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Ultrasonic Absorption in Dodecane Solution of Aerosol OT

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The ultrasonic absorptions of Aerosol OT in dodecane solution were measured in the frequency range 5—95 MHz at various temperatures. An excess absorption caused by single relaxation was observed above the second critical micelle concentration. This is attributed to the conformational change in structure of two kinds of Aerosol OT micelles, since the maximum excess absorption per wave length depends on the concentration and temperature. The thermodynamic and kinetic parameters were determined in relation to the reaction.

The kinetics of micelle formation in surfactant solutions have been extensively studied in aqueous solutions by means of various relaxation methods.[1–10] However, few studies have been performed on the kinetics of reverse micelles in nonpolar solvents.

Aerosol OT (sodium 1,2-bis(2-ethylhexyloxycarbonyl)ethanesulfonate) forms reverse micelles in dodecane and its solution properties have been extensively investigated by static methods.[11–13] The purpose of the present investigation is to clarify the kinetic behavior of dodecane solutions of Aerosol OT by means of ultrasonic absorption.

Experimental

Dodecane was dried on P_2O_5 and distilled under reduced pressure (8 mmHg). Aerosol OT (guaranteed reagent grade) was dried at 105 °C under reduced pressure (8 mmHg) until the weight became constant. The concentration of the sample solution was given in terms of weight.

Ultrasonic absorptions were measured at the odd harmonics of 0.5, 5, and 20 MHz X-cut quartz transducers by means of pulse technique. The frequencies of the measurement were in the range 5—95 MHz. The major mechanical features of the apparatus were reported by Tatsumoto.[14] The sound velocity was measured by the sing-around method operating at 2.0 MHz, the density being determined with a pycnometer. All the measurements were carried out at concentrations 33.4—80 wt % and at temperatures 20—40 °C.

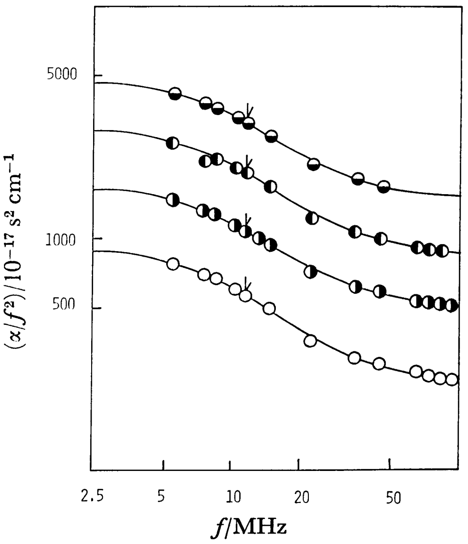

Fig. 1. Ultrasonic absorption spectra in the dodecane solutions of Aerosol OT at 20 °C. ◒ 74.5%, ◐ 67.4%, ◑ 59.1%, ○ 45.4%

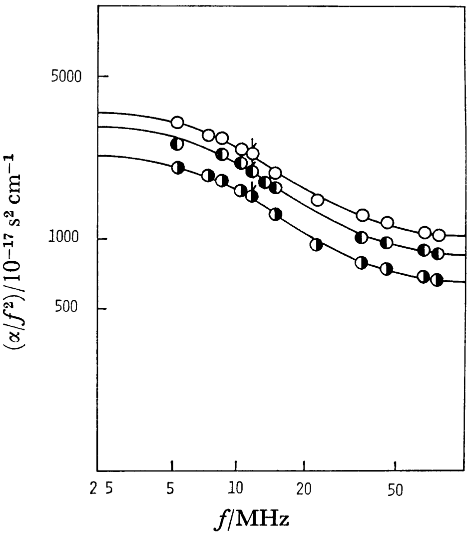

Fig. 2. Temperature dependence of ultrasonic absorption spectra in the 70% dodecane solution of Aerosol OT. ○ 20 °C, ◐ 30 °C, ◑ 40 °C

Results and Discussion

The concentration dependence of the ultrasonic absorption spectra of dodecane solution of Aerosol OT is shown in Fig. 1 and the temperature dependence of the absorption spectra in Fig. 2. All the spectra can be represented by

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

where α is the absorption coefficient, f the frequency, f_r the relaxation frequency, A the amplitude of the excess absorption, and B the residual absorption. The ultrasonic parameters A, B, and f_r were so determined as to give the best fit of the experimental data to Eq. 1. The results are given in Table 1. Figure 3 shows the concentration dependence of the sound velocity at 20 °C. We see anomaly at concentrations of *ca.* 5 and 35%. The former is equal to the first critical micelle concentration(CMC) of Aerosol OT in dodecane reported by Mattoon and Mathews.[15] The latter can thus be assigned to the second CMC. Considering that the excess absorption appears near the second CMC, the cause of the excess absorption is presumed to be associated with the second CMC of Aerosol OT. Peri[11] reported that two types of micelles exist in hydrocarbon solutions of Aerosol OT, their size changing slightly with concentration and temperature. Taking this into account together with our results in which the relaxation frequencies show no concentra-

Table 1. Ultrasonic and thermodynamic parameters of dodecane solutions of Aerosol OT at 20 °C

wt %	A (10^{-15} s^2 cm^{-1})	B	f_r (MHz)	ρ (g cm^{-3})	β (10^{-4} °C^{-1})	c (10^5 s^{-1} cm)
33.4	4.26	1.58	11.5	0.8443	7.98	1.2888
40.0	6.68	1.96	11.5	0.8663	7.82	1.2865
45.4	6.68	2.45	11.5	0.8864	7.76	1.2877
50.0	8.63	3.11	11.5	0.9022	7.54	1.2891
55.0	9.78	3.91	11.5	0.9219	7.41	1.2900
59.1	11.5	5.12	11.5	0.9397	7.23	1.2926
64.7	14.9	7.25	11.5	0.9603	6.97	1.2959
67.4	21.3	8.61	11.5	0.9720	6.67	1.3007
70.0	26.5	10.1	11.5	0.9812	5.95	1.3046
74.5	33.4	14.9	11.5	1.0035	5.22	1.3142
78.6	57.6	18.4	11.5	1.0226	4.59	1.3238
80.0	72.5	19.6	11.5	1.0267	3.80	1.3247

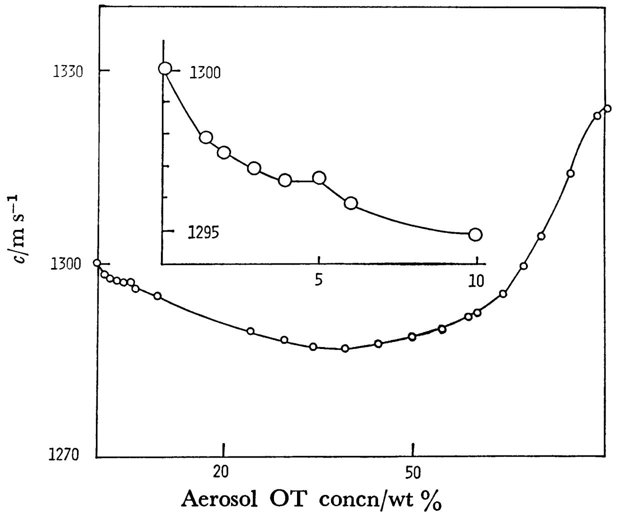

Fig. 3. Concentration dependence of the sound velocity in the dodecane solutions of Aerosol OT at 20 °C.

tion dependence (Table 1), we postulate a two state model for the relaxation mechanism:

$$\mathrm{A} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{B}, \tag{2}$$

where A and B are the two types of micelles. On the assumption that the relaxation strength is much smaller than unity and the total specific heat capacity is equal to the instantaneous specific heat capacity, the relaxation frequency and the maximum excess absorption per wave length $\mu_{\max}$ are expressed by the following equations.[16]

$$2\pi f_r = k_f + k_b, \tag{3}$$

$$\mu_{\max} = \phi\rho\pi c^2 V(\Delta V/V - \Delta H\beta/C_p)^2/2RT, \tag{4}$$

and

$$\phi = K(1-x_{\text{1st CMC}})/(1+K)^2, \tag{5}$$

where k_f and k_b are respectively the forward and backward rate constants, ρ is the density, c the sound velocity, V the molar volume, β the thermal expansion coefficient, C_p the specific heat at a constant pressure, and ΔV and ΔH are the standard volume change and the enthalpy change of the reaction, respectively. The equilibrium constant, K, is defined to be $K=x_b/x_a=k_f/k_b=\exp\{-(\Delta H-T\Delta S)/RT\}$, where x_a and x_b are the mole fraction of species A and B, respectively, and ΔS is the entropy change. With C_p values determined by the interpolation of the values given by Finke *et al.*[17] and Rihani and Doraiswamy,[18] the thermodynamic parameters, K, ΔV, ΔH, and ΔS were so determined as to give the best fit of the experimental values of $\mu_{\max}$ to Eq. 4. The values obtained are given in Table 2; the yields are shown by solid lines in Figs. 4 and 5. The parameters were also determined from the temperature dependence of $\mu_{\max}$ at a constant concentration (Table 2). The thermodynamic parameters determined by these two procedures are very close to each other, indicating that the interpretation of the excess absorption mechanism by the two state

Table 2. Thermodynamic parameters associated with the conformational change in dodecane solution of Aerosol OT

	T (°C)	K	ΔV (cm^3 mol^{-1})	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} K^{-1})
a)	20	0.089	24	9.8	29
	40	0.24	24	9.8	29
b)	20	0.089	23	9.2	27
	25	0.11			
	30	0.15			
	35	0.18			
	40	0.24			

a) Determined from the concentration dependence of $\mu_{\max}$ in the concentration range 33.4—80%. b) Determined from the temperature dependence in 70% solution.

Table 3. Rate constants for the conformational change of the micelle

T (°C)	k_f (10^6 s^{-1})	k_b (10^7 s^{-1})
20	5.9	6.6
25	7.7	6.4
30	9.4	6.3
35	11	6.1
40	14	5.8

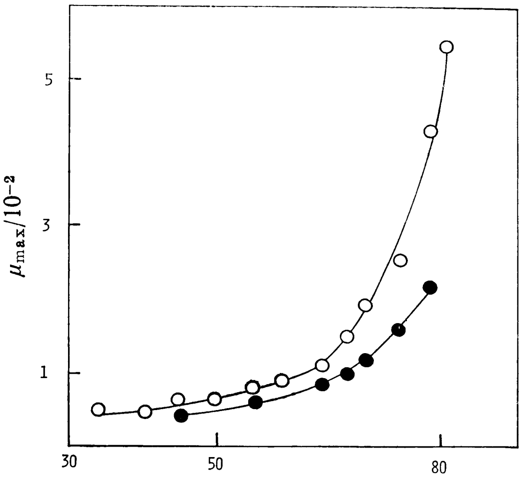

Fig. 4. Concentration dependence of the maximum excess absorption per wavelength at 20 °C (○) and 40 °C (●). The solid lines represent the theoretical curves calculated by Eq. 4 using the parameters in Table 2.

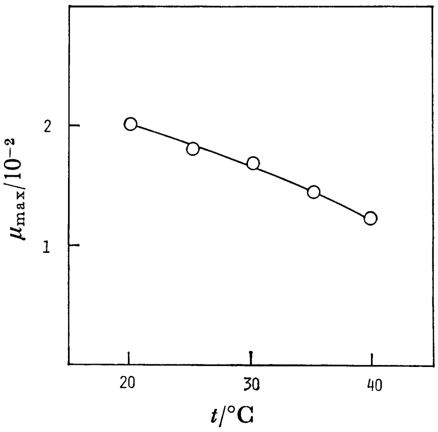

Fig. 5. Temperature dependence of the maximum excess absorption per wavelength in the 70% dodecane solution of Aerosol OT. The solid line was calculated from Eq. 4.

model is reasonable.

The forward and backward rate constants represent the rate of transition from the micelle formed above the first CMC to that above the second CMC and the rate of reverse transition, respectively. The rate constants were calculated from the relaxation frequency and the equilibrium constant at various temperatures (Table 3). The forward rate constant changes with temperature while the backward rate constant remains constant. This indicates that the free energy of activation of state B is almost constant and that of state A decreases with the temperature; micelles formed above the first CMC are destabilized with rise in temperature as compared with other micelles.

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