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Brillouin Scattering Study of Clathrate Hydrate Formation in Acetone-Water Solution

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Light scattering spectra have been observed for binary solutions of acetone and water at 24, 34, and 44 °C in the concentration range of $0 \leq x_{AC} \leq 0.25$, where x_{AC} is the mole fraction of acetone. The hypersonic velocities and the adiabatic compressibilities at 4.5 GHz were obtained from the observed values of Brillouin shifts. The observed concentration and temperature dependencies of the adiabatic compressibility were interpreted by assuming the existence of clathrate hydrate-like local structures in the solutions. The adiabatic compressibilities for binary solutions of *t*-butyl alcohol (TBA) and water were used as reference data. A comparison is made between the local structure formed in the acetone–water solution and that in the TBA–water solution.

Molecules such as tetrahydrofuran, *t*-butyl alcohol (TBA), and acetone are known to form solid clathrate hydrates.[1,2] Recently, Iwasaki *et al.* have observed the concentration and temperature dependencies of the mean-square concentration fluctuations for the binary solutions of TBA–water by means of light scattering.[3] In their study, the existence of local structures of the type $(H_2O)_l$TBA ($l \simeq 20$) has been suggested. The results of the X-ray diffraction analyses for the structure of solid clathrate hydrate have contributed to the following picture for the mixing state of the TBA–water mixtures. In the concentration range of $0 < x_{TBA} < 0.05$, a TBA molecule forms a polyhedron which is surrounded by water molecules; the polyhedra are dispersed in water (x_{TBA} is the mole fraction of TBA). In the concentration range of $0.05 < x_{TBA} < 0.15$, aggregates of several polyhedra are dispersed in TBA. At $x_{TBA} \simeq 0.05$, the number of molecules which take part in the clathrate hydrate formation becomes a maximum.

We believe that the above picture can be applied to the other aqueous solutions of non-electrolytes which are known to form solid clathrate hydrates. In the present study, the mixing state for the acetone–water system will be discussed through the observation of hypersonic velocity obtained from the Brillouin scattering measurements. Hypersonic velocity affords information about the structuring of a solution. For the TBA–water system, Stone *et al.* have shown that the hypersonic velocity takes a maximum value at $x_{TBA} \simeq 0.05$.[4] As the number of molecules which take part in the clathrate hydrate formation becomes maximum at this concentration for the TBA–water system, the characteristic concentration dependence of the hypersonic velocity seems to originate from the formation of the local structure of the type suggested by Iwasaki *et al.* An acetone molecule also forms a solid clathrate hydrate at about −35 °C.[5] We will interpret the concentration dependence of the hypersonic velocity or the adiabatic compressibility of the acetone–water solution based on the assumption that clathrate hydrate-like local structures exist in the solution. The mean-square concentration fluctuations could not be obtained accurately for the present system because the Rayleigh intensity arising from the concentration fluctuation is not so strong as that arising from the entropy fluctuation.

Experimental

The light scattering spectrometer used in the present study was designed and constructed in our laboratoly. Figure 1 shows the schematic diagram of the spectrometer. The light source is a He-Ne laser (NEC GLG 5800) which produces 50 mW power at 632.8 nm. The laser beam is irradiated on a sample cell made of quartz. The scattered light at 90° is directed into a piezoelectrically driven Fabry-Perot interferometer (Burleigh RC 110). After being passed through the interferomer, the light is focussed by a telemeter lens into a pinhole. The central spot of the interferometer ring system is then detected by a photomultiplier (HTV R-649). The photomultiplier signal is amplified, discriminated, and then put into a multichannel analyzer (Camberra Series 30) by which the spectra are averaged over many times. A stabilization system (Burleigh DAS 10, RC 43) was used for the elimination of the axial drift of the interferometer cavity and for maintaining the parallelism of the etalon. The free spectral range was 0.625 cm^{-1} and the finesse was about 20.

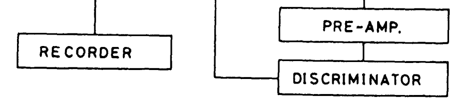

Fig. 1. Block diagram of the light scattering spectrometer.

Acetone was purchased from Wako Pure Chemical Industries, Ltd., and used after distillations. Water was distilled after being passed through an ion exchange resin. The binary mixtures of acetone–water were made dust-free by the use of Millipore filter FG with a pore size of 0.2 μm. The temperature of the sample was controlled by a high temperature cell. A temperature constancy of ±0.5 °C was obtained with the apparatus. The light scattering spectra were observed at 24, 34, and 44 °C. The refractive index of the sample was measured by means of an Atago Abbe refractometer; the results are shown in Table 1.

Table 1. Values of refractive indices (n) and densities (ρ) used for the calculations of v_s and κ_s

x_{AC}	n			$\rho^{a)}$		
	24 °C	34 °C	44 °C	24 °C	34 °C	44 °C
0	1.3326	1.3314	1.3299	0.9972	0.9940	0.9905
0.0200	1.3368	1.3355	1.3338	0.9890	0.9854	0.9810
0.0346	1.3400	1.3362	1.3365	0.9832	0.9790	0.9740
0.0493	1.3427	1.3407	1.3388	0.9760	0.9730	0.9678
0.0600	1.3450	1.3430	1.3407	0.9734	0.9680	0.9620
0.0793	1.3476	1.3452	1.3432	0.9675	0.9613	0.9555
0.0966	1.3497	1.3478	1.3448	0.9618	0.9555	0.9488
0.1256	1.3530	1.4505	1.3475	0.9525	0.9452	0.9378
0.1480	1.3555	1.3522	1.3495	0.9448	0.9372	0.9293
0.2002	1.3584	1.3551	1.3518	0.9291	0.9203	0.9110
0.2490	1.3612	1.3573	1.3538	0.9145	0.9041	0.8950

a) Ref. 9.

Results and Discussion

Hypersonic Velocity and Adiabatic Compressibility. The sound velocity, v_s, and the adiabatic compressibility, κ_s, at 4.56 GHz were obtained from the observed Brillouin shifts, $\Delta\nu$, by the relations[6]

$$v_s = \frac{c\lambda_0}{2n\sin(\theta/2)}$$

and

$$\kappa_s = (v_s^2\rho)^{-1},$$

where c is the velocity of light, λ_0 the wavelength of the incident light in a vacuum, n the reftactive index of the sample, θ the scattering angle, and ρ the density.[9] In Figs. 2 and 3, the observed v_s and κ_s are plotted against the mole fraction of acetone, x_{AC}, for different temperatures. It is seen from these figures that v_s (or κ_s) takes a maximum (or minimum) value at $x_{AC}\simeq 0.1$ for 24 °C and $x_{AC}\simeq 0.05$ for 44 °C. These results suggest that some sort of long-range structures are formed in the binary solution of acetone–water, especially in the concentration range around $x_{AC}=0.1$.

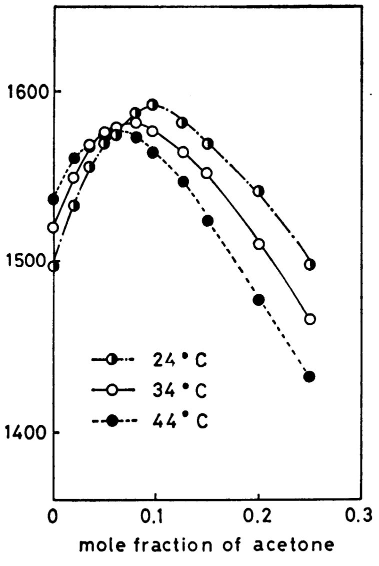

Fig. 2. Concentration dependence of hypersonic velocity for acetone–water system at 24, 34, and 44 °C.

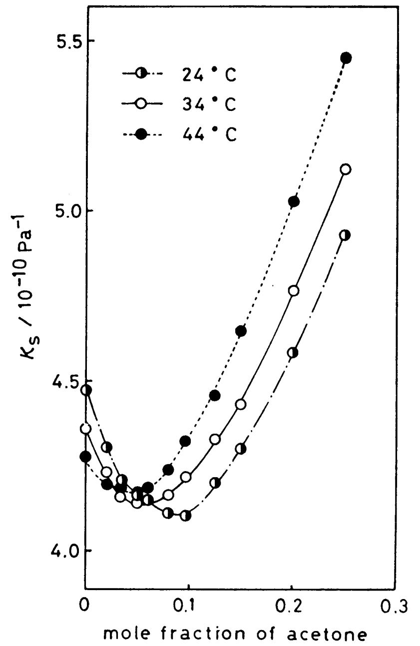

Fig. 3. Concentration dependence of adiabatic compressibility for acetone–water system at 24, 34, and 44 °C.

Mixing State of Acetone–Water Solution. X-Ray diffraction analysis has shown that an acetone molecule forms a solid clathrate hydrate with several water molecules at about −35 °C.[5] The chatacterstic concentration dependence of v_s or κ_s may arise from the clathrate hydrate-like local structure formation in the solution. If the composition of such a structure is of the type $A(H_2O)_l$ where A is acetone, κ_s is expected to take a minimum value at $x_{AC}=1/(l+1)$, because the number of the molecules which do not take part in the clathrate formation becomes minimum at $x_{AC}=1/(l+1)$. Figs. 2 and 3 show that the number ratio of water molecules to acetone molecules in the local structure (we will call this ratio R, from now on) is about 10 at 24 °C and about 20 at 44 °C.

It has been established that water molecules in a solid clathrate hydrate form polyhedra, each of which encages a guest molecule.[1,2] More than 24 water molecules are necessary to form a polyhedron which can encage a molecule as large as an acetone molecule. In the case of a solid hydrate, however, several polyhedra share one of their faces (we will call this "association of polyhedra") and, therefore, R can become less than 24. For example, R is 7⅔ or 5¾ for "structure I" and 17 for "Structure II."[1,2] As R obtained from the observed κ_s is 10 at 24 °C, it may be concluded that polyhedra associate to some extent in the solution at this temperature.

If the concentration of acetone is very low, however, association of polyhedra cannot be expected. Therefore, R may be 24 or more. As the concentration increases, it is expected that the polyhedra begin to associate with each other near $x_{AC}\simeq 0.04$ because almost all the water molecules form polyhedra at this concentration. The slowing down of the gradient change of κ_s near

$x_{AC}\simeq 0.05$ at 24 °C may reflect this situation.

In the concentration range of $0.05<x_{AC}<0.1$, κ_s continues to decrease with the increase of x_{AC}. This fact suggests the growth of the local structures with the increase of the concentration. With the increase of x_{AC} up to 0.1, the association degree of the polyhedra increases and, therefore, R decreases down to 10. Since an acetone molecule is known to form a solid clathrate hydrate of the Structure II ($R=17$), at least 17 water molecules are thought to be necessary to form a stable local structure of a clathrate hydrate type. Therefore, the local structure formed at $x_{AC}\simeq 0.1$ ($R=10$) may be more unstable than the local structure formed at $x_{AC}\simeq 0.05$ ($R=20$). In fact, κ_s increases as the temperature increases near $x_{AC}\simeq 0.1$, while κ_s is almost independent of the temperature near $x_{AC}\simeq 0.05$.

In the concentration range of $x_{AC}>0.1$, κ_s increases rapidly with the increase of the concentration. This suggests that the number of acetone molecules which are not encaged by water molecules increases with the increase of x_{AC}. Thus, it can be imagined that the associated polyhedra begin to be separated by acetone molecules at $x_{AC}\simeq 0.1$.

Burton has measured the ultrasonic velocity at 1 MHz for the acetone–water solution at 27 °C and found that v_s takes a maximum value at $x_{AC}\simeq 0.05$.⁷⁾ However, our results at 4.5 GHz show that v_s takes a maximum value at $x_{AC}\simeq 0.1$ at room temperature. This difference is considered to come from the fact that the life-time of the local structure, τ, is dependent of concentration. τ at $x_{AC}\simeq 0.1$ may be much shorter than the period of the ultrasonic wave, but may be longer than that of the hypersonic one. On the other hand, τ at $x_{AC}\simeq 0.05$ may be longer than the period of the ultrasonic wave.

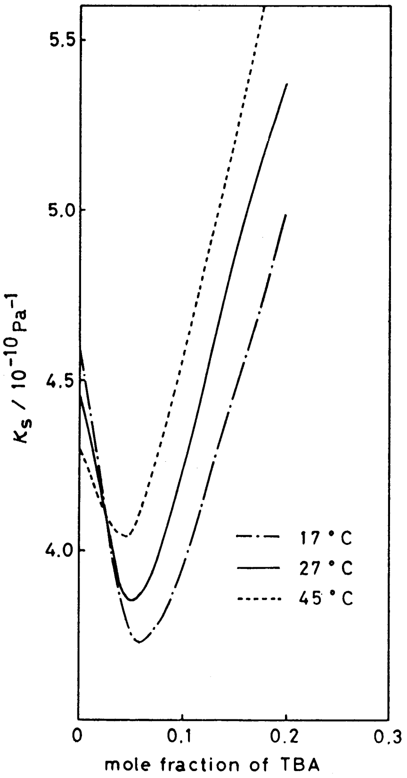

Fig. 4. Concentration dependence of adiabatic compressibility for *t*-butyl alcohol (TBA)–water system at 17, 27, and 45 °C calculated from the hypersonic velocity data of Stone *et al.*⁴⁾

Comparison with TBA–Water System. Stone *et al.* have measured the hypersonic velocity for the TBA–water system at 6 GHz. Figure 4 shows the adiabatic compressibility for the system calculated from their sound velocity data. It is seen from the figure that κ_s takes a minimum value at x_{TBA} is about 0.06 (at 17 °C), 0.05 (at 27 °C), or 0.045 (at 45 °C). These data can be reduced to the R values of 16 (at 17 °C), 19 (at 27 °C), and 21 (at 45 °C). Iwasaki *et al.* have obtained the R values of 17 ± 2 at 17 °C and 21 ± 2 at 65 °C from the analyses of the concentration dependence of the concentration fluctuation.³⁾ The R value at 17 °C obtained from the adiabatic compressibility is in agreement with that obtained from concentration fluctuation at the same temperature. Moreover, those R values obtained from the measurements of the adiabatic compressibility and the concentration fluctuation have similar temperature dependences. These facts confirm the R values obtained for the acetone–water system in our present study. The R value for the acetone–water system at room temperature is smaller than that for the TBA–water system. This difference seems to come from the difference between acetone and TBA in the size of the hydrophobic group of the molecule. The number of molecules which can encage an acetone molecule may be smaller than that for a TBA molecule.⁸⁾

Figures 3 and 4 also show that the minimum values of κ_s for the acetone system are larger than those for the TBA system. This difference may also originate from the difference in hydrophobicity between acetone and TBA. The more hydrophobic a solute molecule is, the more stabilization energy is required for dissolution. Thus, the hydrate-like structure for the TBA system becomes more stiff than that for the acetone system.

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