An Ultrasonic Absorption Study of the DMF–Water System

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Using the pulse method, the ultrasonic absorption was measured for binary mixtures of water and *N*,*N*-dimethylformamide (DMF) at 5.5 and 57 MHz in the temperature range of 5—45 °C. At lower temperatures α/f^2 as a function of the concentration produces a plateau up to x (x is the mole percent of DMF in solution) = 1.5, a minimum point at $x=6$, and a maximum point at $x=25$. An increase in the temperature causes these characteristic features of α/f^2 to disappear. At 45 °C the values of α/f^2 increase monotonically. No relaxation process is observed in the frequency range of this work. The general features of the concentration dependence of α/f^2 resemble those of the urea–water system in a water-rich region and those of the dioxane–water system in a DMF-rich region. The mechanism of the plateau can be explained by the cooperative nature of the formation and breaking of water clusters. The maximum of α/f^2 is ascribed to the complex formation between DMF and water molecules, while the minimum of α/f^2 arises from the competition between the breaking-down of the water structure and the complex formation in solution. The maximum behavior in the ultrasonic absorption can be interpreted in terms of a kinetic model, $\mathrm{DMF}+m\mathrm{H_2O}\rightleftarrows\mathrm{DMF}\cdot(\mathrm{H_2O})_m$. m is determined to be 3, and the following values have been obtained for the model mentioned above: $\Delta V_m \simeq 1$ cm³/mol, $K_m = 10\pm2$.

In a previous paper[1] the ultrasonic and volumetric behavior of aqueous solutions of amides (*N*-methylformamide, *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide) was studied at 25 and 35 °C over the entire concentration range. The velocity maxima were observed for all three of the amide solutions, while the minima in the partial molar volume were observed for DMF and DMAA. A tentative interpretation has been proposed that the velocity maxima are ascribable to the complex formation between water and amide molecules, while the minima in the partial molar volume are to be ascribed to the competition between the volume increase due to the complex formation and the volume decrease due to the breaking-down of the water structure.

In order to obtain further information on the interaction between water and amide molecules, ultrasonic absorption measurements have been carried out on the DMF–water system. From among three types of amide–water systems investigated previously, the DMF–water system is chosen because this system is one of the most widely used systems of polar mixed solvents.

Experimental

The DMF used was of a spectral grade obtained from Nakarai Chemicals and was used without further purification. The distilled water was degassed prior to each measurement.

The ultrasonic pulse method was used for the measuremet of the absorption coefficients of solutions. The details of the apparatus and the experimental procedures have been reported previously.[2,3] The measurements of the absorption coefficient were done at 5.5 and 57 MHz in the temperature range of 5—45 °C. The data are reproducible within ±1% at 57 MHz and within 5% at 5.5 MHz. The temperature was controlled to ±0.1 °C.

Results

Temperature and Concentration Dependences of α/f^2. Figure 1 shows the concentration dependences of α/f^2 at various temperatures. At lower temperatures, the curves show a minimum point at x (x is the mole percent of DMF in solution) = 5—8 and a maximum point at *ca.* $x=25$. With the rise in the temperature, the height of $(\alpha/f^2)_{max}$ and the depth of $(\alpha/f^2)_{min}$ decrease, and the width of the maximum peak shows a broadening with a slight shift of PSAC (the peak sound absorption concentration) towards higher concentrations of DMF. At temperatures higher than 35 °C, the minimum and the maximum points disappear and the values of α/f^2 increase monotonically. The appearance of the minimum point in the relation of α/f^2 *vs.* concentration in a small concentration of solute has not been observed in other aqueous solutions of nonelectrolytes except the work of Takenaka *et al.*[4] who found the appearance of the minimum in the α/f^2 *vs.* concentration curves for this system (20 and 25 °C, 15—45 MHz), but who mentioned nothing further about it.

Figure 2 is an expanded representation of Fig. 1 in the water-rich region. Two characteristic features should be noted regarding the temperature dependence of α/f^2 in this region. The first is, as has been described above, the appearance of the minimum point, while the second is the appearance of the plateau, in which α/f^2 is relatively insensitive to the quantity of DMF added. With a decrease in the temperature, this region increases from $x=0$ at 45 °C to $x=2$ at 5 °C. At 35 °C, the values of α/f^2 remain constant up to $x=7$, but this constant-value region does not correspond to the true plateau. From the comparison of the plateau region at different temperatures, it may be concluded that the constant-value region observed at 35 °C is the result of the opposite effects of the decrease of α/f^2 in the 2—6 mol% concentration range and the increase of α/f^2 in the concentration range of more than 6 mol%. The overlooking of the plateau in this system by Takenaka *et al.*[4] is due to the incompleteness of their measurements.

The general behavior of the DMF–water system in a small concentration of a solute shown in Fig. 2 resembles the results observed by Arakawa *et al.*[5] in the aqueous solutions of urea and guanidine hydrochloride. In urea solutions, the magnitudes of α/f^2 first decreased very slowly (it is more correct to say that the α/f^2 remains constant) with the concentration, and then, decreased rapidly in the range *ca.* 0.5 to

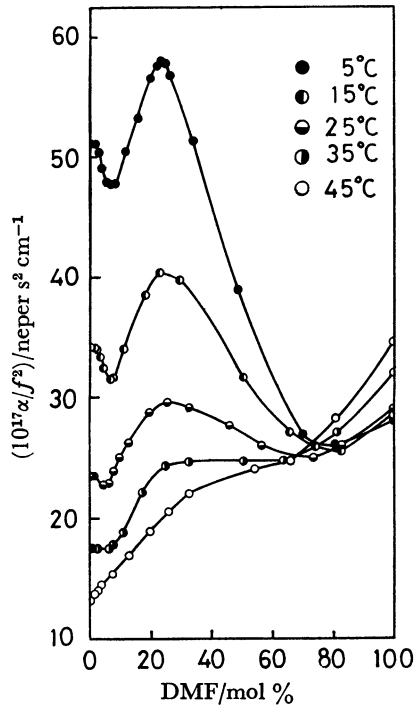

Fig. 1. Temperature and concentration dependence of α/f^2 in DMF–water system.

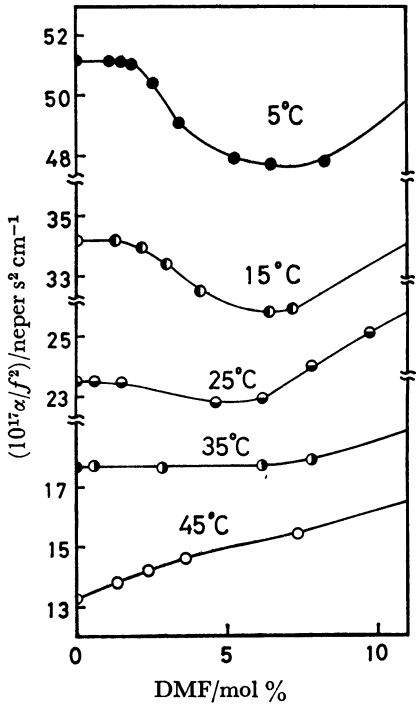

Fig. 2. Expanded representation of Fig. 1 in water-rich region.

3 M. The temperature rise causes these concentration dependences to disappear. The similarities between the urea–water system and the present one will be clearer if the results shown in Fig. 2 are represented in a molar scale (see Fig. 6(a) of Ref. 5).

As is shown in Fig. 1, in the DMF-rich region the values of α/f^2 measured at higher temperatures are larger than those measured at lower temperatures. These phenomena correspond well to those observed in the dioxane–water system.[5]

Frequency Dependence of α/f^2. The values of α/f^2 at 5.5 MHz are always larger than those at 57 MHz. However, the differences are so small (at most 4×10^{-17} neper s^2 cm^{-1} at 25 °C) that it is reasonable to conclude that the relaxation process does not exist in the present frequency range. Takenaka *et al.*[4] have also reported that the relaxation process is not observed in the frequency range of 15—45 MHz.

Discussion

Plateau and Minimum in the Water-rich Region. In spite of many theories of water structure and the ambiguities involved in them, it is widely recognized that the temperature-rise breaks down the hydrogen-bonding of water, resulting in increases in the fraction of unbonded or smaller-cluster molecules in water. The ultrasonic absorption coefficient of water, expressed as α/f^2 decreases monotonically with the temperature. The variation in the relation of α/f^2 *vs.* concentration in a small concentration of solute reflects the effects of the addition of DMF upon the water structure. The present experimental results indicate that the added DMF molecules have the same effects as the temperature-rise upon the ultrasonic absorption coefficient. Therefore, DMF molecules act as a structure breaker in water. Some experimental evidences have been found that DMF is a water-structure breaker.[7–9]

As has already been mentioned in the preceding section, the behavior of α/f^2 observed in the urea–water system and in the present one in their water-rich regions is very similar. Urea acts as a water-structure breaker. Both urea and DMF molecules have the $>$N–C(=O)– group. These facts led us to adopt the same interpretation of the concentration dependence of α/f^2 in the DMF–water system in a small concentration region of the solute as that proposed for the urea–water system.[5] Arakawa *et al.*[5] have argued that the characteristic feature in the α/f^2 *vs.* concentration curve found in the small concentration region is attributable to the cooperative nature of the formation and breaking of water clusters. When a very small amount of DMF is added to water, the influence of the DMF molecules upon the structure of water is isolated and the cooperative formation of clusters is not affected by the added DMF. When the amount of DMF is greater, however, the influence becomes appreciable and DMF affects the clusters cooperatively, disrupting them into unbonded monomers and/or small clusters.

Blandamer[6] has insisted that, if the liquid clathrate model is accepted, the plateau region is the zone of the enhanced water structure in the system of water–alcohols (alcohols are water-structure formers). His interpretation, however, can not be applied in the present system, for the DMF molecule is a water-structure breaker.[7–9]

The minimum sound absorption concentration

(hereafter abbreviated as MSAC) corresponds to the concentration at which the partial molar volume of DMF reaches a minimum point. MSAC becomes more remarkable with a decrease in the temperature. This phenomenon suggests that MSAC is intimately related to the structure of water. In the preceding paper,[1] the minimum in the partial molar volume of DMF in the aqueous solution is ascribed to the competition between the volume increase due to the complex formation and the volume decrease due to the breaking-down of the water structure. A similar conclusion can be drawn in the case of MSAC observed in the present work. In other words, MSAC arises from the competition between the decrease in α/f^2 due to the breaking-down of the water structure and the increase in α/f^2 due to the complex formation in DMF with water, which will be discussed below from another point of view.

PSAC and Excess Absorption due to the Complex Formation between DMF and Water. Two different approaches are possible to account for the abnormal ultrasonic absorption in the liquid mixture. One is the fluctuation theory proposed by Romanov *et al.*,[10] while the other is a kinetic model of complex formation between solute and solvent. The following factors indicate that the interpretation based on the complex formation is more suitable in the present system. First, Assarsson and Eirich[11] have shown the complex formation of such alkyl-substituted amides as *N,N*-dimethylacetamide with water from the data of viscosity and the phase diagram of these systems. Therefore, the complex formation in the DMF-water system is higly probable. Second, PSAC agrees fairly well with the concentration of the velocity maximum, *ca.* $x=20$. Third, the peak in the ultrasonic absorption observed in the present system is less steep than in the system consisting of water and alcohols, to which the fluctuation theory has been applied. Finally, the effects of the temperature rise on the PSAC and the width of the maximum peak in the ultrasonic absorption are small in comparison with those found in the aqueous solutions of alcohols.

Various kinetic models of complex formation have been put forward.[12] The model adopted by the present authors to interpret the ultrasonic absorption behavior observed in the DMF–water system is represented by this equation:

$$\mathrm{A} + m\mathrm{B} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{AB}_m \qquad \text{(I)}$$

The principal reason for adopting this model is the extreme unsymmetry in the relationships of α/f^2 with the concentration of DMF. In Model (I), it is assumed that the DMF molecule, represented by the symbol A, combines in a single step with m water molecules, represented by the symbol mB. Let the mole fraction, x, of the solute and the z of the complex be such that when the total number of solute and water molecules, including those in the complex, is unity, x is the total number of solute molecules and z is the number of complexes in the A+B⇌AB model. If the variables x and z are transformed to

$$x_m = \frac{x}{x+(1-x)/m} \quad \text{and} \quad z = \frac{z}{x+(1-x)/m},$$

PSAC is situated at $x_m=0.5$ or PSAC$=x=1/(1+m)$. Therefore, in this model, $m=(1-\mathrm{PSAC})/\mathrm{PSAC}$ is the optimum water-to-solute ratio. Using the usual analysis of the ultrasonic absorption data, the following physical properties concerning the excess absorption can be obtained;

$$\mu_{\max}^{\text{excess}} = \frac{\pi}{4}\cdot\frac{dc^2}{V_m RT}(\Delta V_m)^2\frac{(1-\beta_m)}{K_m\beta_m} \qquad (1)$$

$$\Delta V_m = (\partial V/\partial z_m)_{p,T} \qquad (2)$$

$$\beta_m{}^2 = 1 - 4x_m(1-x_m)K_m{}^2/(1+K_m)^2 \qquad (3)$$

and;

$$K_m = z_m/(x_m-z_m)(1-x_m-z_m), \qquad (4)$$

where $\mu_{\max}^{\text{excess}}$, V_m, and K_m refer to the excess absorption per wavelength at the maximum, the molar volume of the complex, and the equilibrium constant in Model (I) respectively. The theory enables a match to be made of the position of the experimental absorption peak by adjusting the value of m, of the height of the peak, by adjusting ΔV_m, and of the mean width of the peak by adjusting K_m. Here m is taken to be 3, as PSAC is found at *ca.* $x=25$ in Fig. 1. μ^{excess} is given by this relation; $\mu^{\text{excess}}=(\alpha/f^2)^{\text{excess}}\cdot fc$, where f is the frequency, and c, the velocity of the ultrasonics.

In the course of calculation, the values of the ultrasonic velocity, c, and the density, d, introduced on the right-hand side of Eq. 1 should not be the real values, but the ones at the "*hypothetical state*" of the solution without complex formation, because only the excess contribution originating from the complex formation is considered. The values of d and c at these "*hypothetical state*," d_{hyp}, and c_{hyp} respectively, were estimated on the basis of the ideal additivity of the volume of solution and the ideal additivity of the compressed volume in solution:

$$V_{\text{hyp}} = x_1V_1 + x_2V_2 = \frac{M_1x_1+M_2x_2}{d_{\text{hyp}}} \qquad (5)$$

$$V_1x_1\kappa_1 + V_2x_2\kappa_2 = V_{\text{hyp}}\kappa_{\text{hyp}} = \frac{M_1x_1+M_2x_2}{d_{\text{hyp}}}\cdot\frac{1}{(c_{\text{hyp}})^2d_{\text{hyp}}} \qquad (6)$$

The final results of calculation are shown in Fig. 3, where PSAC is at $x_m=0.5$, as predicted by Eqs. 1 and 3. The improper choice of m does not lead to the results shown in Fig. 3. The small non-symmetry in the curve of Fig. 3 is not significant and the variation in the mean width of the peak with the temperature can be taken to be negligible if due consideration is paid to the experimental errors and the analysis of the data. The average values of $(x_m)_{1/2}$ are found to be 0.72 and 0.28. As $(x_m)_{1/2}$ is obtained by solving Eq. 3 at $\mu_{\max}^{\text{excess}}/2$, the sum of the two values of $(x_m)_{1/2}$ is always 1. The most appropriate values of K_m compatible with these values of $(x_m)_{1/2}$ were numerically determined through the use of Eqs. 1 and 3: $K_m=10\pm2$. This value and the values of μ^{excess} at PSAC make possible the evaluation of ΔV_m. At this stage, the sign of ΔV_m remains undetermined. It is, however, the same as that of ΔH_m (see Eq. 7 below). The temperature dependence of the latter leads to the assignment of the negative sign to ΔH_m. The values of ΔV_m thus obtained are

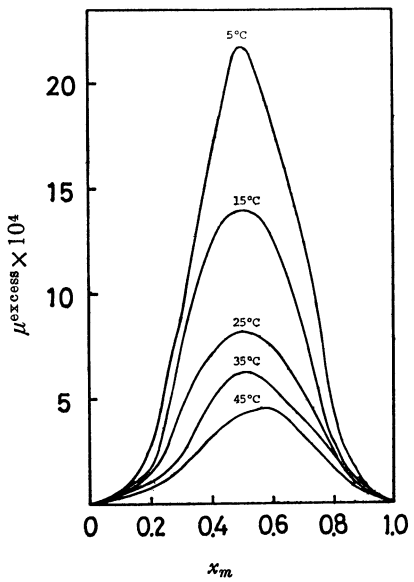

Fig. 3. Excess absorption plotted against x_m at various temperatures.

T/°C	5	15	25	35	45
ΔV_m/cm^3 mol^{-1}	1.12	0.93	0.74	0.67	0.61

These values have been determined on the assumption that the thermal contribution to the relaxation strength of the ultrasonic absorption is negligible compared with the isothermal one. In other words, the observed behavior in the ultrasonic absorption has been ascribed to the volume changes of complex formation between DMF and water. Denote these values of ΔV_m by ΔV_m^{ls}. If we consider that the thermal contribution is dominant in the ultrasonic absorption behavior, the contribution denoted by the enthalpy change, ΔH_m^{th}, can also be estimated. ΔH_m^{th} is obtained with recourse to this equation:

$$V\theta\Delta H_m^{th} = C_p\Delta V_m^{ls} \quad (7)$$

where θ is the volume expansibility of the solution. The basis of Eq. 7 is that the same value of μ_{max}^{excess} is produced either by ΔV_m^{ls} or ΔH_m^{th}. Therefore, the values of ΔH_m^{th} determined by Eq. 7 correspond to those at the maximum contribution. Using the values of $\Delta V_m \simeq 1$ cm^3/mol and θ and C_p data at $x=$ 25 found in the literature,[13] $\Delta H_m^{th} \simeq 5.06$ J/mol. This value gives the temperature dependence of K_m: 10.7 at 5 °C and 9.4 at 45 °C. The small variations in K_m with the temperature well correspond to the experimental fact that the mean width of the peak in Fig. 3 is almost independent of the temperature in the present system.

The values of ΔV_m^{ls} is small in comparison with the results found in the systems of acetone–, dimethylamine–, methyldiethylamine–, and *n*-amylamine–water.[14] The complex formation in the aqueous solution of DMF produces rather minor changes in the intermolecular distances between DMF and water molecules. The complex formed in the solution becomes looser with an increase in the temperature, as is seen in the variation of ΔV_m with the temperature. This fact confirms the views described in our preceding paper[1] that the structure of the complex in amide–water systems may not be similar to those in an ordinary clathrate-like 17 hydrate or $8X \cdot 136H_2O$.

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