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Ultrasonic and Thermodynamic Studies on the Aqueous Solutions of Tetramethylurea

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Ultrasonic absorption and sound velocity were measured for aqueous solutions of tetramethylurea at temperatures 10—30 °C. Excess compressibility and partial molar volume were obtained. The curves for the concentration dependence of density, viscosity, and absorption show a maximum at about 60 vol% (20 mol%). The excess compressibility curve shows a minimum at the same concentration. It is concluded that a molecular complex of the molar ratio 4: 1 (water: tetramethylurea) linked with hydrogen-bonds is formed at 20 mol%. In a dilute solution (below 4 mol%), the magnitude of ultrasonic absorption of tetramethylurea solutions is equal to that of 1,3-dimethylurea solutions, but is less than that of 1,3-diethylurea solutions. The tetramethylurea–water interaction is of a similar nature to that between 1,3-dimethylurea and water in a dilute solution.

From the results of our ultrasonic studies on the effects of guanidine hydrochloride, urea and its alkyl derivatives upon the structure of water, it was concluded that guanidine hydrochloride and urea molecules behave as a structure breaker for liquid water.[1–3]

Recently, Subramanian *et al.*[4] have shown from NMR and specific heat capacity data on aqueous solutions of urea and its derivatives that the relative decreasing order of structure making propensities (in water) is tetramethylurea>1,3-dimethylurea>urea, and they stated to have reached the same conclusion as ours. However, they have misinterpreted our study, for we made no mention of the aqueous solutions of tetramethylurea in our report.[2] Finer *et al.*[5] pointed out that the results of proton chemical shift studies on aqueous solutions of urea strongly disagree with that by Subramanian *et al.*[4] Therefore, the conclusion on the order of structure making propensities given by Subramanian *et al.* is doubtful.

In the present paper we report on ultrasonic studies on aqueous solutions of tetramethylurea with an intention to investigate alkyl group–water interactions, and compare it with the results for 1,3-dimethylurea and 1,3-diethylurea solutions. Despite the usefulness of the material as a good solvent for many organic substances, physicochemical studies on tetramethylurea solutions are very few.[6] Tetramethylurea is one of the few urea derivatives which is liquid at room temperatures and acts only as a hydrogen bond acceptor without an ability as a proton donor. We discuss in this paper the solute-solvent interactions in tetramethylurea solutions.

Experimental

Measurements of sound velocity and absorption coefficient were carried out by an ultrasonic pulse technique. The apparatus and procedure of measurements were already described.[7] The absorption coefficient was determined in the frequency range 15—45 MHz. Temperature range was 10—30 °C, the accuracy being within ±0.1 °C. The sound

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[1] K. Arakawa and N. Takenaka, This Bulletin, **40**, 2739 (1967).

[2] K. Sasaki and K. Arakawa, *ibid.*, **42**, 2485 (1969).

[3] K. Arakawa, N. Takenaka, and K. Sasaki, *ibid.*, **43**, 636 (1970).

[4] S. Subramanian, T. S. Sarma, D. Balasubramanian, and J. C. Ahluwalia, *J. Phys. Chem.*, **75**, 815 (1971).

[5] E. G. Finer, F. Franks, and M. J. Tait, *J. Amer. Chem. Soc.*, **94**, 4424 (1972).

[6] A. Lüttringhause and H. W. Dirksen, *Angew. Chem. internat. edt.*, **3**, 260 (1964)

[7] K. Arakawa and N. Takenaka, This Bulletin, **40**, 2063 (1967).

velocity was measured at 5 MHz.

Tetramethylurea (Aldlich Co. Ltd., USA) was used after being refluxed with calcium hydride under nitrogen atmosphere and distilled at 10 mmHg. Density of aqueous solutions was measured with an Ostwald type pycnometer at 20 °C, and partial molar volume was calculated. Viscosity coefficients for the solutions were measured with an Ostwald type viscometer (flow time for pure water, 270 s at 20 °C).

Results

Sound Velocity and Compressibility. The accuracy of sound velocity was within ±1 m/s. The values obtained are plotted against concentration (vol%) in Fig. 1. The density data at 20 °C are shown in Fig. 2. Excess compressibility $(V\kappa_s)_{\text{excess}}$ is defined by

$$(V\kappa_s)_{\text{excess}} = (V\kappa_s) - (x_1V_1\kappa_{s,1}+x_2V_2\kappa_{s,2}) \qquad (8)^{8)}$$

where V, V_1, and V_2 are molar volume of solution, solvent, and solute, respectively, κ_s, $\kappa_{s,1}$, and $\kappa_{s,2}$, adiabatic compressibility of solution, solvent, and solute, respectively, and x_1 and x_2, mole fraction of solvent and solute, respectively. The results are plotted against concentration (mol%) in Fig. 3. We see that the excess compressibility curve has a minimum at about 20 mol%. The partial molar volume obtained from density data is given in Fig. 4. The partial molar volume of solute rapidly decreases up to about 4 mol% (20 vol%) while that of solvent water increases only slightly. Sound velocity *vs.* concentration curves at various temperatures intersect at about 20 vol% (4 mol%) (Fig. 1).

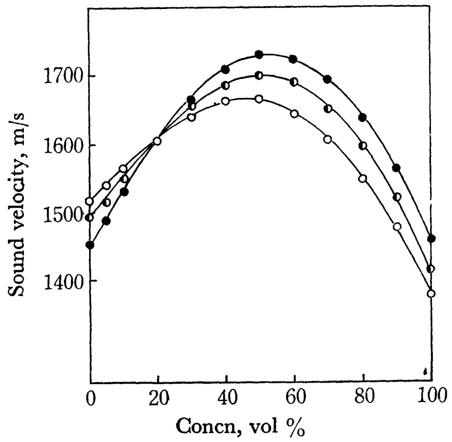

Fig. 1. Sound velocity for tetramethylurea solutions.
●: 10 °C, ◐: 20 °C, ○: 30 °C

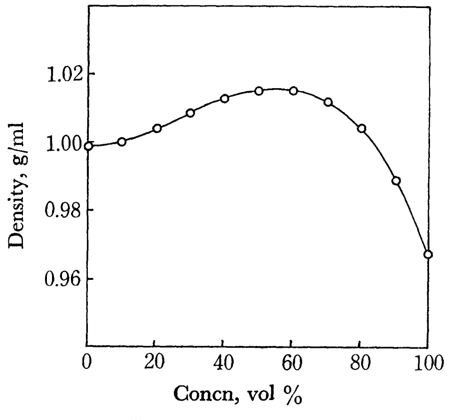

Fig. 2. Concentration dependence of density for tetramethylurea solutions at 20 °C.

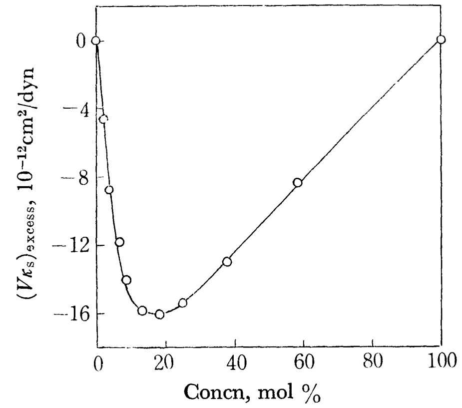

Fig. 3. Concentration dependence of excess compressibility for tetramethylurea solutions at 20 °C.

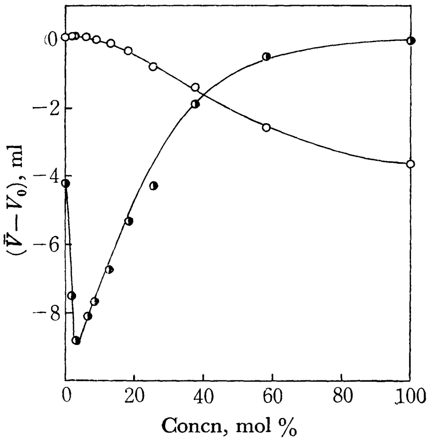

Fig. 4. Partial molar volume for tetramethylurea solutions at 20 °C.
○: water, ◑: tetramethylurea

Ultrasonic Absorption and Viscosity. The data of ultrasonic absorption are reproducible within ±2%. The α/f^2 *vs.* concentration curves (α, absorption coefficient and f, frequency) are given in Fig. 5. The magnitude of absorption increases slowly up to about 20 vol% (4 mol%), and rapidly from 20 to about 60 vol%.

Viscosity coefficients were measured in order to obtain classical absorption. The results are given in Fig. 6. The classical absorption is given by

$$(\alpha/f^2)_{\text{class.}} = \frac{8\pi^2\eta}{3\rho V^3} \qquad (2)$$

where ρ is density, V sound velocity and η viscosity coefficient. The structural absorption is given by

$$(\alpha/f^2)_{\text{struct.}} = (\alpha/f^2)_{\text{obsd.}} - (\alpha/f^2)_{\text{class.}} \qquad (3)$$

The results at 20 °C as compared with the data of observed and classical absorption are given in Fig. 7. The increase of observed absorption is primarily at-

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[8] The definition of excess compressibility from Eq. (1) is identical with that given previously. O. Kiyohara and K. Arakawa, This Bulletin, **44**, 1224 (1971).

tributed to the structural absorption. The magnitude of absorption on the solutions of low concentration is compared with that of 1,3-dimethylurea and 1,3-diethylurea solutions (Fig. 8). The absorption is equal in magnitude to that of 1,3-dimethylurea solutions in the same region of concentration.

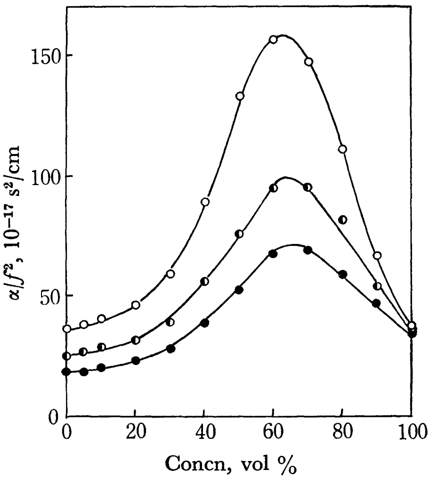

Fig. 5. Ultrasonic absorption (35 MHz) for tetramethylurea solutions.
○: 10 °C, ◐: 20 °C, ●: 30 °C

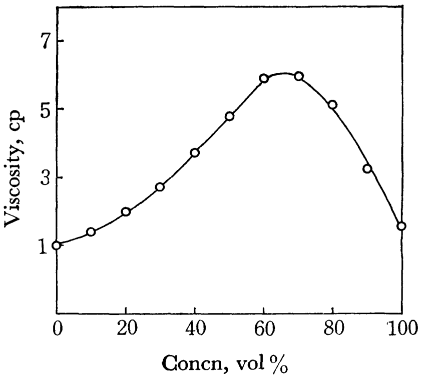

Fig. 6. Concentration dependence of viscosity for tetramethylurea solutions at 20 °C.

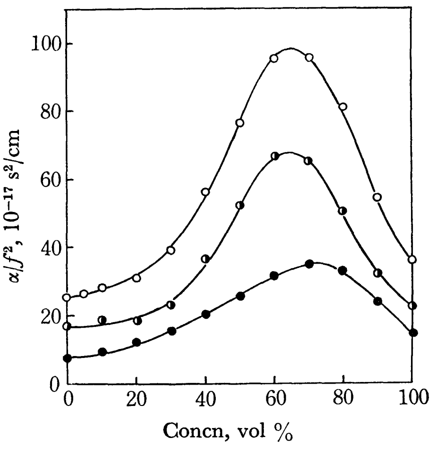

Fig. 7. Concentration dependence of ultrasonic absorption (35 MHz) for tetramethylurea solutions at 20 °C.
○: observed absorption, ◑: structural absorption, ●: classical absorption

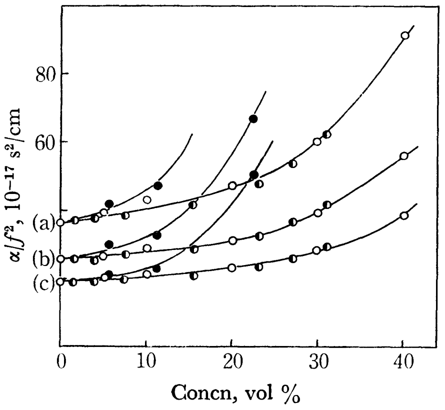

Fig. 8. Ultrasonic absorption for the solutions of alkyl derivatives. (a): 10 °C, (b): 20 °C, (c): 30 °C.
○: tetramethylurea, ◐: 1,3-dimethylurea, ●: 1,3-diethylurea

Discussion

Alkyl Group-Water Interaction. All curves intersect nearly at a point at about 20 vol% (4 mol%) (Fig. 1). An intersection point in a family of sound velocity *vs.* concentration curves at different temperatures appears in various aqueous systems.[9,10] The concentration at the crossing point (Fig. 1) corresponds to that of the sharp minimum of partial molar volume curve of solute (Fig. 4). The partial molar volume of solvent increases only slightly up to about this concentration. Below the concentration of 20 vol% (4 mol%), solute molecules might enter the cavities of water structure causing no conceivable rearrangement of the structure of water. This is due to the cooperative nature of structure formation in liquid water.[3] Since the magnitude of α/f^2 for pure tetramethylurea dose not differ much from that of pure water (Fig. 5), substitution of tetramethylurea molecules for solvent molecules in aqueous solutions causes no appreciable change in α/f^2 for solutions in a dilute region.

From a comparison of the magnitude of α/f^2 for tetramethylurea, 1,3-dimethylurea and 1,3-diethylurea solutions (Fig. 8), we can discuss alkyl group-water interactions. It is seen that the magnitude of absorption for tetramethylurea solutions is equal to that of 1,3-dimethylurea solutions, while the magnitude of α/f^2 for 1,3-diethylurea solutions is fairly larger. 1,3-Diethylurea molecules behave as a structure former on the structure of water.[2] The rapid increase of α/f^2 with concentration for 1,3-diethylurea solutions is ascribed to the structure formation around ethyl groups of solute molecules in water. In tetramethylurea and 1,3-dimethylurea solutions the situation is different.

Barone *et al.*[11] pointed out that from a spectroscopic study the structure forming ability of tetramethylurea in liquid water was stronger than that of 1,3-dimethlyurea and 1,3-diethylurea. However, the low "structure

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9) R. Parshad, *J. Acoust. Soc. Amer.*, **20**, 66 (1948).
10) G. W. Willard, *ibid.*, **12**, 438 (1940).
11) G. Barone, E. Rizzo, and V. Vitagliano, *J. Phys. Chem.*, **74**, 2230 (1970).

temperature" [12,13] of tetramethylurea they gave should be ascribed to some other source, since their measurements were carried out in a higher concentration region. Study on iceberg formation should be made in a relatively dilute concentration region in order to avoid the effect from other factors of solute–solvent interactions.

The difference in α/f^2 *vs.* concentration curves (Fig. 8) is thus attributed to the difference between the behavior of the methyl group and ethyl group in water. The van der Waals radius of methyl group given by Pauling is about 2.0 Å.[14] The value is not much larger than that of water molecule,[14,15] and the methyl group seems to rotate nearly free from the absence of steric hindrance in water. Thus, the tetramethylurea-water interaction is found to be essentially similar to that of 1,3-dimethylurea solutions in low concentrations. This is in agreement with the result of viscosity increment (coefficient B) for solutions of tetramethylurea, 1,3-dimethylurea and 1,3-diethylurea by Herskovits *et al.*[16] The present result seems to be in line with that of the gas solubility study by Wetlaufer *et al.*[17]

Formation of Tetramethylurea Hydrate. The concentration of maximum density is found at about 60 vol% (18.5 mol%) (Fig. 2). The excess compressibility curve has a minimum at about 20 mol% (Fig. 3). It is thus expected that a tetramethylurea hydrate is formed. A maximum of α/f^2 was found at 63 vol% (20.4 mol%) at each temperature (Fig. 5) and a maximum of viscosity coefficient at 64 vol% (21.1 mol%) (Fig. 6).

Lüttringhause and Dirksen[6] proposed from density measurements that a molecular complex is formed with the molar ratio 6: 1 (water: tetramethylurea). However, we see a maximum or a minimum at a concentration of about 20 mol% in each curve for density, compressibility, ultrasonic absorption and viscosity coefficient. This corresponds to the molar ratio 4: 1 (solvent: solute). Tetramethylurea acts only as a hydrogen-bond acceptor, since all hydrogens of amide nitrogen are substituted by the CH_3 groups. Thus, it is tentatively assumed that tetramethylurea tetrahydrates are formed in aqueous solutions by hydrogen bonding. From the temperature dependence of maximum values of absorption, the apparent activation energy was calculated to be 6.9 kcal/mol. This value seems to be adequate for the tetrahydrate formation. The increase of observed absorption is mainly due to the increase of structural absorption (Fig. 7). Thus, we can conclude that the maximum value of ultrasonic absorption at 60 vol% is ascribed to the presence of tetrahydrate.

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13) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths and Co. Ltd., London, (1959), p. 309.

14) L. Pauling, "The Nature of the Chemical Bond", 3rd., Cornell University, (1961), p. 260.

15) J. Morgan and B. E. Warren, *J. Chem. Phys.*, **6**, 666 (1938).

16) T. T. Herskovits, H. Jaillet, and A. T. DeSena, *J. Biol. Chem.*, **245**, 6511 (1970).

17) D. B. Wetlaufer, S. K. Malik, C. Stoller, and R. L. Coffin, *J. Amer. Chem. Soc.*, **86**, 508 (1964).