; ●, 283.15 K; ▲, 288.15 K; ▼, 298.15 K; and ♦, 308.15 K. Lines for $\bar{V}_2$ and $\bar{V}_1^E$ from eqs 5 and 7, respectively. Lines for $\bar{V}_{2,E}$ and $\bar{V}_{1,E}^E$ are arbitrary ones, only to show tendencies.

to 1.7 mol·kg^{-1}. The solvent excess partial molar entropy and enthalpy here is the most negative.[8]

The intersection point of the $\bar{V}_1^E$ isotherms should correspond to the uniform solute−solvent structural arrangement, without any equilibrium among different species.

c. $m > 1.7$ mol·kg^{-1}. Above $m = \approx 1.7$ mol·kg^{-1}, there is not sufficient water molecules for the complete (intact) "host" clathrate network, and the structural integrity of the network is disrupted. Here the concentration of the nonbonded solvent species is rapidly increasing, i.e., $\bar{V}_1^E$ is decreasing. (The high energy of the H-bonds arises from their cooperativity.[22])

The concentration behavior of $\bar{V}_1^E$(TBuAmBr) supports our earlier conclusion, based on the $H_2O + D_2O$ vapor pressure study,[8] that the "clathrate-hydrate-like" solute−solvent arrangement is the consequence of the hydrophobic interaction; consequently, at high dilution (hydrophobic hydration), some different structure dominates. It is also worth pointing out that with the TBuAmBr solution the adiabatic compressibility (β) isotherms intersect at $m = \approx 0.7$ mol·kg^{-1}, i.e., corresponding to the $m(\bar{V}_{2,\mathrm{min}})$ composition. Following Endo's hypothesis,[23] the β-intersections of polar organic compounds have often been related to clathrate-hydrate-like solute−solvent arrangements;[24,25] however, according to our interpretation, it seems to be only a general consequence of the interstitial solution (caging) process.

Solvent Excess Partial Molar Expansibility, $\bar{V}_{1,E}^E$. It is expected that $\bar{V}_{1,E}^E$ contains more structural information than $\bar{V}_1^E$, being a higher-order derivative of the free energy.[16] On the other hand, $\bar{V}_1^E$ should reflect the spatial structural changes of the solvent, while through the relation $(\partial C_p/\partial P)_{T,m} = -T(\partial^2\bar{V}_1/\partial T^2)_{P,m}$ the sign of $(\partial\bar{V}_{1,E}^E/\partial T)_{P,m}$ [$= (\partial^2\bar{V}_1/\partial T^2)_{P,m}$] should characterize the "structure-making/breaking" influence of the solute, and its size should reflect the stability of the structure.[16]

The basic difference among the three $\bar{V}^{E}_{1,E}$ results (Figures 1d to 3d) seems to be that those of the DMU and TMU undergo radical changes in the water-rich composition region (i.e., below $m(\bar{V}_{2,\min})$, reflected by the intersections), while $\bar{V}^{E}_{1,E}$(TBuAmBr) monotonously increases up to $m = \approx 1.7$ mol·kg^{-1} composition. This behavior of $\bar{V}^{E}_{1,E}$(TBuAmBr) is in accordance with our earlier conclusion (from excess solvent enthalpy[8]) that shearing the hydration spheres between the neighboring solutes is energetically favorable; i.e., it further increases the stability of the hydrogen bonded "host" network. (The excess solvent enthalpy at ≈ 1.7 mol·kg^{-1} is the most negative,[8] while $\partial\bar{V}^{E}_{1,E}/\partial T$ is large and positive.)

The polar−apolar character of the DMU molecule is well balanced, and therefore its structural effect on water highly depends on concentration and temperature. Due to its symmetry, 1,3-DMU has two H-bond donor and two acceptor sites, therefore it is capable of "substitutional" participation in the hydrogen-bonded water clusters. According to its $\partial\bar{V}^{E}_{1,E}/\partial T$ behavior (Figure 1d), below ≈ 2.5 mol·kg^{-1} composition it is hydrophilic, while above ≈ 2.5 mol·kg^{-1} its hydrophobic character dominates; however, due to their competitions, both effects are very weak (small $\partial\bar{V}^{E}_{1,E}/\partial T$ values). With the H_2O + D_2O solvent excess enthalpy and entropy,[6] an extreme has also been observed at the composition of ≈ 2 mol·kg^{-1}.

In contrast to the 1,3-DMU molecule, TMU is not capable of "substitutional" solution, having only H-bond acceptor capability on its carbonyl group. Although the interaction of the carbonyl group with the solvent proves to be significant,[26] at low compositions ($m \leq \sim 1$ mol·kg^{-1}) the hydrophobic character of the TMU dominates, and $\partial\bar{V}^{E}_{1,E}/\partial T$ is positive (Figure 2d). At ≈ 1 mol·kg^{-1}, the intersection of the $\bar{V}^{E}_{1,E}$ isotherms indicates a structural rearrangement, which has also been observed by Bezzabotnov et al.[27] in their small-angle neutron scattering study on the TMU solution. From the sizes of the detected particles, they concluded that contact TMU pairs appear above ≈ 0.7 mol·kg^{-1} composition, where two TMU molecules are coupled through water molecules. With TMU solution $m(\bar{V}_{2,\min}) = \approx 1.7$ mol·kg^{-1}, above that composition one expects stronger interaction (overlapping) of the hydrated species. Nevertheless, the interaction here results in a unique behavior of the solution, which is reflected besides the anomalous $\bar{V}^{E}_{1,E}$ isotherms; by a maximum of the heat of mixing at ~ 4 molality,[28] by the unique behavior of positron annihilation[10] and also by an azeotropic vapor pressure maxima over the (~2 to 4) molality range.[7] A slight vapor pressure maxima appears already at ~ 320 K and increases up to 50 % above the Raoult's law value at 283 K. From the strong nonideality of the solution, one can conclude that below 283 K the hydration interaction results in microheterogenity, and the solution structure is very close to phase separation with an "upper critical solution temperature", UCST. According to Koga's analysis, with an equilibrium resulting in UCST, both the enthalpy and entropy contribution of the free energy ($G = H - TS$) should be negative.[16]

Conclusions

The solute and solvent partial molar volumes and their thermal expansibilities of the title solutions reflect that their structure is determined by a variety of structural equilibriums, depending mainly on the polar/apolar balance of the "mixed" solute molecule, on their H-bond donor/acceptor ability, and on the solute/solvent ratio.

With the 1,3-dimethylurea, having two H-bond donor and two acceptor sites, below ~2 mol·kg^{-1} composition, hydrophilic hydration dominates ("substitutional" solution), while above that composition, hydrophobic hydration (caging process) dominates. After all the bulk water is "used up" in the hydration process ($m > 4$ mol·kg^{-1}), the caging effect becomes very week.

The tetramethylurea molecule has only H-bond acceptor sites, and the strong interaction of its carbonyl group with water molecules at ~1 mol·kg^{-1} composition results in water-separated solute pairs. With the TMU solution, the bulk water is "used up" at ~ 1.7 *m* composition, suggesting a hydrophobic cage with 1:33 solute/solvent ratio. With further increase of the composition, the interaction (overlapping) of the hydrophobic cages results in microheterogeneity of the solution over the (2 to 4) *m* composition range, indicating a phase separation with an "upper critical solution temperature".

The tetrabutylammonium bromide solution shows dominant hydrophobic hydration and interaction, resulting in hydrophobic cages at ~0.9 mol·kg^{-1} composition with ~1:60 solute/solvent ratio. Their interaction (overlapping) results in a clathrate-hydrate-like "host−guest" arrangement at 1.7 molality, corresponding to 1:32 solute/solvent ratio.

Appendix 1. Experimental Density Results of the 1,3-Dimethylurea, Tetramethylurea, And Tetrabutylammonium Bromide Solutions

Experimental Property Data:

Table A1.

System type: Binary

Chemical Systems: Dimethylurea + Water

Property: density

Experimental Method: vibrating tube densimeter

Combined Expanded Uncertainty for the Property: $2\delta(\rho) = 0.00004$

State Variables and Constraints: temperature *T*, mole fraction of dimethylurea x_2, laboratory pressure

Standard Uncertainty for Variables and Constraints: $\delta(T) = 0.01$ K; $\delta(x_1) = 0.0001$

Table A2.

System type: Binary

Chemical Systems: Tetramethylurea + Water

Property: density

Experimental Method: vibrating tube densimeter

Combined Expanded Uncertainty for the Property: $2\delta(\rho) = 0.00004$

State Variables and Constraints: temperature *T*, mole fraction of Tetramethylurea x_2, laboratory pressure

Standard Uncertainty for Variables and Constraints: $\delta(T) = 0.01$ K; $\delta(x_1) = 0.0001$

Table A3.

System type: Binary

Chemical Systems: Tetrabutylammonium bromide + Water

Property: density

Experimental Method: vibrating tube densimeter

Combined Expanded Uncertainty for the Property: $2\delta(\rho) = 0.00004$

State Variables and Constraints: temperature *T*, mole fraction of Dimethylurea x_2, laboratory pressure

Standard Uncertainty for Variables and Constraints: $\delta(T) = 0.01$ K; $\delta(x_1) = 0.0001$

Table A1. Mole Fraction (x_2) and Densities (ρ) of 1,3-Dimethylurea in Water at the Temperatures (274.15 to 308.15) K

	$\rho/(\mathrm{g \cdot cm^{-3}})$												
x_2	T/K = 274.15	T/K = 275.15	T/K = 276.15	T/K = 277.15	T/K = 278.15	T/K = 279.15	T/K = 280.15	T/K = 281.15	T/K = 282.15	T/K = 283.15	T/K = 288.15	T/K = 298.15	T/K = 308.15
0	0.999902	0.999943	0.999967	0.999975	0.999967	0.999943	0.999905	0.999850	0.999784	0.999703	0.999103	0.997048	0.994035
0.000898	1.000361	1.000390	1.000401	1.000412	1.000410	1.000385	1.000345	1.000287	1.000217	1.000133	0.999526	0.997452	0.994420
0.001800	1.000829	1.000850	1.000858	1.000871	1.000856	1.000832	1.000780	1.000726	1.000650	1.000565	0.999930	0.997853	0.994802
0.004480	1.002259	1.002252	1.002259	1.002267	1.002232	1.002193	1.002144	1.002059	1.001978	1.001879	1.001225	0.999058	0.995947
0.008930	1.004684	1.004651	1.004636	1.004634	1.004558	1.004501	1.004440	1.004335	1.004222	1.004115	1.003353	1.001076	0.997861
0.017710	1.009582	1.009479	1.009399	1.009350	1.009258	1.009161	1.009050	1.008915	1.008750	1.008599	1.007667	1.005095	1.001700
0.024610	1.013505	1.013350	1.013244	1.013136	1.013052	1.012890	1.012740	1.012562	1.012360	1.012172	1.011044	1.008236	1.004628
0.031410	1.017268	1.017118	1.016940	1.016803	1.016699	1.016437	1.016243	1.015996	1.015766	1.015582	1.014346	1.011281	1.007429
0.038150	1.021018	1.020731	1.020540	1.020374	1.020224	1.019905	1.019661	1.019469	1.019192	1.019006	1.017551	1.014238	1.010164
0.044710	1.024432	1.024135	1.023921	1.023741	1.023579	1.023293	1.023017	1.022790	1.022471	1.022226	1.020594	1.017042	1.012756
0.051260	1.027795	1.027447	1.027200	1.027029	1.026865	1.026570	1.026264	1.025974	1.025614	1.025272	1.023541	1.019750	1.015270
0.067220	1.035639	1.035227	1.034866	1.034556	1.034296	1.033898	1.033520	1.033210	1.032762	1.032445	1.030341	1.025982	1.021161
0.082460	1.042408	1.042024	1.041673	1.041259	1.040877	1.040446	1.040005	1.039610	1.039053	1.038581	1.036440	1.031415	1.026062
0.097550	--	--	--	--	1.046814	1.046324	1.045782	1.045390	1.044752	1.044351	1.041596	1.036307	1.030329

Table A2. Mole Fraction (x_2) and Densities (ρ) of Tetramethylurea in Water at the Temperatures (274.15 to 308.15) K

	$\rho/(\mathrm{g \cdot cm^{-3}})$												
x_2	T/K = 274.15	T/K = 275.15	T/K = 276.15	T/K = 277.15	T/K = 278.15	T/K = 279.15	T/K = 280.15	T/K = 281.15	T/K = 282.15	T/K = 283.15	T/K = 288.15	T/K = 298.15	T/K = 308.15
0	0.999902	0.999943	0.999967	0.999975	0.999967	0.999943	0.999905	0.999850	0.999784	0.999703	0.999103	0.997048	0.994035
0.000932	1.000033	1.000060	1.000086	1.000082	1.000074	1.000041	0.999998	0.999936	0.999869	0.999784	0.999158	0.997079	0.994030
0.001850	1.000186	1.000201	1.000220	1.000208	1.000196	1.000160	1.000108	1.000040	0.999970	0.999880	0.999227	0.997119	0.994035
0.004620	1.000697	1.000700	1.000688	1.000652	1.000631	1.000581	1.000519	1.000431	1.000340	1.000236	0.999510	0.997289	0.994088
0.009240	1.001741	1.001699	1.001663	1.001601	1.001546	1.001453	1.001372	1.001250	1.001141	1.001003	1.000128	0.997677	0.994319
0.018310	1.004219	1.004105	1.004012	1.003873	1.003757	1.003592	1.003454	1.003273	1.003135	1.002906	1.001795	0.998817	0.994962
0.025500	1.006386	1.006193	1.006052	1.005903	1.005685	1.005467	1.005274	1.005047	1.004857	1.004571	1.003225	0.999880	0.995682
0.032600	1.008560	1.008322	1.008093	1.007898	1.007616	1.007345	1.007099	1.006827	1.006575	1.006286	1.004670	1.000924	0.996403
0.039620	1.010660	1.010356	1.010080	1.009835	1.009490	1.009167	1.008873	1.008551	1.008253	1.007861	1.006092	1.001944	0.997067
0.046540	1.012669	1.012392	1.011974	1.011679	1.011268	1.010919	1.010576	1.010205	1.009835	1.009422	1.007435	1.002906	0.997696
0.053410	1.014595	1.014188	1.013792	1.013462	1.012999	1.012620	1.012207	1.011803	1.011383	1.010915	1.008699	1.003848	0.998338
0.066040	1.017879	1.017350	1.016880	1.016415	1.015918	1.015428	1.014956	1.014475	1.013961	1.013424	1.010914	1.005436	0.999385

Table A3. Mole Fraction (x_2) and Densities (ρ) of Tetrabutylammonium Bromide in Water at the Temperatures (276.15 to 308.15) K

	$\rho/(g \cdot cm^{-3})$												
x_2	$T/K = 276.15$	$T/K = 277.15$	$T/K = 278.15$	$T/K = 279.15$	$T/K = 280.15$	$T/K = 281.15$	$T/K = 282.15$	$T/K = 283.15$	$T/K = 288.15$	$T/K = 293.15$	$T/K = 298.15$	$T/K = 303.15$	$T/K = 308.15$
0	0.999967	0.999975	0.999967	0.999943	0.999905	0.999850	0.999784	0.999703	0.999100	0.998207	0.997045	0.995650	0.994035
0.000900	1.001350	1.001350	1.001320	1.001280	1.001230	1.001165	1.001089	1.000998	1.000350	0.999405	0.998180	0.996740	0.995085
0.001800	1.002750	1.002730	1.002690	1.002650	1.002580	1.002490	1.002400	1.002300	1.001600	1.000600	0.999320	0.997820	0.996140
0.003590	1.005600	1.005520	1.005470	1.005391	1.005286	1.005176	1.005065	1.004948	1.004100	1.002980	1.001590	0.999990	0.998220
0.007150	1.011369	1.011226	1.011089	1.010956	1.010784	1.010608	1.010444	1.010263	1.009150	1.007760	1.006130	1.004300	1.002320
0.010690	1.017091	1.016875	1.016664	1.016454	1.016215	1.015979	1.015724	1.015500	1.014040	1.012370	1.010490	1.008430	1.006210
0.014210	1.022490	1.022161	1.021906	1.021630	1.021315	1.020992	1.020685	1.020379	1.018720	1.016750	1.014530	1.012260	1.009840
0.017700	1.027720	1.027303	1.026963	1.026611	1.026219	1.025833	1.025442	1.025064	1.023060	1.020770	1.018300	1.015770	1.013130
0.022020	1.033533	1.033007	1.032571	1.032113	1.031619	1.031176	1.030695	1.030211	1.027790	1.025180	1.022430	1.019650	1.016740
0.026310	1.038460	1.037941	1.037413	1.036887	1.036316	1.035797	1.035235	1.034685	1.031870	1.028990	1.026000	1.022970	1.019880
0.030560	1.042530	1.040983	1.040407	1.039823	1.039107	1.038632	1.038045	1.037437	1.035330	1.032220	1.029060	1.025850	1.022540
0.034780	-	1.045387	1.044756	1.044111	1.043438	1.042818	1.042160	1.041487	1.038350	1.035020	1.031680	1.028340	1.024970
0.043100	-	1.050630	1.049926	1.049244	1.048505	1.048230	1.047118	1.046413	1.042930	1.039410	1.035890	1.032360	1.028780
0.051280	-	1.054863	1.054129	1.053396	1.052647	1.051944	1.051206	1.050457	1.046340	1.042740	1.039060	1.035440	1.031820
0.074990	-	1.060808	1.060071	1.059332	1.058551	1.057830	1.057048	1.056301	-	-	-	-	-

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