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Apparent Molal Volumes of Urea Derivatives in Water-Methanol Mixtures

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Apparent molal volumes (ϕ_v) at 25 °C have been obtained for the following urea derivatives in water–methanol mixtures from measurements of the density using an Anton Paar digital densimeter: urea (U), methylurea (MU), ethylurea (EU), 1,1-dimethylurea (1,1-DMU), 1,3-dimethylurea (1,3-DMU), 1,1-diethylurea (1,1-DEU), and 1,3-diethylurea (1,3-DEU). The limiting values $\phi_v{}^\circ$ were calculated by linear extrapolation using the least-squares method. A plot of $\phi_v{}^\circ$ vs. X_2, the mole fraction of methanol, showed a minimum for each alkylurea studied at low methanol concentrations ($X_2 \simeq 0.1$), but none for unsubstituted urea: the more alkyl-substituted the urea was, the sharper the minimum. Inspection of the data shows that the assumption of independent solvation on both sides of the urea molecules also holds to a good approximation to the apparent molal volumes both in the pure solvents and in the mixtures.

It has long been known that alcohol–water mixtures often show abnormalities in their properties, such as the viscosity-composition and the ultrasonic velocity-composition maximum. Although they are not fully understood, such peculiarities are considered to be structural in origin. Thus, Franks and Ives postulated an enhancement of the structure of water by interactions between alkyl groups and water in the water-rich region; they therefore surveyed the properties of these systems with special reference to their structural implications.[1] Aqueous urea also has long been the subject of study, in particular the effect of urea on the water structure, and many biophysicochemical studies have been carried out on aqueous urea. The theoretical treatment of the mixture has been performed by Frank and Franks, who pictured dissolved urea as acting like a statistical water-structure breaker.[2] It is generally accepted that urea does not appreciably interact with either hydrophobic or hydrophilic molecules or groups, and so several thermodynamic and transport properties of aqueous urea solutions with added electrolytes or nonelectrolytes have been interpreted in terms of the nonspecific interaction of urea with the solute, as has been noted by Mathieson and Conway.[3] We feel that, in order to understand the effect of urea on the structure of water, it would now be useful to carry out the systematic study of urea solutions over the whole mole-fraction range of alcohol and water. Since the infinite-dilution apparent molal volumes are independent of solute–solute interactions, being determined only by the respective intrinsic value and solute–solvent interactions, they can be used to examine the solute–solvent interactions.

In the present work, densities were measured at 25 °C for the urea(or alkylurea)–methanol–water ternary system at various concentrations. The apparent molal volumes and their limiting values were obtained from these data.

Experimental

The density of the methanol, which was a guaranteed reagent from Wako Chemical Industries, Ltd., was 0.78663 g cm^{-3} at 25 °C; the reported densities are 0.78665[4] and 0.78660.[5] As will be seen later, the infinite apparent molal volume of urea in this solvent was 36.98 cm^3 mol^{-1}, which was in excellent agreement with the value (36.97) reported by Hamilton and Stokes.[5] The methanol, therefore, was used without further purification as a solvent or cosolvent. The urea (Wako Chemical Industries, Ltd.) and 1,1-dimethylurea (Sigma Chemical Company) were used as received. The methylurea (Wako Chemical), and the 1,1-diethylurea and 1,3-diethylurea, which have both been obtained from the Aldrich Chemical Company, Inc., were recrystallized from ethanol. The ethylurea and 1,3-dimethylurea, which were both from the Tokyo Kasei Kogyo Co., Ltd., were recrystallized from an ethanol–ethyl ether mixture.

Ternary systems are very complicated, and special interest is usually taken in their properties in the water-rich region. Thus, the densities of the urea solutions were measured at 25 °C in 0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, and 1.0 by the use of mole-fraction methanol X_2 in water. All the solutions were prepared by weight in the concentration range of 0.2—0.9 mol kg^{-1} (the number of moles of urea per kg of the mixed solvent whenever the mixed solvent was used). The mixed solvent was prepared for each series of measurements, and its density was determined respectively. The densities were measured to $\pm 2\times10^{-6}$ g cm^{-3} with an Anton Paar DMA 02D Densimeter as before.[6] The temperature control of the thermostated bath system regulating the densimeter was better than ±0.005 °C.

Results

The apparent molal volumes were obtained using Eq. 1:

$$\phi_v = \frac{M}{d} + \frac{1000(d_0 - d)}{m d_0 d} \tag{1}$$

where M is the molecular weight of the urea; m, its molal concentration, and d_0 and d, the densities of the solvent and the solution respectively. The apparent molal volumes of a nonelectrolyte such as urea are usually expressed as in Eq. 2 below ca. 1 mol kg^{-1}:

$$\phi_v = \phi_v^\circ + S_v m \qquad (2)$$

where ϕ_v° is the infinite-dilution apparent molal volume and where S_v is the experimental slope. At an infinite dilution, ϕ_v° is equal to $\overline{V}^\circ$ (the infinite-dilution partial molal volume). The ϕ_v° values were calculated by a linear extrapolation using the least-squares fit to Eq. 2. The derived values for ϕ_v° are summarized in Table 1. The standard deviations are less than 0.03 cm^3 mol^{-1}. Those for amino-acid-alkali-chloride–water ternary systems previously reported by the present authors were mostly less than 0.02 cm^3 mol^{-1};[6] the volatility of methanol probably makes the standard deviations a little larger in the present work. The ϕ_v° values in water for U, 1,1-DMU, and 1,3-DMU are reported by Philip et al. as 44.24, 78.88, and 80.04 cm^3 mol^{-1} respectively.[7] Our value for U is in excellent agreement, and for 1,1-DMU and 1,3-DMU our values are in good agreement, with the literature values. For the other alkylureas no accurate ϕ_v° values have yet been reported, although Herskovits and Kelly evaluated the partial specific volumes for the ureas using the density data;[8] their densities, however, were measured with 10-cm^3 pycnometers in order to obtain viscosity coefficients for the ureas and so can not be compared with our data. As has been mentioned earlier, the ϕ_v° value of urea in methanol was reported to be 36.97 cm^3 mol^{-1} by Hamilton and Stokes,[5] a value in excellent agreement with ours. As for the others, however, no comparable data have been reported.

Discussion

Apparent Molal Volume of Urea. First of all let us consider the results for the unsubstituted urea. The thermodynamic properties of aqueous urea solutions, including the volume, were intensively discussed by Stokes,[9] who reported apparent molal volumes of urea at 0, 40, and 50 °C to supplement the existing volume data. He showed that ϕ_v° is strongly temperature-dependent; 41.75 cm^3 mol^{-1} at 0 °C, 44.20 at 25, 44.55 at 30, 45.10 at 40, and 45.60 at 50. The estimated thermal expansion coefficient α of the limiting apparent molal volumes, defined by:

$$\alpha(\phi_v^\circ) = \mathrm{d}\ln\phi_v^\circ/\mathrm{d}T$$

is abnormally large at low temperatures, but decreases as the temperature is raised. The ϕ_v° values measured by Hamilton and Stokes[5] in various organic solvents, such as methanol, ethanol, and formamide, show a large variation in different solvents, though the temperature dependence of the limiting apparent molal volumes in nonaqueous solvents is slight, in marked contrast to the situation in water. Of the several properties of the solvents they examined, the compressibility of the solvent has the only clear correlation with the ϕ_v° values of urea; the ϕ_v° value increases as the compressibility of the solvent decreases. Regarding the compressibility as a measure of the void space in the liquid, they argued that the solute molecule does not have to create a hole for itself of the full dimensions demanded by its intrinsic size. Thus, methanol, with the largest compressibility of the solvents studied by them at 25 °C, gave the smallest ϕ_v° value of urea, 36.97 cm^3 mol^{-1}. As has been mentioned earlier, water–alcohol systems are well-known to enhance the structure of water considerably when alcohol is added to water in low mole fractions; as a result, the water–alcohol systems show often abnormalities in their properties. The isentropic compressibilities of water–methanol mixtures studied separately by Kiyohara and Benson[10] and by Lara and Desnoyers[11] show a minimum around X_2=0.13—0.14 at 25 °C. As is shown in Fig. 1, in which the volumes of the transfer of urea from water to the mixtures are plotted against X_2, U shows a volume maximum in the water-rich region. Though the maximum of the volume does not agree with that of its adiabatic compressibility, there is an indication that urea has a larger volume in the less compressibility solvents, as has been noted by Hamilton and Stokes.

Table 1. Limiting Apparent Molal Volumes ϕ_v° in Water–Methanol Mixtures

X_2	ϕ_v°/cm^3 mol^{-1}						
	U	MU	EU	1,1-DMU	1,3-DMU	1,1-DEU	1,3-DEU
0.0	44.24	62.40	79.26	78.53	80.32	111.63	113.74
0.1	44.34	61.64	77.86	77.11	78.53	109.33	110.86
0.2	44.89	62.18	78.84	77.77	79.18	110.48	112.34
0.3	45.16	62.45	79.64	78.06	79.73	111.80	114.20
0.4	44.65	62.51	80.26	78.10	80.02	112.42	115.47
0.6	43.36	61.75	79.88	77.48	80.03	112.17	116.64
0.8	40.98	60.44	78.67	76.10	79.64	111.20	116.76
1.0	36.98	57.38	76.15	73.26	77.57	109.55	115.47

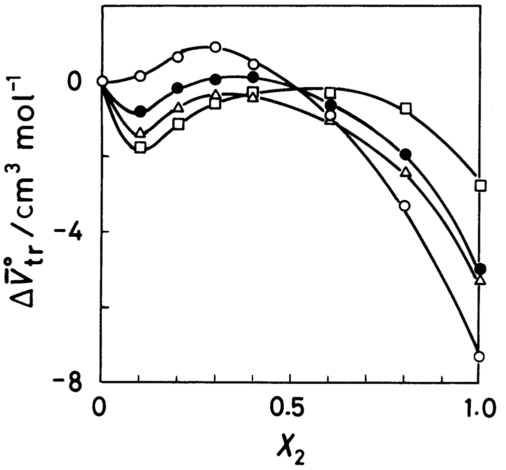

Fig. 1. Volumes of transfer for methylureas from H_2O to mixtures of $MeOH+H_2O$. ○: Urea, ●: methylurea, △: 1,1-dimethylurea, □: 1,3-dimethylurea.

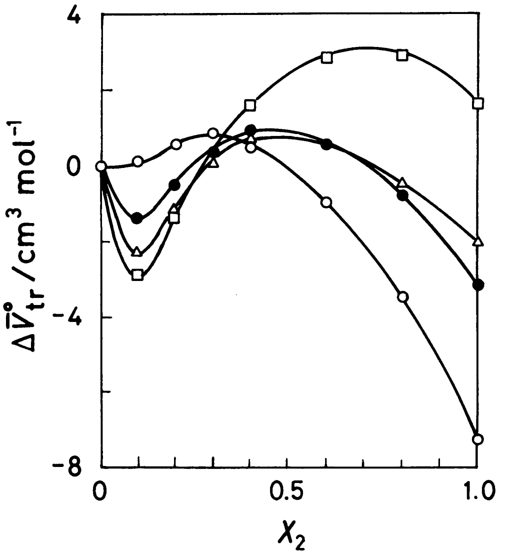

Fig. 2. Volumes of transfer for ethylureas from H_2O to mixtures of $MeOH+H_2O$. ○: Urea, ●: ethylurea, △: 1,1-diethylurea, □: 1,3-diethylurea.

ϕ_v° in Water. The ϕ_v° values of the six alkylsubstituted ureas studied here are listed in Table 1. The contribution of a methyl or ethyl group to the apparent molal volume can be thought of as the intrinsic volume of the group plus volume terms originating from interactions between the solute and solvent molecules. Thus, when a hydrogen atom bonded to a nitrogen of a urea molecule is replaced by a methyl group, which is hydrophobic in nature, the ϕ_v° values of the urea molecules are influenced by the following: (1) a contribution from the methyl group itself (intrinsic and hydrophobic), (2) a hindrance of the hydrogen-bonding ability of the substituted amino group, and (3) finally a decrease in the hydrogen-bonding ability of the carbonyl group.[7] By comparing the ϕ_v° values of two pairs of isomers, 1,1-DMU and 1,3-DMU, and 1,1-DEU and 1,3-DEU, the 1,3-isomers are seen to have definitely larger volumes than the corresponding 1,1-isomer, as Table 1 shows. In accounting for this difference the second effect mentioned above may be most important. The 1,1-isomer has one unsubstituted amino group, and so it has more hydrogen-bonding ability than the corresponding 1,3-isomer; that is, the former exhibits a greater volume decrease due to hydrogen-bonding. Next, half of the sum of the ϕ_v° values of U and 1,3-isomer is roughly equal to the value of the corresponding mono-substituted urea: $(44.24+80.32)/2=62.28$ and 62.40 for methylderivatives, $(44.24+113.74)/2=78.99$ and 79.26 for ethyl derivatives. This fact supports the assumption of independent solvation on both sides of the urea molecules, as reported by Rouw and Somsen from their measurements of the enthalpies of solutions.[12] From the additivity of the group contributions to the partial molar volumes for various kinds of organic analogues, such as carboxylic acids, alkylamines, amino acids, ketones, and alcohols, the group volume increment of CH_2 was calculated as 16.0 ± 0.2 cm^3 mol^{-1} by Shahidi[13] except for cyclic compounds, for which the group volume increment is ca. 2 cm^3 mol^{-1} smaller than for acyclic compounds.[14] Thus, for open-chain compounds, a volume increment of 16 cm^3 mol^{-1} is usually brought about by the replacement of a hydrogen atom by a methyl group. As may be seen from Table 1, the volume difference between urea and methylurea in water is 18.16 cm^3 mol^{-1}, much larger than 16. In the case of alkylamines, this large volume increment may be due to the hindrance of hydrogen-bonding formation of the substituted amino group, as well as to the contribution from the methyl group itself, mentioned above: this brings about a smaller volume decrement. In this connection, it is very interesting to note the volume-change relationships of alkylamine compounds. The partial molal volumes at an infinite dilution reported by Verrall and Conway for the compounds are as follows:[15] CH_3NH_2 40.0, $(CH_3)_2NH$ 58.6, $(CH_3)_3N$ 77.9, and $(C_2H_5)_3N$ 119.7 cm^3 mol^{-1}. A value of 18.6 cm^3 mol^{-1}, much larger than 16, is observed in passing from CH_3NH_2 to $(CH_3)_2NH$, and one of 19.3, in passing from $(CH_3)_2NH$ to $(CH_3)_3N$.

ϕ_v° in Methanol. As may be seen from Table 1, the ϕ_v° values in methanol are smaller than the corresponding values in water except for 1,3-DEU. By comparing the transfer volumes from water to methanol, urea is found to have a more negative value than the other alkylureas studied. The transfer volumes at an infinite dilution from water to methanol $\Delta\bar{V}^\circ_{tr}$ increase in the following order:

U<1,1-DMU<MU<EU<1,3-DMU<1,1-DEU<1,3-DEU.

Thus, alkyl groups, methyl and ethyl, make a larger contribution to the volume in methanol than in water. In other words, a larger volume increment is observed in methanol than in water when urea is substituted by the methyl group, i.e., 20.40 $cm^3 mol^{-1}$ from U to MU in methanol compared with 18.16 in water.

The assumption of the independent solvation of both sides of the urea molecules mentioned above can be applied also to the volume in methanol and in each water–methanol mixture studied as well.

Recently, Edward et al. have expressed volumes in CCl_4 and other organic solvents by using this equation:[16)]

$$\bar{V}^\circ = V_c + \sum n_i I_i + \delta Z_g \qquad (3)$$

where V_c is independent of the solute and is defined as the co-volume, and where n_i and I_i are the number of and characteristic volume of group i. Z_g is the average number of gauche conformations of a molecule at a given temperature, and δ is the volume decrement associated with a gauche interaction. More recently, it has been demonstrated by French and Criss that the group-additive relationships can be expressed for volumes of organic nonelectrolyte solutes, such as alkanes, amines, ethers, and alkanols, in methanol also at 25 °C.[4,17)] They obtained a V_c value of 15.8 $cm^3 mol^{-1}$ and the I_i values by analyzing the volume data in methanol. Some of the I_i values in $cm^3 mol^{-1}$ are as follows:

$-CH_3$ 25.83; $-CH_2-$ 17.72; $-\overset{|}{\underset{|}{C}}H$ 10.44; $-\overset{|}{\underset{|}{C}}-$ 3.4; $-NH_2$ −0.8;
$-OH$ −1.1; $\rangle C{=}O$ 3.8; $-CONH-$ 6.4; $-H$ 8.1.

As was pointed out by these authors, the group parameters for volumes are based upon the key assumption that each group contribution is independent of the location of the group and the nature of other groups in the molecule. As may be seen from the data, $I(NH_2)+I(CO)$ are not equal to $I(CONH)+I(H)$. This fact may suggest that amino and carbonyl groups adjacent each other do interact. In fact, as for U with no gauche interaction, the calculated values of the partial molal volume are 18.0 ($V_c+2I(NH_2)+I(CO)$) and 29.5 ($V_c+I(CONH)+I(H)+I(NH_2)$), compared with the experimental value of 36.98 $cm^3 mol^{-1}$. Group additivity is apparently not applicable to the urea molecule, although the assumption of the independent solvation of both sides of the urea derivatives produced a good approximation of the molal volume.

$\phi_v{}^\circ$ in the Mixed Solvents. In Figs. 1 and 2 volumes of the transfer from water to the methanol–water mixtures are plotted against the mole fraction of methanol in the mixture. As may be seen from these figures, each curve of $\Delta\bar{V}^\circ{}_{tr}$ in the water-rich region goes through a minimum and then turns upward except for the non-hydrophobic solute U. Upon the introduction of more or larger alkyl groups into the urea molecule, the curves gradually come to show deeper minima. The order of decreasing (more negative) $\Delta\bar{V}^\circ{}_{tr}$ values at $X_2=0.1$ is:

U<MU<1,1-DMU≃EU<1,3-DMU<1,1-DEU<1,3-DEU.

It is considered that this reflects the order of the hydrophobicity of the compounds. In this connection, it is interesting to note Rouw and Somsen's report concerning the enthalpies of transfer, $\Delta\bar{H}^\circ{}_{tr}$, from water to mixtures of DMF+H_2O for various alkyl-substituted ureas.[12)] They show that the enthalpies of solution of these compounds (except for U) show an endothermic shift (i.e., $\Delta\bar{H}^\circ{}_{tr}>0$) upon the addition of small amounts of DMF to the water. The order of increasing $\Delta\bar{H}^\circ{}_{tr}$ values in the water-rich region is:

U<MU<1,1-DMU≃EU<1,3-DMU<TMU,

where TMU indicates tetramethylurea. These two sequences agree perfectly with each other, demonstrating that the 1,3-isomer is more hydrophobic than the 1,1-isomer and that 1,1-DMU has about the same hydrophobicity in nature as ethylurea. On the other hand, a volume increment is brought about upon the addition of a small amount of water to methanol. The volumes of transfer from CH_3OH to CH_3OH+H_2O increase in the following sequence:

1,3-DEU<1,1-DEU<1,3-DMU<EU<1,1-DMU<MU<U.

Here, the less hydrophobic the solute is, the more the volume increases. More studies will be necessary in order to elucidate further the behavior of the ternary water–methanol–urea system.

References

1) F. Franks and D. J. G. Ives, *Q. Rev. Chem. Soc.*, **20**, 1 (1966).

2) H. S. Frank and F. Franks, *J. Chem. Phys.*, **48**, 4764 (1968).

3) J. G. Mathieson and B. E. Conway, *J. Solution Chem.*, **3**, 781 (1974).

4) R. N. French and C. M. Criss, *J. Solution Chem.*, **10**, 231 (1981).

5) D. Hamilton and R. H. Stokes, *J. Solution Chem.*, **1**, 213 (1972).

6) T. Ogawa, K. Mizutani, and M. Yasuda, *Bull. Chem. Soc. Jpn.*, **57**, 2064 (1984).

7) P. R. Philip, G. Perron, and J. E. Desnoyers, *Can. J. Chem.*, **52**, 1709 (1974).

8) T. T. Herskovits and T. M. Kelly, *J. Phys. Chem.*, **77**, 381 (1973).

9) R. H. Stokes, *Aust. J. Chem.*, **20**, 2087 (1967).

10) O. Kiyohara and G. C. Benson, *J. Solution Chem.*, **10**, 281 (1981).

11) J. Lara and J. E. Desnoyers, *J. Solution Chem.*, **10**, 465

(1981).

12) A. Rouw and G. Somsen, *J. Chem. Soc., Faraday Trans. 1*, **78**, 3397 (1982).

13) F. Shahidi, *J. Solution Chem.*, **12**, 295 (1983).

14) S. Cabani, G. Conti, L. Lepori, and G. Leva, *J. Phys. Chem.*, **76**, 1343 (1972).

15) R. E. Verrall and B. E. Conway, *J. Phys. Chem.*, **70**, 3961 (1966).

16) J. T. Edward, P. G. Farrell, and F. Shahidi, *J. Phys. Chem.*, **82**, 2310 (1978); *Can. J. Chem.*, **57**, 2585 (1979).

17) R. N. French and C. M. Criss, *J. Solution Chem.*, **10**, 699, 713 (1981).