November, 1982] © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *55*, *3403—3406 (1982)* 3403

Kinetic Studies of the Micelle System of Octylammonium Alkanoates in Hexane Solution by the Ultrasonic Absorption Method

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(Received April 21, 1982)

Ultrasonic absorption was measured in hexane solutions of octylammonium alkanoates (nonanoate, decanoate, dodecanoate, and tetradecanoate). The value of critical micelle concentration (CMC) was determined to be 0.02 M (1 M = 1 mol dm^{-3}) for all the surfactants. The excess ultrasonic absorption, observed in the solutions above the CMC, was ascribed to the association-dissociation of the monomer to and from the micelle. From the concentration dependences of the ultrasonic parameters, the mean aggregation number of the micelle, the rate constants, and the enthalpy change of the above reaction were obtained. These results were discussed in relation to the shape of the reversed micelle and the solute-solvent interactions.

A large amount of experimental information has been provided for the physicochemical properties of micelles in aqueous solution. In the field of the kinetics, two distinct reaction processes of micelle formation have been observed in different time regions:[1-4] one is a micelle formation and decomposition and the other is an association-dissociation of the monomer to and from the micelle. On the other hand, relatively little is known with regard to the micelles in organic solvents[5-8] in spite of their important roles as catalysis, solubilizing agents, and model systems for the membranes and molecular aggregations. Especially, their kinetics have rarely been studied.[8,9] The difficulty of this study seems to be due to the following reasons: (i) since the aggregation number of the micelle is very low, an abrupt and large change of the physicochemical properties of the solution cannot be expected at the CMC, and (ii) micelle formation and monomer exchange reactions are too rapid to be observed by conventional techniques. To overcome these difficulties, the ultrasonic absorption method is a very valuable technique for the study of the dynamic features of the micelle in organic solution. In the present work we applied the technique to the hexane solution of octylammonium alkanoates of different chain lengths: *i.e.*, octylammonium nonanoate (OAN), decanoate (OADe), dodecanoate (OAD), and tetradecanoate (OAT).

The purposes of this work are to decide the reaction responsible for the relaxation absorption. to obtain the kinetic parameters concerning the reaction, and to see the effect of the chain length of the detergents.

Experimental

Octylammonium alkanoates were prepared by the method already reported,[10] and dried at room temperature under reduced pressure until the weight became constant. The melting points of the detergents were satisfactorily consistent with the corresponding literature values.[11] Hexane was dried on P_2O_5 and distilled.

Ultrasonic absorption was measured by the pulse technique in the frequency range 5—95 MHz for the solutions of the concentrations from 0.05 to 0.35 M at intervals of 0.05 M at 30 °C. Details of the apparatus have been described elsewhere.[12] The sing-around method was employed for the measurement of sound velocity. The density was measured by a pycnometer.

Results and Discussion

Since many physicochemical properties of the detergent solution change at the CMC, a number of methods have been applied for the determination of the CMC. The velocity of sound, which is used in this work, is one of them: the CMC is determined from the break point of the velocity *vs.* concentration plot. As an example, the concentration dependence of the sound velocity of OAN is shown in Fig. 1, where the CMC was determined to be 0.02 M. In the same way, the value of the CMC was obtained to be 0.02 M for OADe, OAD, and OAT. Consequently, we could not observe any difference in the CMC's of the four detergents. The relationship between the alkyl chain length and the CMC is not clear in organic solution, in contrast to that in aqueous solution. Generally, the CMC increases with increase of the lipophilic part of the detergent in organic solution.[13] But the relationship is not always straightforward. In some cases, no effect was observed, *e.g.*, octylammonium alkanoates in CCl_4;[13] the present result, constant CMC irrespective to the chain length, is another example.

Ultrasonic relaxation absorptions were observed in

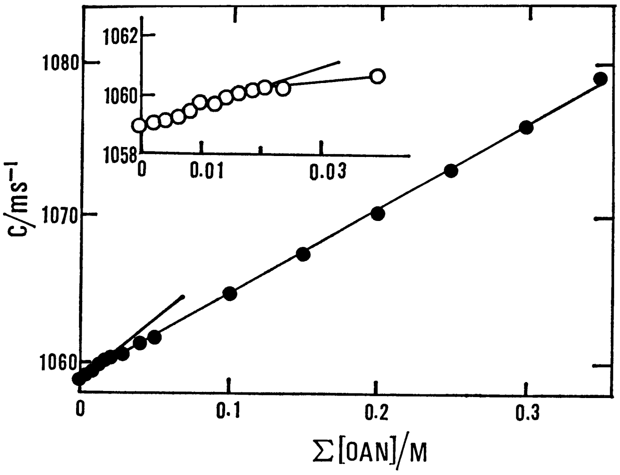

Fig. 1. Concentration dependence of the sound velocity of OAN in hexane at 30 °C.

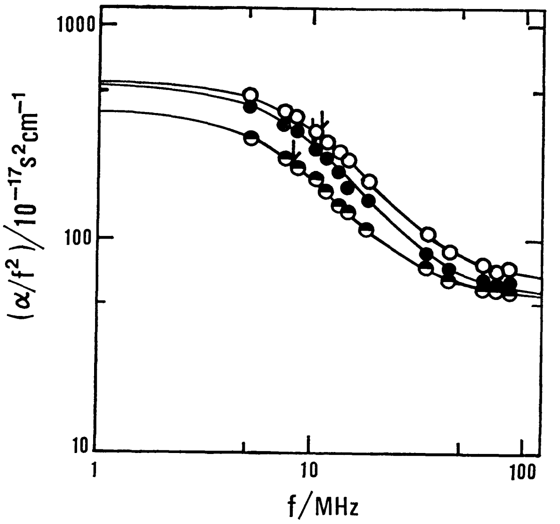

Fig. 2. Ultrasonic absorption spectra of OAT in hexane at 30 °C.
The solid lines are theoretical curves calculated by Eq. 1 with f_r, A, and B in Table 1. The arrows indicate the relaxation frequency: ◓: 0.15 M, ●: 0.25 M, ○: 0.35 M.

TABLE 1. ULTRASONIC PARAMETERS OF OCTYLAMMONIUM ALKANOATES IN HEXANE

$\frac{C}{\text{M}}$	$\frac{A}{10^{-17}\,\text{s}^2\,\text{cm}^{-1}}$	$\frac{B}{10^{-17}\,\text{s}^2\,\text{cm}^{-1}}$	$\frac{f_r}{\text{MHz}}$
	OAN		
0.05	299	54.6	5.3
0.10	303	58.6	5.9
0.15	422	55.6	6.7
0.20	485	56.6	7.1
0.25	503	58.5	7.8
0.30	519	58.1	8.7
0.35	536	60.7	9.1
	OADe		
0.05	264	50.5	5.9
0.10	354	55.6	6.6
0.15	407	60.3	7.1
0.20	485	60.6	7.6
0.25	520	61.3	8.1
0.30	537	64.1	9.1
0.35	598	64.1	9.4
	OAD		
0.05	305	54.7	6.3
0.10	304	54.7	6.9
0.15	388	62.7	7.5
0.20	432	62.7	8.3
0.25	458	60.3	9.2
0.30	511	64.7	9.7
0.35	486	61.3	10.6
	OAT		
0.05	282	48.1	6.7
0.10	331	54.6	7.5
0.15	349	54.7	8.1
0.20	443	58.5	9.0
0.25	483	54.5	9.6
0.30	468	60.3	10.1
0.35	492	64.1	10.9

all the detergent solutions in the concentration range above the CMC. Representative absorption spectra of OAT are shown in Fig. 2. Similar absorption spectra were obtained in other detergent solutions. All of the spectra were represented by the single relaxation equation:

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

where α is the absorption coefficient, f the frequency, f_r the relaxation frequency, A and B are the relaxing and nonrelaxing absorptions, respectively. The absorption parameters, f_r, A, and B, were determined by a computor so as to give the best fit of the experimental data to Eq. 1 and are listed in Table 1.

Since the relaxation absorption is observed only in the solutions above the CMC, it is clear that the present absorption is related to the micelle. As plausible reactions responsible for the present absorption, micelle formation and decomposition and association-dissociation of the monomer to and from the micelle were investigated. However, the micelle formation reaction,

$$nS \rightleftharpoons S_n, \tag{2}$$

(S=detergent monomer and S_n=micelle composed of n detergent molecules) could not give any satisfactory interpretations to the present data.

The association-dissociation of the monomer to and from the micelle,

$$S_n + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S_{n+1}, \tag{3}$$

was examined as follows. By assuming that $[S_n]=[S_{n+1}]$, the equilibrium constant is given by

$$K = \frac{k_1}{k_{-1}} = \frac{1}{[S]}. \tag{4}$$

For Reaction 3, the reciprocal relaxation time, τ^{-1} is expressed by

$$\tau^{-1}(=2\pi f_r) = k_1([S]+[S_n]) + k_{-1}, \tag{5}$$

and, furthermore, rewritten by Eq. 4 to be

$$\tau^{-1} = k_{-1}([S_n]/[S]+2). \tag{6}$$

With the relationship between the micelle concentration, $[S_n]$, and the overall concentration, C, of detergent,

$$[S_n] = \frac{C-[S]}{2n}, \tag{7}$$

Eq. 6 is rewritten as follows:

$$\tau^{-1} = k_{-1}\left\{\frac{C}{2n[S]}+\left(2-\frac{1}{2n}\right)\right\}. \tag{8}$$

The plots of the experimental data, τ^{-1} *vs.* C, are shown in Fig. 3. The fact that these points form a straight line indicates that the present absorption is based on Reaction 3. The values of k_{-1} and n were determined from the slope and the intercept of the straight line, respectively, and k_1 was calculated from k_{-1} and the equilibrium constant by Eq. 4. The values obtained are listed in Table 2.

Attribution of the absorption to Reaction 3 was further examined from the standpoint of absorption am-

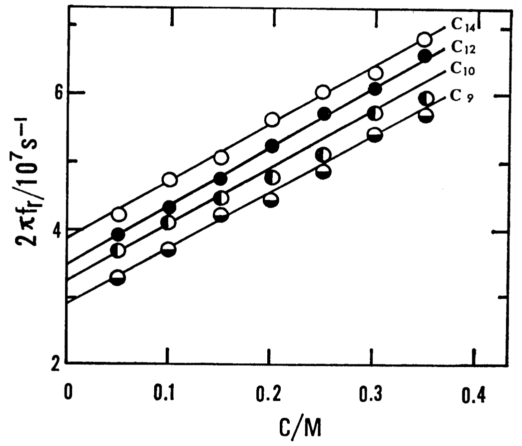

Fig. 3. Concentration dependence of the relaxation frequencies of detergent in hexane at 30 °C.

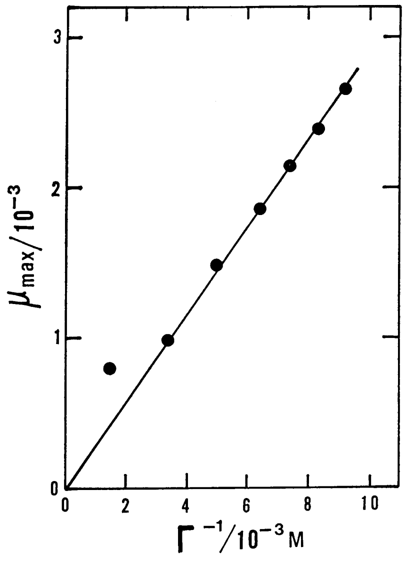

Fig. 4. The plot of $\mu_{\max}$ *vs.* Γ^{-1} for OAN in hexane at 30 °C.
The solid line represents the theoretical curve calculated by Eq. 9 using the parameters in Table 2.

Table 2. Physicochemical parameters of the micelle and the association-dissociation of the monomer to and from the micelle

Detergent	CMC / M	n	k_1 / 10^8 M^{-1} s^{-1}	k_{-1} / 10^7 s^{-1}	ΔH / kcal M^{-1}
OAN	0.02	4.8	7.6	1.5	−4.9
OADe	0.02	5.3	8.6	1.7	−5.1
OAD	0.02	5.4	9.2	1.8	−5.2
OAT	0.02	5.9	10.1	2.0	−5.4

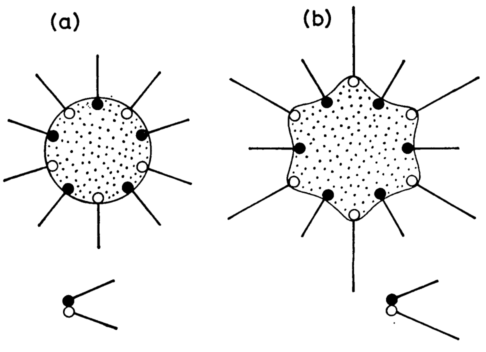

Fig. 5. Schematic representations of the reversed micelles and the monomers in hexane: (a) OAN, (b) OAT, (●——) octylammonium, and (○——) alkanoate.
The dotted region means the polar core.

plitude. The relaxation absorption per wavelength, $\mu_{\max}$, is expressed by

$$\mu_{\max} = \frac{\pi\rho C^2}{2RT}\left(\Delta V - \frac{\alpha}{\rho C_p}\Delta H\right)^2 \Gamma^{-1}, \tag{9}$$

with

$$\Gamma = \frac{1}{[S]} + \frac{1}{[S_n]} + \frac{1}{[S_{n+1}]}, \tag{10}$$

where ρ is the density, C the sound velocity, α the thermal expansion coefficient, C_p the specific heat at constant pressure and ΔV and ΔH are the standard volume change and the enthalpy change of the reaction, respectively. Since the values in the parentheses are constant for a reaction, the plot of $\mu_{\max}$ *vs.* Γ^{-1} will give a straight line which goes through the origin of the coordinates. The plots for OAN are shown in Fig. 4. Similar plots were obtained for OADe, OAD, and OAT. These results are in agreement with the above prediction, and suggest that the present relaxation absorption is based on the association-dissociation of the monomer to and from the micelle. Additional support of this assignment of the relaxation absorption will be given by the fact that the time constant of the present system falls in the range of the reported lifetime of the detergent monomers in the presence of the higher aggregates in nonpolar solvents: *i.e.*, 10^{-5}—10^{-8} s.[14]

For the reactions in organic solutions, the ΔV term is usually much smaller than the ΔH term because of the small value of ΔV and the large value of $\alpha/\rho C_p$ in the ΔH term.[15] Therefore, neglecting the ΔV term, ΔH value was obtained from the slope of the plot in Fig. 4 and is listed in Table 2.

As is well known, detergents in nonpolar solvents aggregate to form a reversed micelle, where the polar head groups locate around a polar solvent core which is often called the polar core, with the hydrocarbon chains directed outside to the solvent. Schematic second-order models of the reversed micelles of the present systems are shown in Fig. 5. In the case of OAN, since the alkyl chain length of alkanoate is about the same as that of ammonium, the lipophilic effects on them are of the same magnitude. Consequently, the surfaces of the micelle and the polar core will be as shown in Fig. 5 (a). On the other hand, in the case of OAT, the lipophilic effect on carboxylate is larger than that on ammonium. This fact will result in pulling the carboxylate out a little and enlarging the sizes of the polar core and the micelle, as shown in Fig. 5 (b). If we accept these pictures, we can attribute the increase of the aggregation number with increase of the chain length of the alkanoate, seen in Table

2, to the enlargement, or the variation of the shape, of the micelle.

Kinetics of the association-dissociation of the monomer to and from the micelle have been studied only in the aqueous solution.[16] The result indicated that there is a progressive decrease in both rate constants, k_1 and k_{-1}, with increasing the chain length of the detergent. The reason of the decrease of k_1 has been ascribed to the degree of packing, *i.e.*, how closely the monomer units are distributed on the surface of the micelle; that of k_{-1} has been thought to be due to the increase of cohesive forces between the hydrophobic ends.

These ideas were applied to the present system. With increase of the chain length of the alkanoate, the degree of packing in the micelle will decrease, in spite of the increase of the aggregation number, and therefore the detergent monomer can move into micelle more easily, *i.e.*, k_1 will increase. The increase of k_{-1} will be ascribed to the decrease of the electrostatic cohesive force between the polar head groups, which are packed less closely with increase of the chain length.

The chain length dependence of $|\Delta H|$ seems to be too small to develop a meaningful discussion now; we will attempt this after gathering the data for other surfactants in organic solvents.

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