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Effect of an Ionic Surfactant on the Kinetic Properties of an Aqueous Nonelectrolyte Solution Studied by Ultrasonic Methods

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In order to investigate the effect of ionic surfactant on the dynamic properties of nonelectrolyte aqueous solutions, the ultrasonic absorption, velocity and the conductivity have been measured for aqueous solutions of triethylene glycol monobutyl ether (TGBE) in the presence of sodium dodecyl sulfate (SDS) at 25 °C. In aqueous solution of TGBE, a clear single relaxational ultrasonic absorption is observed in the MHz frequency range. When SDS is added the relaxation process is observed in the more dilute solutions, the relaxation frequency shifts to lower frequency and the amplitude of the excess absorption increases in the TGBE concentration range of less than 1.0 mol dm^{-3}. Further, for TGBE concentration greater than 1.0 mol dm^{-3}, the relaxation frequency is found to be almost independent of SDS concentration and the amplitude of the excess absorption decreases with increasing SDS concentration. The observed relaxation is well accounted for by a kinetic scheme involving the interaction between the nonelectrolyte and water. From the concentration dependence of TGBE, the rate and thermodynamic parameters have been determined as a function of SDS concentration. The obtained data have been interpreted in terms of the structural changes of the solvent water by SDS molecules. As the results, it has been proposed that the hydrophobic parts of SDS have a considerable effect on water structure.

It has been proposed that the MHz frequency ultrasonic absorptions in aqueous solutions of nonelectrolytes containing hydroxyl groups are well accounted for the two relaxations by mechanisms involving an interaction between the solute and solvent and a molecular aggregation of the solutes.[1-4] The former process is observed in most of the solutions studied, whereas the latter is limited to solutions of solutes containing large hydrophobic groups.

On the other hand, it is generally accepted that micellar surfactant solutions solubilize sparingly water-soluble compounds. Many nonelectrolytes are not soluble enough to allow examination of their dynamic properties by ultrasonic methods. The ability of the surfactant to solubilize the nonelectrolyte provides an apparent homogeneous aqueous nonelectrolyte system and also allows studies of the phenomena associated with cosurfactants, which are very important in understanding microemulsions.

Zana et al.[5,6] have measured ultrasonic absorptions in aqueous solutions of butanol and hexanol in the presence of surfactants. They have interpreted the observed relaxation by a model involving an exchange reaction of the nonelectrolyte between the micellar and bulk phase in these solutions. Hall et al.[7-9] have also analyzed the relaxation process observed in aqueous alcohol solutions of other surfactants using a similar kinetic model and also a phenomenological treatment. In addition, an ultrasonic study concerning the effect of surfactant on the relaxation properties of aqueous solutions of 2-butoxyethanol (ethylene glycol monobutyl ether) was also performed by Verrel et al.[10] and they also accounted for the observations by the same analysis as Zana's. A very recent study by Verrall's[11] group showed that there exist a clathrate aggregate of alcohol with water in aqueous solution of 2-butoxyethanol and a surfactant. However, it is evident that the excess absorption or relaxational absorption of the ultrasound in the MHz frequency range exists in aqueous solutions of highly soluble alcohols. In the solution of 2-butoxyethanol, for example, a clear excess absorption is observed even at 0.7 mol dm^{-3}.[12] It is very important to prove if the observed relaxation corresponds to the interconversion of such nonelectrolytes between micelles and the bulk phase. For this purpose, we have chosen triethylene glycol monobutyl ether (TGBE) and sodium dodecyl sulfate (SDS) as solutes. In aqueous solutions of TGBE,[4] a clear single relaxational absorption is observed in the frequency range of 6.5 to 220 MHz, while in aqueous SDS solution, no excess absorption is found in the same frequency range up to 0.1 mol dm^{-3} concentration.[13] Therefore, such a ternary system may be very suitable for studying the effect of surfactant on the ultrasonic properties. Though too much time has been required to accumulate such desirable ultrasonic data by a pulse method, our recent semiautomatic equipment[2] has made it possible to perform such experiments much faster.

Experimental

Triethylene glycol monobutylether (TGBE) was purchased from TOKYO Kasei Co. Ltd. and was distilled once. Sodium dodecyl sulfate (SDS) was from BDH Chemicals Ltd. and was used without further purification. Doubly distilled water was used as a solvent. The concentrations of TGBE were determined by weighing. A stock solution of SDS was prepared and it was added to TGBE solutions in order to obtain the desired concentrations of SDS.

Ultrasonic absorption measurements were performed by the computerized pulse method in the frequency range from 6.5 to 220 MHz using three cells with 0.5, 5, and 20 MHz fundamental x-cut transducers. The detailed description of the apparatus was reported elsewhere.[2] Sound velocity was measured by means of an interferometer at 2.5 MHz and by a sing around method at 1.92 MHz. By both methods, the absolute values of the sound velocity were obtainable with a precision of ±1 m s^{-1} and the relative values by the sing around method were reproducible to within ±5 cm s^{-1}. All ultrasonic measurement cells were immersed in a water bath which was controlled to within ±0.002 °C. Conductivity measurements were carried out on a conductivity meter (Yanagimoto Model MY-7). All measurements were made at 25 °C.

Results and Interpretation

Figure 1 shows a representative ultrasonic absorption spectrum in aqueous solutions of TGBE with SDS present at 25 °C. In the concentration range of TGBE from 0.2 to 1.7 mol dm^{-3} and that of SDS from 1 to 100 mmol dm^{-3}, the observed spectra are all satisfactorily fitted to an equation which is characteristic of a single relaxation process:

$$\alpha/f^2 = A/[1+(f/f_r)^2]+B, \tag{1}$$

where α is the absorption coefficient, f the frequency, A the amplitude of the excess absorption, f_r the relaxation frequency and B the background absorption including the classical absorption.[14] These parameters, f_r, A, and B, have been determined by a least mean square method described in detail elsewhere.[4] Figure 2 shows the TGBE concentration dependence of the relaxation frequency at various concentrations of SDS. At low concentrations of SDS (less than 5 mmol dm^{-3}), the plot indicates a minimum, while it seems to increase monotonically when SDS is present at a concentration greater than 20 mmol dm^{-3}. Another interesting feature is that the relaxation frequency at more than 1.0 mol dm^{-3} of TGBE falls on almost a same line even if the concentration of SDS is changed.

The excess absorption amplitudes as a function of TGBE are shown in Fig. 3 at various concentrations of SDS and it is seen that they indicate maxima, i.e. the peak sound absorption concentrations. Without SDS, the excess absorption is only observed in the TGBE concentration range of more than 0.60 mol dm^{-3}. However, when SDS is added the excess absorption is found in more dilute solutions of TGBE. For example when the SDS concentration is 100 mmol dm^{-3}, the

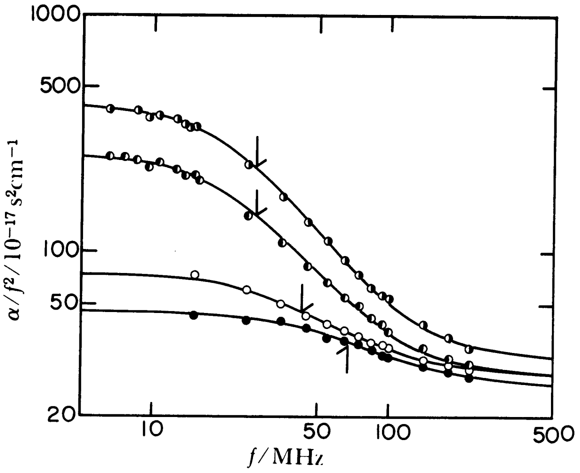

Fig. 1. Representative ultrasonic absorption spectra in 0.60 mol dm^{-3} TGBE aqueous solution at various SDS concentration at 25 °C. The arrows show the positions of the relaxation frequencies. ●; 0 mmol dm^{-3}, ○; 1.5 mmol dm^{-3}, ◐; 20 mmol dm^{-3}, ◑; 100 mmol dm^{-3}.

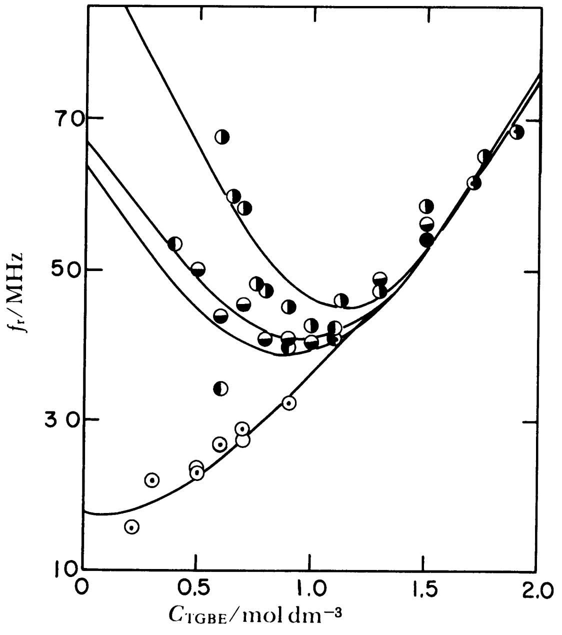

Fig. 2. TGBE concentration dependence of the relaxation frequency as a function of SDS at 25 °C. The solid curves are those calculated using the determined β, k_b, K_{12} values. The calculated values at 20 and 100 mmol dm^{-3} SDS solutions are almost same. ◑; 0 mmol dm^{-3}, ◒; 1.5 mmol dm^{-3}, ◐; 5 mmol dm^{-3}, ⊙; 20 and 100 mmol dm^{-3}.

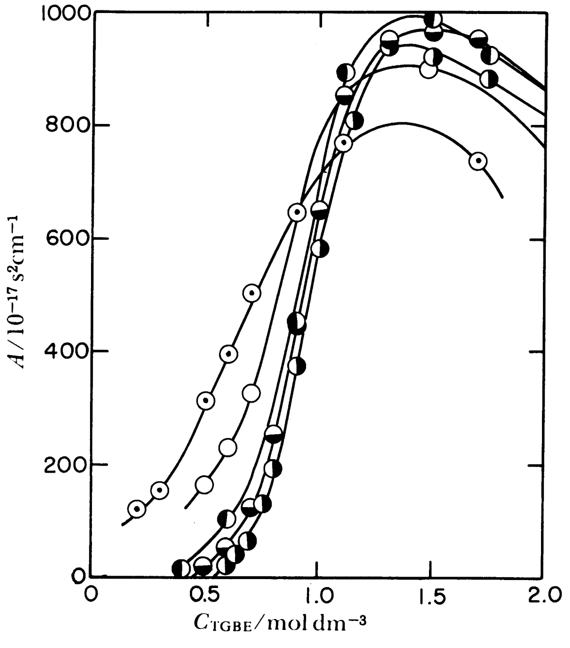

Fig. 3. TGBE concentration dependence of the amplitude of the excess absorption at different SDS concentrations. ◑; 0 mmol dm^{-3}, ◒; 1.5 mmol dm^{-3}, ◐; 5 mmol dm^{-3}, ○; 20 mmol dm^{-3}, ⊙; 100 mmol dm^{-3}.

excess absorption is clearly observed even at 0.20 mol dm^{-3} of TGBE. The amplitude of the excess absorption depends on the concentrations of both SDS and TGBE.

In order to see if micelles are formed in the solutions, sound velocity and conductivity measurements have been carried out. The former results are shown in Fig. 4 and the latter in Fig. 5. In 0.60 mol dm^{-3} solution of TGBE, a break point has been found in the sound velocity at 6.2 mmol dm^{-3} SDS concentration and in the conductivity at about 7 mmol dm^{-3}. These results indicate that the addition of TGBE decreases the critical micelle concentration (cmc) because the cmc for SDS solution is 8.3 mmol dm^{-3}.[15]

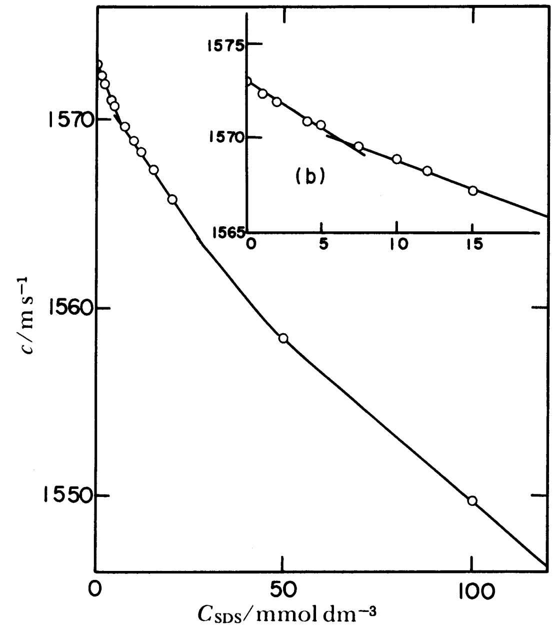

Fig. 4. SDS concentration dependence of the sound velocity at 0.60 mol dm^{-3} TGBE. The break point has been seen at about 6.2 mmol dm^{-3}. In (b), the scale of the concentration is expanded.

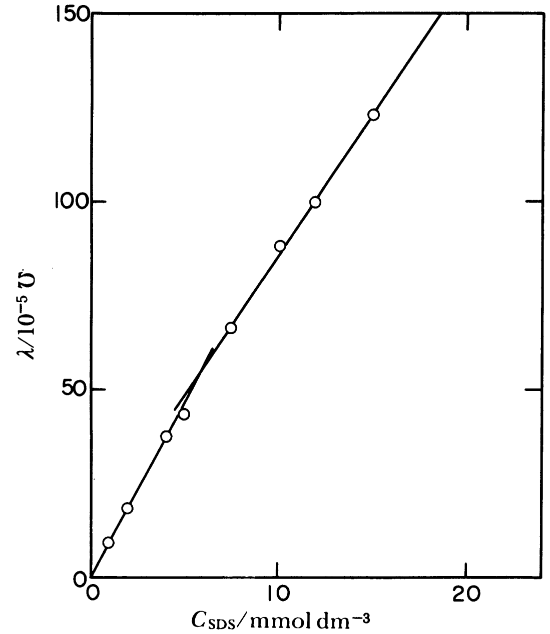

Fig. 5. SDS concentration dependence of the conductivity at 0.60 mol dm^{-3} at 25 °C. At 7 mmol dm^{-3} SDS, the two straight lines intercect.

In aqueous solution of SDS it has been reported that the ultrasonic relaxational absorption is observed far below the MHz frequency range.[13] Even if the surfactant is added to the aqueous solutions of TGBE, the ultrasonic spectra can be well expressed by a single relaxational equation and the ultrasonic relaxation parameters change gradually with the concentration of SDS. Therefore, it may be considered that the cause of the excess absorption in the TGBE solutions with SDS present is associated with the same mechanism as that observed in the absence of SDS. Therefore, we may interpret the relaxation phenomena in terms of a similar reaction mechanism. It is represented as follows:[3]

$$\mathrm{AB} \underset{k_f}{\overset{k_f}{\rightleftarrows}} \mathrm{A}+\mathrm{B} \tag{2}$$

where k_f and k_b are the forward and reverse rate constants, A the solute and B the solvent, and AB the complex formed between the solute and the solvent. In order to analyze the relaxation process, it is a reasonable assumption that water exists in hydrogen honded and nonhydrogen bonded states. Only the latter molecules may participate in the reaction. The relationship between the relaxation frequency and the analytical concentrations is derived to be[3]

$$2\pi f_r = k_b[(C_{TGBE} - \beta C_w + K_{12})^2 + 4\beta C_w K_{12}]^{1/2}, \tag{3}$$

where C_{TGBE} and C_w are the analytical concentrations of TGBE and water, β the fraction of nonhydrogen bonded water and K_{12} is defined as $K_{12}=k_f/k_b$. Under the assumption that the rate and thermodynamic parameters in Eq. 3 are independent of TGBE concentration, a nonlinear least mean square computer program has been used in order to determine the three parameters, β, k_b, and K_{12} at the various concentrations of SDS. In Table 1, the experimental results are shown and the solid lines in Fig. 2 represent f_r's which are calculated according to Eq. 3 and using these values.

The excess absorption amplitude is related to the reaction parameters as follows:[16]

$$\mathrm{A} = (\rho c/f_r)(\Gamma/RT)(\Delta V - \alpha_p \Delta H/\rho C_p)^2 (C_p^\infty/C_p), \tag{4}$$

Table 1. Rate and Thermodynamic Constants for Aqueous Solutions of Triethylene Glycol Monobutyl Ether with Sodium Dodecyl Sulfate at 25 °C

SDS	k_f	k_b	β
mmol dm^{-3}	10^7 s^{-1}	10^8 mol^{-1}dm^3 s^{-1}	
0	4.6±0.3	3.5±0.2	0.0285±0.0006
1.5	5.3±0.4	3.1±0.2	0.0225±0.0004
5.0	5.1±0.4	2.9±0.2	0.0216±0.0011
20	4.9±1.5	2.2±0.7	0.0051±0.0019
100	5.0±2.0	2.2±0.7	0.0046±0.0011

where ρ is the solution density, c the sound velocity, ΔV the standard reaction volume change, α_P the thermal expansion coefficient in the high frequency limit, C_P^∞ the specific heat in the high frequency limit, ΔH the standard enthalpy change of the reaction, C_p the specific heat in the low frequency limit, and Γ the concentration term expressed by,

$$\Gamma=(1/[A]+1/[B]+1/[AB]-1/([A]+[B]+[AB]))^{-1}. \quad (5)$$

The relaxational specific heat and the relaxational thermal expansion coefficient are very small compared with those values in the low frequency limit, and the concentration dependences of these two values are not expected to contribute so much to the dependence of the amplitude of the excess absorption, A. Therefore, the most important term that controls the dependence of the excess absorption amplitude may be $\rho c\Gamma/f_r$. In order to see how they depend on the analytical concentration, the terms have been calculated as a function of TGBE concentrations at various concentrations of SDS and they are shown in Fig. 6. These calculations indicate that the amplitude of the excess absorption should increase in the low concentration range of TGBE when SDS is added, and the calculated results are consistent with the experimental data shown in Fig. 3. However, we are reluctant to make the quantitative analysis for the amplitude of excess absorption because of the lack of the definitive thermodynamic constants, e.g. the specific heat and the thermal expansion coefficient.

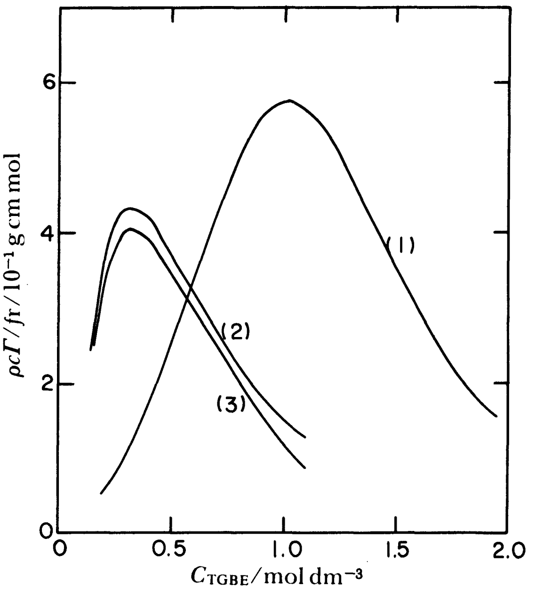

Fig. 6. The calculated $\rho c\Gamma/f_r$ values as a function of TGBE concentration. Those at 0, 1.5, and 5 mmol dm^{-3} SDS are almost identical. When SDS increases, the position of the maximum decreases. (1): 0, 1.5, and 5 mmol dm^{-3} SDS, (2): 20 mmol dm^{-3} SDS, (3): 100 mmol dm^{-3} SDS.

Discussion

Previous investigations[5-9] by ultrasonic relaxation methods for aqueous solution containing both surfactants and alcohols as solutes seem to have been focussed on the findings that no relaxation was observed for either pure surfactant solutions or for alcohol solutions, and that a relaxational absorption appears when the surfactant and alcohol are mixed. Those experiments were carried out above cmc of the surfactants because the solubilities of the solutes were limited. The relaxation time depends on the concentrations of both surfactant and alcohol. From these results the source of the relaxation was attributed to the perturbation of the equilibrium involving the exchange process of the alcohols between micelles and bulk solvent.[5-8,11] However, our ultrasonic studies[1,4] for aqueous solutions of various nonelectrolytes bearing a hydroxyl group have indicated that the water structure may be changed when a certain amount of nonelectrolyte is added, and then the relaxational absorption appears suddenly and the cause of the relaxation is due to the interaction between the solute and solvent. Under these circumstances, the present experimental study indicates that when SDS is added to the aqueous solution of TGBE the ultrasonic parameters are affected considerably by the surfactant as is seen in Figs. 2 and 3. However, the observed ultrasonic spectra are all characterized by a single relaxation process in the concentration range employed of both TGBE and SDS, and the ultrasonic parameters seem to change gradually with concentration. These experimental results lead us to believe that the cause of the excess absorption in aqueous solution of TGBE in the presence of SDS is the same as that observed when SDS is absent. That is, the equilibrium associated with the solute-solvent (TGBE-water) interaction is perturbed. The exchange reaction of the nonelectrolyte between the micellar and bulk phase may be ruled out as the cause of the observed excess absorption, though such process does exist in an other frequency range. It is worth noting that when the SDS concentration is greater than 10 mmol dm^{-3} the dependence of the relaxation frequency on TGBE concentration is quite similar to those reported so far for aqueous solutions of some alcohols in the presence of some surfactants. That is, the relaxation frequency increases approximately linearly with TGBE concentration. However, it might be expected that the exchange reaction may be observed in the pulse frequency range if the appropriate system had been chosen. That is, we do not deny the analysis for other systems studied so far.

It is easily seen that the concentration dependences of the relaxation frequency and the amplitude of the relaxational absorption are controled by the reactant concentration according to Eqs. 3—5. The reason why the relaxation frequency look to increase monotonically with TGBE concentration when SDS is more than 10 mmol dm^{-3} may be speculated as follows. The concentration of water participating in the reaction may decrease when SDS is added, and then the dominant variable for the relaxation frequency becomes the concentration of TGBE. This situation is reflected in the change of β value. The β representing the fraction of nonhydrogen bonded water or less structured water decreases with increasing concentration of SDS. This means that the SDS may also act as a water structure promoter. It should be noted that the difference in the value of parameter, β above and below cmc is remarkable.

Next, it is examined the kinetic results obtained by this investigation in light of the reaction kinetics of solute-solvent interaction. The rate constant for the dissociation of the solute-solvent complex seems to be SDS concentration independent, while the association rate constant decreases with increasing SDS concentration. This result may imply that some of the nonelectrolytes are bound to the SDS micelles and the electrorepulsive force may hinder the interaction between the water and nonelectrolyte, or that the mobility of the cosurfactants may decrease because of the existence of the micelles.

A similar micelle effect has also been observed in the kinetics of a proton-transfer reaction: the rate constant diminished when the ionic surfactants formed micelles.$^{17)}$ In order to interpret the observations more quantitatively, other surfactants should be selected and such studies are now under investigation.

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