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The Ultrasonic Study of Aqueous Solutions of Alkyl-Substituted Urea

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An ultrasonic investigation of aqueous solutions of alkyl-substituted urea was made by means of an ultrasonic pulse technique in order to study the influence of the solutes upon the structure of solvent. The ultrasonic velocity and absorption were measured in solutions of 1,3-dimethylurea and 1,3-diethylurea in the frequency range from 5 to 45 Mc/sec. The temperature was varied from 10 to 40°C, and the concentration from 0.2 to 4 mol/*l*. Within the range of frequency no relaxation frequency was observed for both solutions. From the data on absorption coefficent and viscosity, the magnitude of absorption due to structural relaxation was calculated. It was found that structural absorption in dimethylurea solutions is slightly larger, and in diethylurea solutions much larger than that of the urea solutions. From these results, it is concluded that 1,3-dimethylurea is a structure breaker for the open-packed structure in water, the ability being smaller than that of urea, and that, for the behavior of 1,3-diethylurea molecule in water, the structure-forming ability of the ethyl group is found to surpass the structure-breaking effect of the residual part of the molecule.

In the preceding paper[1] one of the authors reported the results of an ultrasonic study on aqueous solutions of urea, and stated from experimental grounds that urea behaves as a structure breaker for the "open-packed structure" or the "ice-like structure" in liquid water. Recently, H. S. Frank and coworker[2] have discussed the behavior of urea molecules in water and have concluded that urea is a structure breaker for water, based on a two state model of water,[3] which has been made clear

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

[2] H. S. Frank and F. Franks, *J. Chem. Phys.*, **48**, 4746 (1968).

[3] L. Hall, *Phys. Rev.*, **73**, 775 (1948).

by the authors[4] to be a useful model for thermodynamical behaviors of liquid water. Urea is well known as a typical reagent for the denaturation of protein.[5] The effect of the addition of urea in aqueous solutions of polymers is said to consist of two factors;[6] the direct interactions between polymer molecules and urea[7,8] and the influence upon the configuration of polymer molecules through the change of the structure of water caused by the addition of urea.[1,9]

We have studied the structure of water[4] and the influence of the various addends upon it.[1,10] It is interesting to investigate the behavior of alkyl-substituted urea in water in comparison with those of urea, aiming at the effect of alkyl-substitution, especially the change in the ability as structure breaker which is attributed to the introduction of alkyl group. We measured the ultrasonic velocity and absorption of aqueous solutions of alkyl urea.

The denaturation effect of Lysozyme by 1,3-dimethylurea has recently been investigated by Hamaguchi and Sasaki.[11] Concerning the influence of alkane molecules upon the structure of water, Wetlaufer *et al.* have studied the solubility of hydrocarbons in 7M urea and 4.9M guanidine hydrochloride solutions,[12] and appreciable differences have been observed between the behavior of methane and that of higher homologues. Thus we carried out an ultrasonic study of aqueous solutions of 1,3-dimethylurea and 1,3-diethylurea.

Experimental

An ultrasonic pulse method was used for the measurements of the sound velocity and of the absorption. The apparatus used and the procedure for the measurements were described in the preceding paper.[13] The absorption coefficient was determined over the fequency range of 15—45 Mc/sec and at temperatures from 10 to 40°C with 10°C intervals. The sound velocity was measured at 5 Mc/sec. The temperature was held constant to within ±0.1°C. The absorption data were reproducible within 2% and the velocity data within 1 m/sec. Two commercial samples, 1,3-dimethylurea[*1] and 1,3-diethylurea,[*2] were used without further purification. The melting points of the samples were 106.6 ±0.5°C and 103.8±0.5°C, respectively. The viscosity coefficient, η, was measured on the aqueous solutions by means of an Ostwald capillary viscometer (flow time for pure water 77.7 sec at 20°C). From the values of η the classical absorption (Stokes loss) was calculated.

Results

Ultrasonic Velocity. The results obtained for the aqueous solutions of 1,3-dimethylurea and of 1,3-diethylurea are plotted against temperature in Figs. 1(a) and (b), respectively. The sound velocity data obtained for pure water by Greenspan and Tschiegg[14] are also given. We see that the concentration dependence of the velocity *vs.* temperature curves is similar to that for urea solutions.[1]

Ultrasonic Absorption. The absorption coefficient, α, was measured for solutions of 1,3-dimethylurea in the concentration range, 0.2—4 mol/*l*, and for solutions of 1,3-diethylurea in the range, 0.5—2 mol/*l*. The frequency dependency of α is given

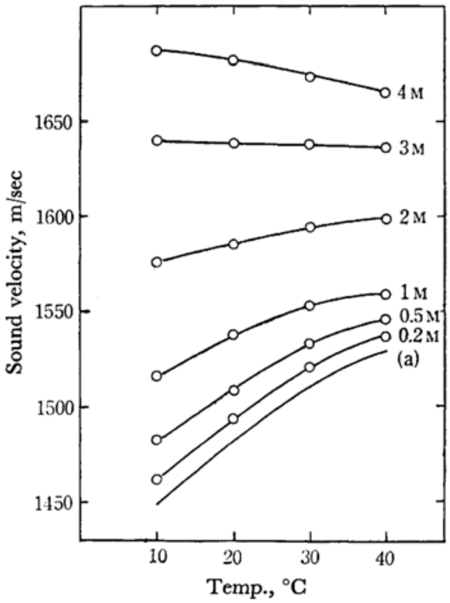

Fig. 1(a). Sound velocity of aqueous solutions of 1,3-dimethylurea.
(a) Pure water

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4) K. Arakawa and K. Sasaki, This Bulletin, **42**, 303 (1969).

5) W. Kauzmann, *Advances Protein Chem.*, **14**, 1 (1959).

6) M. Watase and K. Arakawa, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **89**, 383 (1968).

7) D. R. Robinson and W. P. Jencks, *J. Am. Chem. Soc.*, **87**, 2462 (1965).

8) J. A. Gordon and W. P. Jencks, *Biochemistry*, **2**, 47 (1963).

9) G. G. Hammes and P. R. Schimmel, *J. Am. Chem. Soc.*, **89**, 442 (1967).

10) K. Arakawa and N. Takenaka, This Bulletin, **42**, 5 (1969).

11) K. Hamaguchi and H. Sakai, *J. Biochem.*, **57**, 721 (1965).

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

13) K. Arakawa and N. Takenaka, This Bulletin, **39**, 447 (1966); **40**, 2063 (1967).

[*1] Aldrich Chemical Co., Inc., Milwaukee, Wisconsin, U.S.A.

[*2] Tokyo Chemical Industry Co., Ltd., Tokyo.

14) M. Greenspan and C. E. Tschiegg, *J. Res. Natl. Bur. Std.*, **58**, 249 (1957); *J. Acoust. Soc. Am.*, **31**, 75 (1959).

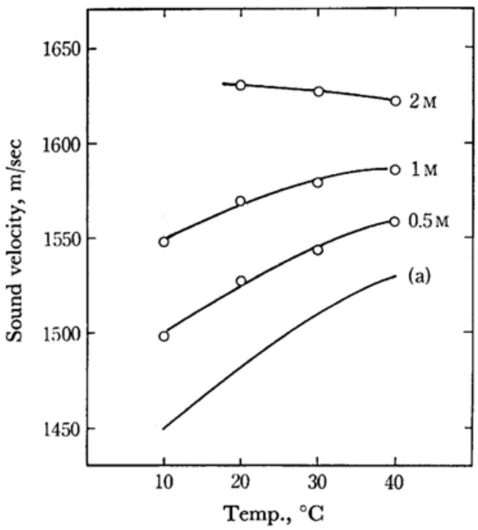

Fig. 1(b). Sound velocity of aqueous solutions of 1,3-diethylurea.
(a) Pure water

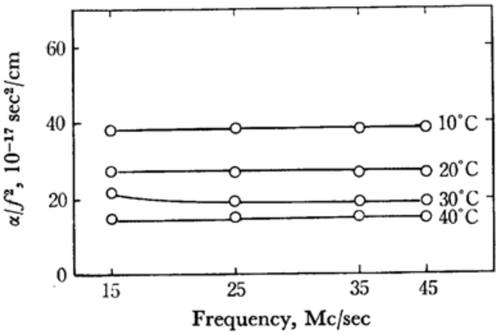

Fig. 2(a). Ultrasonic absorption of aqueous solutions of 1,3-dimethylurea.
Concn., 2 mol/*l*

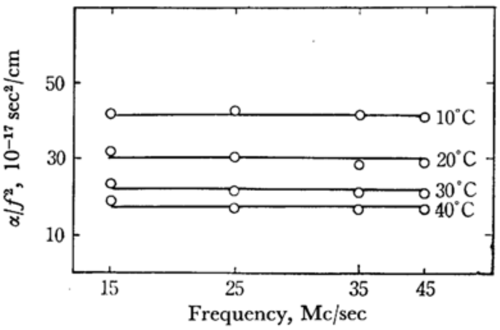

Fig. 2(b). Ultrasonic absorption of aqueous solutions of 1,3-diethylurea.
Concn., 1 mol/*l*

in Figs. 2(a) and (b) in the form of α/f^2 *vs.* log f relation, where f is frequency, for 2 mol/*l* solution of dimethyl urea and for 1 mol/*l* solution of diethyl urea, as examples. Both groups of curves are flat throughout the frequency range. This means that no relaxation frequency is observed.

In Figs. 3(a) and (b) the (α/f^2) *vs.* concentration curves are given for the solutions of dimethylurea and diethylurea, respectively. For solutions of diethylurea the magnitude of α/f^2 is seen to increase more rapidly than for solutions of dimethylurea with the increase in concentration. The (α/f^2) *vs.* concentration curves for aqueous solutions of urea, 1,3-dimethylurea, and 1,3-diethylurea at 20°C and 40°C are compared in Figs. 4(a) and (b). Concentrations are given in volume %. The dotted lines represent the magnitude of absorption,*3 which is attributed only to water as solvent when no structural change is assumed.

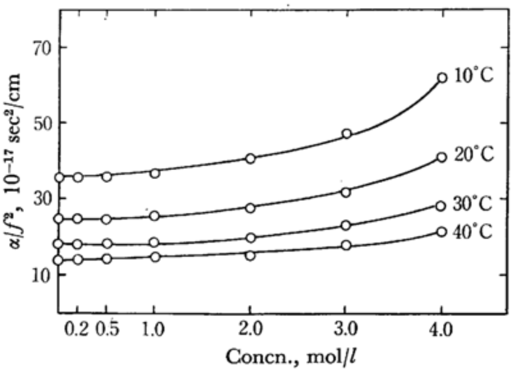

Fig. 3(a). α/f^2 *vs.* concn. relation 1,3-dimethylurea solution.

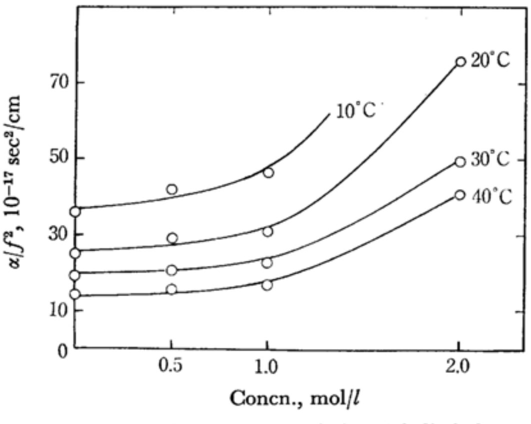

Fig. 3(b). α/f^2 *vs.* concn. relation 1,3-diethylurea solution.

In order to calculate the classical absorption $(\alpha/f^2)_\eta$, the viscosity coefficient η, was measured. The result is given in Fig. 5. The classical absorption is given by

$$(\alpha/f^2)_\eta = \frac{8\pi^2\eta}{3\rho V^3} \qquad (1)$$

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*3 This is calculated according to the volume fraction of water as solvent from the absorption of pure water.

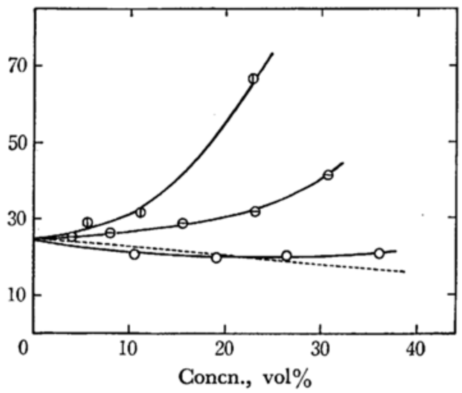

Fig. 4(a). α/f^2 *vs.* concn. relation at 20°C.
○ urea solution,
⊖ 1,3-dimethylurea solution
⦶ 1,3-diethylurea solution

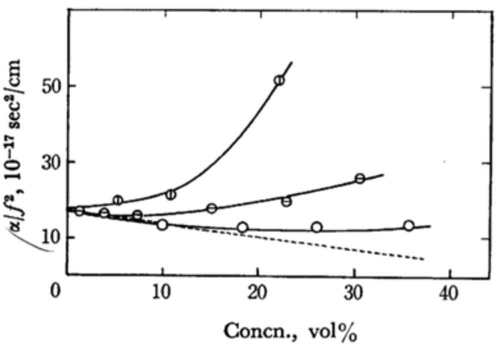

Fig. 4(b). α/f^2 *vs.* concn. relation at 40°C.
○ urea solution
⊖ 1,3-dimethylurea solution
⦶ 1,3-diethylurea solution

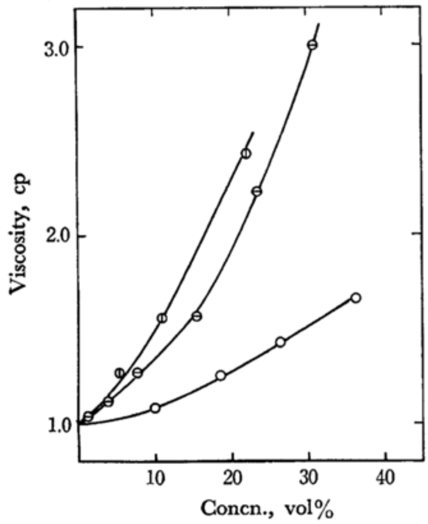

Fig. 5. Viscosity of solutions at 20°C.
○ urea solution
⊖ 1,3-dimethylurea solution
⦶ 1,3-diethylurea solution

where ρ is density and V is sound velocity. The absorption due to structural relaxation, $(\alpha/f^2)_{\rm struct.}$ is given by subtracting $(\alpha/f^2)_\eta$ from $(\alpha/f^2)_{\rm obs.}$

$$(\alpha/f^2)_{\rm struct.} = (\alpha/f^2)_{\rm obs.} - (\alpha/f^2)_\eta \qquad (2)$$

The result is shown in Figs. 6(a) and (b) for each temperature.

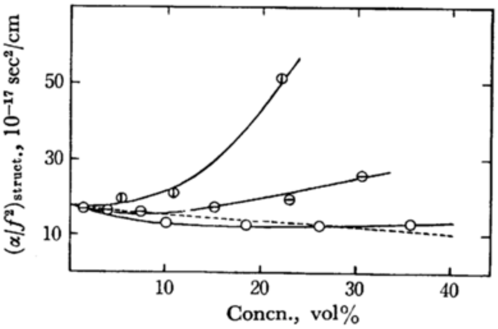

Fig. 6(a). $(\alpha/f^2)_{\rm struct.}$ *vs.* concn. relation at 20°C.
○ urea solution
⊖ 1,3-dimethylurea solution
⦶ 1,3-diethylurea solution

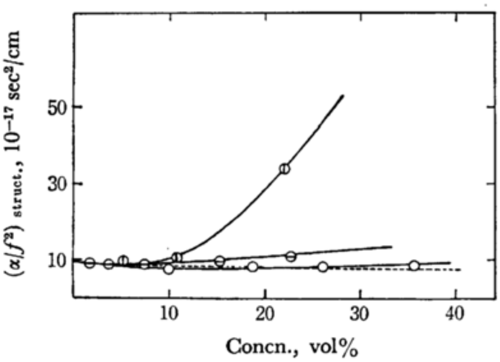

Fig. 6(b). $(\alpha/f^2)_{\rm struct.}$ *vs.* concn. relation at 40°C.
○ urea solution
⊖ 1 3-dimethylurea solution
⦶ 1 3-diethylurea solution

Discussion

The Influence of Solute Molecules upon the Structure of Liquid Water. Urea is known as hydrogen bond breaker. However, there is some ambiguity[15] about the behavior of urea in water. From recent studies by us[1] and by Hammes *et al.*,[9] it has been concluded that urea behaves as a structure breaker for the ice-like structure in liquid water. In the case of alkyl-substituted urea the situation is different, because, in addition to the effect of substitution of hydrogen attached to amino radical, the alkyl group is believed to cause iceberg-

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[15] M. Abu-Hamdiyyah, *J. Phys. Chem.*, **69**, 2720 (1965).

formation around it in water.[16,17] That is, alkyl-substituted urea has two opposite functions, *viz.*, as a structure breaker and as a structure former.

It is clearly seen from Figs. 6(a) and (b) that the magnitude of ultrasonic absorption due to structural relaxation becomes larger in the order 1,3-diethylurea $>$ 1,3-dimethylurea $>$ urea. As pointed out previously,[1] the absorption in urea solutions decreases with the addition of the solute to water, and becomes smaller than the absorption caused by water component only (shown by dotted curves as seen in Figs. 4(a) and (b)). It is similar in the case of structural absorption as seen in Figs. 6(a) and (b). This fact supports definitely the idea that the urea molecules behave as the structure breaker for the ice-like structure in liquid water. This also seems to be the case in 1,3-dimethylurea solutions. The absorption of the solution of 1,3-dimethylurea due to structural relaxation is nearly equal to that in the solutions of urea for a concentration less than about 10 vol%. The magnitude of $(\alpha/f^2)_{\text{struct.}}$ for dimethylurea solutions decreases first with the increase in concentration, and is nearly equal to or a little smaller than that shown by the dotted line for a concentration range of less than about 10 vol%. This behavior is similar essentially to that of urea solutions, though the features observed are not so striking. 1,3-Dimethylurea molecules may be said to act as the structure breaker for the ice-like structure in water, though that ability is supposed to be smaller than that of urea.

In the case of the 1,3-diethylurea solutions, the situations are definitely different. The structural absorption in the solution is found to be much larger than that in the dimethylurea solution within the whole range of concentration. The difference between diethylurea solutions and the other two solutions becomes appreciable in the range of concentration greater than 0.1 volume fraction. This difference is, of course, ascribed to the presence of ethyl groups in place of methyl groups. In order to investigate the change of ultrasonic absorption accompanying the increase in the number of carbon atoms in homologous series, the absorption data for various compounds are given in Table 1. No appreciable change of absorption is observed. It seems that the variation of ultrasonic absorption induced by the introduction of C_2H_5 group in place of CH_3 is not great. Therefore, from the absorption data given in Figs. 6(a) and (b), the fact that the absorption in diethylurea solutions is greater than that in dimethylurea solutions is explained by the structure-forming effect of C_2H_5 group in liquid water. This is in line with the suggestion given by Wetlaufer *et al.*,[12] based on the solubility data of hydrocarbons in urea and guanidine hydrochloride solutions. According to their data, an essential difference between CH_4 and C_2H_6 has been observed with respect to the interaction of alkane molecules with water around themselves. It has been suggested that, at temperatures above about 20°C, C_2H_6 molecules and those of higher homologues have a structure-forming effect upon water molecules around them, with the exception of CH_4. Thus we conclude that in the diethylurea solution the comparatively large absorption is attributed at least partly to the local water structure around C_2H_5 groups, and that the structure-forming effect of C_2H_5 groups may surpass the structure-breaking effect of residual groups in the diethylurea molecule.

TABLE 1. ULTRASONIC ABSORPTION OF VARIOUS LIQUIDS

Liquid	Temp. °C	f Mc/sec	α/f^2 10^{-17} sec^2/cm
C_6H_{14}	20	5—30	57.6[a]
C_7H_{16}	20	5—30	58[a]
C_8H_{18}	20	5—30	51[a]
$C_{10}H_{22}$	20	21	56.7[b]
$HCOOCH_3$	24.1	104	49.3[c]
$HCOOC_2H_5$	24.1	104	49.9[c]
$C_3H_7COOCH_3$	24.5	104	35.5[c]
$C_3H_7COOC_2H_5$	24.5	104	38.6[c]
CH_3COCH_3	24.4	104	25.7[c]
$CH_3COC_2H_5$	25	10—100	26.5[d]

a) N. I. Koshkin, *Primenenie ultraakustiki k issledovaniyo beshchestva*, **1**, 101 (1955).

b) S. Parthasarathy, M. Pancholy and A. F. Chapgar, *Nuovo Cimento* **10**, 111, 118, 1053 (1958).

c) E. L. Heasell and J. Lamb, *Pro. Phys. Soc.*, **B69**, 869 (1956).

d) M. S. de Groot and J. Lamb, *ibid.*, **A242**, 36 (1957).

Summary and Conclusion

From the ultrasonic data obtained by means of a pulse technique, it is concluded that in the aqueous solution of 1,3-dimethylurea the solute molecules behave as a structure breaker for the ice-like structure in liquid water, though the structure-breaking ability is smaller than that of urea. For the aqueous solution of 1,3-diethylurea it may be said that the structure-forming ability of ethyl group surpasses the structure-breaking effect of the residual part in the solute molecule.

The authors wish to thank Mr. Nobuo Takenaka and Miss Yuko Endo for their cooperation in performing this study.

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[16] G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3401 (1962).

[17] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).