Kinetics for Micelle-Monomer Association-Dissociation Reaction of Surfactants with Hydrophobic Counterions

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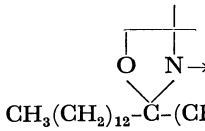
A pressure-jump technique and a spin label technique were applied to the kinetic investigation of the association-dissociation reactions between monomer and micelle in surfactant solutions of STS, TMTS, TETS, and TPTS.** The rate constants for the reactions were determined at several temperatures by the pressure-jump experiment. The ESR spectra of a spin probe, 5-SAL, solubilized in the micelles were analyzed in terms of the rotational correlation time, τ_c. A linear relationship was found between k_d, the dissociation rate constant, and τ_c^{-1}. This indicates that the dissociation rate depends on the fluidity of the micellar interior, and is in accord with the picture drawn by Aniansson *et al.* for the dissociation process. A qualitative discussion is presented on the activation parameters estimated from the present results according to the scheme presented by Aniansson *et al.*

Kinetics of relaxation processes occuring in micellar solutions have been extensively investigated using fast chemical relaxation techniques. It is established experimentally that in many surfactant solutions at least two relaxation processes exist in well-separated time domains. Kinetic information on the association-dissociation process of the monomer with the micelle is obtained from the fast relaxation time, and that on the micellization-dissolution process is obtained from the slow relaxation time.[1]

The behavior of the relaxation times associated with these two processes is affected by the counterion;[2-4] a relaxation study for micellar systems of *N*-alkylpyridinium salts with hydrophobic counterion has been reported by Hoffmann *et al.*[5] In the present work, the pressure-jump measurements were carried out for the micellar systems of tetradecyl sulfate having several types of tetraalkylammonium ions as counterion; the dissociation and association rate constants of the monomer from and with the micelle were determined from the relaxation data.

Aniansson *et al.*[1] have treated the dissociation of a surfactant monomer from the micelle as a diffusion process of a monomer in micelle perpendicular to the micellar surface; they derived an expression for the dissociation rate constant in terms of the diffusion coefficient of the leaving monomer and the free energy barrier which a monomer has to overcome to dissociate from the micelle. This model predicts that some correlation will occur between the dissociation rate and the fluidity of the micellar interior. The direct information about the fluidity can be obtained from the ESR spectra of a spin probe solubilized in the micelle. In this work, therefore, ESR measurements were also carried out with the same surfactant systems using 5-SAL (a fatty acid spin label) as a probe. The ESR spectra were analyzed in terms of the rotational correlation time, τ_c, and the relationship between τ_c and dissociation rate constant was examined.

**Abbreviations used in this paper:
STS; sodium tetradecyl sulfate, TMTS; tetramethylammonium tetradecyl sulfate, TETS; tetraethylammonium tetradecyl sulfate, TPTS; tetrapropylammonium tetradecyl sulfate, 5-SAL; 2-tridecyl-2-[3-(carboxyl)propyl]-4,4-dimethyloxazolidin-3-yloxyl



$CH_3(CH_2)_{12}$-C-$(CH_2)_3COOH$.

Experimental

Materials. The surfactants used in this study were prepared by the following procedure.[6]

STS was prepared by the usual method from tetradecyl alcohol purified by the fractional distillation. This STS was converted to silver tetradecyl sulfate (AgTS) by repeated crystallization in aqueous solution of $AgNO_3$ at about 30 °C followed by repeated recrystallization from water. The content of Ag^+ in AgTS was assayed to be in agreement with the calculated value within 0.5% by titrating ethanolic solution of AgTS with a standard aqueous solution of NaCl, using K_2CrO_4 as an indicator.

TMTS, TETS, and TPTS were prepared by double decomposition of the above mentioned AgTS with tetramethylammonium chloride, tetraethylammonium chloride, and tetrapropylammonium iodide, respectively, in ethanol. These halides were commercial products and purified by recrystallization from ethanol. To AgTS was added a stoichiometric amount of the corresponding halide. The precipitated silver halide was removed by filtration, and a small amount of the reagents was added to the filtrate. This procedure was repeated until no precipitation was observed. The final filtrate was evaporated and the residue was dried *in vacuo*.

The spin label reagent, 5-SAL, was purchased from Syva (Palo Alto, Calif.).

Critical Micelle Concentration (CMC). The CMC's of TMTS, TETS, and TPTS were determined by the conductivity method at different temperatures. The results are summarized in Table 1, together with those of STS.

Relaxation Measurement. The pressure-jump (P-jump) apparatus with conductivity detection was described previously.[4]

ESR Measurement. ESR spectra were recorded on a JEOL model FEIX ESR spectrometer at room temperature (24±1 °C).

Sample solutions were prepared by the following procedure. A required amount of stock solution of 5-SAL in chloroform was taken into a volumetric flask to give the desired probe/surfactant molar ratio, and the solvent was completely evaporated *in vacuo*. A stock solution of the surfactant was added, and the mixture was then shaken in

the dark overnight to assure the solubilization of the probe in micelle. This surfactant-probe stock solution was diluted to prepare the solution of desired surfactant concentration.

Table 1. Critical micelle concentration (CMC) determined by electroconductivity
(10^{-3} mol dm^{-3})

Surfactant	Temperature/°C			
	10	15	20	25
TMTS	1.36	1.35	1.35	—
TETS	0.96	0.95	0.94	—
TPTS	0.55	0.57	0.59	—
STS	—	—	—	2.10

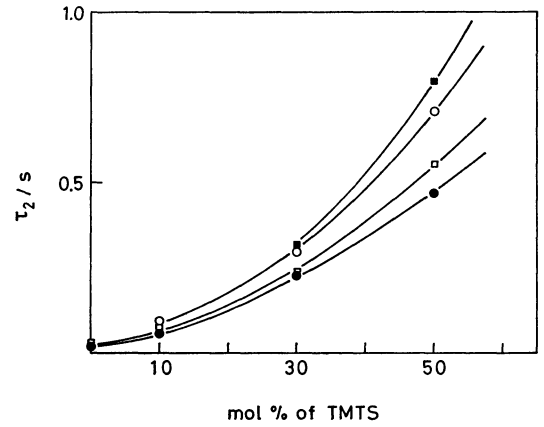


Fig. 1. The slow relaxation time, τ_2, for TMTS–STS mixed system at 25 °C.
Total surfactant concentration (mol dm^{-3}); 2.4×10^{-3} (●), 2.2×10^{-3} (□), 2.0×10^{-3} (○), 1.8×10^{-3} (■).

Results

Pressure-jump Study. It is usually difficult to observe both of the relaxation processes in micellar solution using a single relaxation technique, because of the restricted time range available for a single apparatus. Fortunately, in the case of STS, two relaxation processes can be observed by the P-jump technique.[1,7,8] However, for the present three surfactant systems, only one of the relaxations could be detected

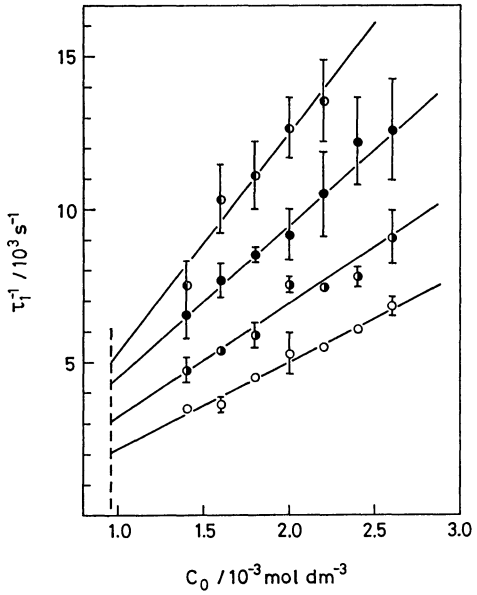


Fig. 2b. Plot of τ_1^{-1} *vs.* total surfactant concentration, C_0, for TETS at different temperatures.
○: 5 °C, ◑: 10 °C, ●: 15 °C, ◐: 20 °C. Dashed line indicates the CMC. Straight lines represent the best fit of the data by the least-squares method.

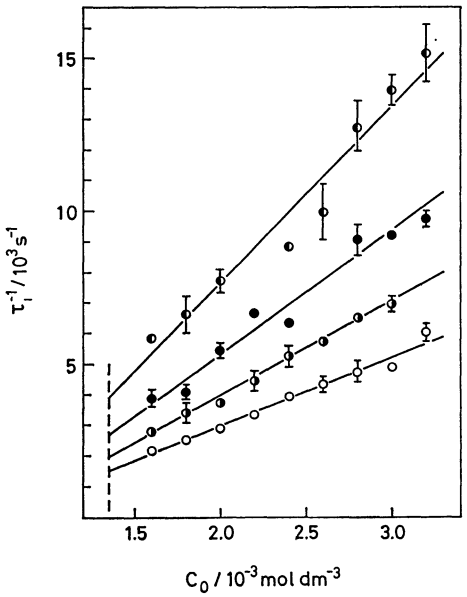


Fig. 2a. Plot of τ_1^{-1} *vs.* total surfactant concentration, C_0, for TMTS at different temperatures.
○: 5 °C, ◑: 10 °C, ●: 15 °C, ◐: 20 °C. Dashed line indicates the CMC. Straight lines represent the best fit of the data by the least-squares method.

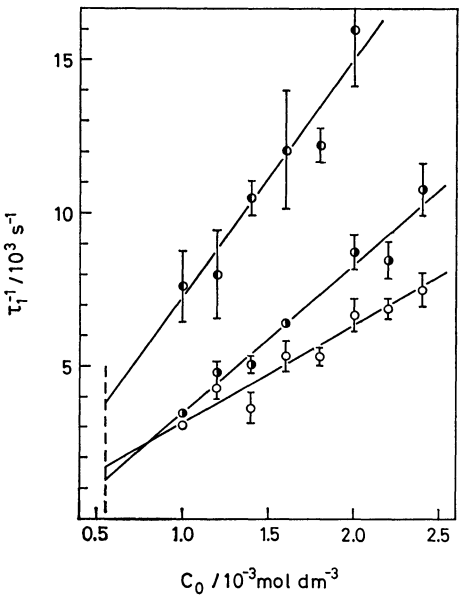


Fig. 2c. Plot of τ_1^{-1} *vs.* total surfactant concentration, C_0, for TPTS at different temperatures.
○: 5 °C, ◑: 10 °C, ◐: 20 °C. Dashed line indicates the CMC. Straight lines represent the best fit of the data by the least-squares method.

TABLE 2. VALUES OF THE KINETIC PARAMETERS FOR TETRADECYL SULFATE WITH VARIOUS COUNTERIONS

	Temp/°C	TMTS	TETS	TPTS	STS[a)]
$\frac{k_d}{10^3\ s^{-1}}$	5	$3.1_1\pm0.1_8$	$2.7_7\pm0.1_9$	$1.7_4\pm0.1_9$	—
	10	$4.1_6\pm0.1_2$	$3.5_4\pm0.3_6$	$2.6_8\pm0.2_5$	—
	15	$5.5_2\pm0.5_3$	$4.7_1\pm0.1_9$	—	—
	20	$7.9_2\pm0.6_9$	$6.8_2\pm0.9_0$	$4.7_3\pm0.6_4$	—
	25	9.8 ± 0.5	8.1 ± 0.6	6.2 ± 0.4	12.1 ± 1.5
$\frac{k_a}{10^6\ mol^{-1}\ dm^3\ s^{-1}}$	5	0.99	1.2	1.4	—
	10	1.3	1.6	2.1	—
	15	1.8	2.1	—	—
	20	2.5	3.1	3.4	—
	25	3.1	3.7	4.5	2.5
σ^2/m	5	2.1	1.4	1.0	—
	10	2.1	1.2	2.1	—
	15	2.1	1.1	—	—
	20	2.1	1.4	1.3	—
	25	—	—	—	10.8(4.3[b)])
E_d/kJ mol^{-1}		41.2 ± 2.5	39.3 ± 3.3	43.0 ± 3.8	31.4 ± 3.8

a) From the data in Ref. 7. b) From the data in Ref. 1.
Errors are standard deviations computed by linear regression analysis.

by P-jump measurement in spite of the identity of the long-chain ion with STS. From the relaxation time range and their concentration dependences, this appears to be the faster of the two processes. In order to confirm this assignment, P-jump measurements were carried out for the systems of TMTS and TETS mixed with STS. In these cases two relaxation processes were observed. The slow relaxation time, τ_2, obtained for TMTS–STS mixed system is plotted in Fig. 1 as a function of the mixing ratio at different surfactant concentration. It is seen from Fig. 1 that τ_2 increases with the fraction of TMTS and finally vanishes beyond the observation limit. A similar result was also obtained for TETS–STS mixed system. Thus, it can be concluded that the slow relaxation process for the present surfactants is too slow to be observed by the P-jump apparatus used in this study, whose effective time range is limited to within about 2 s because of the restricted stability of a high frequency bridge.

The plots of the reciprocal of the fast relaxation time, τ_1^{-1}, against the total surfactant concentration, C_0, are shown in Figs. 2a—c for TMTS, TETS, and TPTS, respectively. τ_1^{-1} increases linearly with C_0 in the measured concentration range.

The fast relaxation process in micellar solution has been assigned to the perturbation of the exchange equilibrium of a monomer between micellar and bulk phases. Some workers have applied the theory developed by Aniansson and Wall[9] for the analysis of the relaxation data.[1-3,5,8] In the previous paper,[10] some contradictions were pointed out in the kinetic parameters deduced from the Aniansson-Wall model, and a modification of the model was proposed to settle the contradictions. According to the modified treatment, the fast relaxation time is expressed by the following equation:

$$\tau_1^{-1} = \frac{mk_d}{\sigma^2} + k_d\frac{C_0-\bar{A}_1}{\bar{A}_1}, \quad (1)$$

where k_d is the dissociation rate constant of a monomer from the micelle, m the average aggregation number of the micelle, σ^2 the variance of the micellar size distribution curve which is assumed to be Gaussian, and $\bar{A}_1$ the equilibrium monomer concentration which may be approximated by the CMC.

According to Eq. 1, k_d and σ^2/m are obtained from the slope and intercept at the CMC of the straight line of τ_1^{-1} *vs.* C_0 plot. Furthermore, the association rate constant of a monomer with the micelle, k_a, is estimated from the following relation:

$$k_a = \frac{\alpha}{1-\alpha}\frac{k_d}{\bar{A}_1}, \quad (2)$$

where α represents the fraction of the surface area occupied by monomers at the micellar surface.

Applying Eqs. 1 and 2 to the present experimental results, the rate constants and σ^2/m value, which is a measure of the relative width of the distribution curve of the aggregation number, were determined. They are summarized in Table 2, together with those for STS. For the evaluation of these parameters, the CMC values listed in Table 1 were used as $\bar{A}_1$, and α was assumed to be 0.3.[10] Some uncertainty is associated with the absolute values of k_a because the exact values of α are not available for the respective surfactants. However, the relative values of k_a listed in Table 2 can be compared for the different surfactants under the following assumptions: (i) α is mostly determined by the type of the amphiphile ion and the aggregation number of the micelle; (ii) the aggregation numbers of the relevant surfactant micelle do not differ so significantly. At 25 °C, the relaxation was too fast to be measured by the P-jump apparatus used in this study. Thus, the values in Table 2 at this temperature, which are listed for comparison with STS, are those extraporated from the temperature dependence of the rate constants (see Fig. 3).

It is seen from Table 2 that k_d values for the present systems are smaller than that for STS and also decrease with increasing hydrophobicity of the counterion. On the other hand, k_a shows the reverse change. Furthermore, σ^2/m values decrease with increasing hydrophobicity of the counterion, although

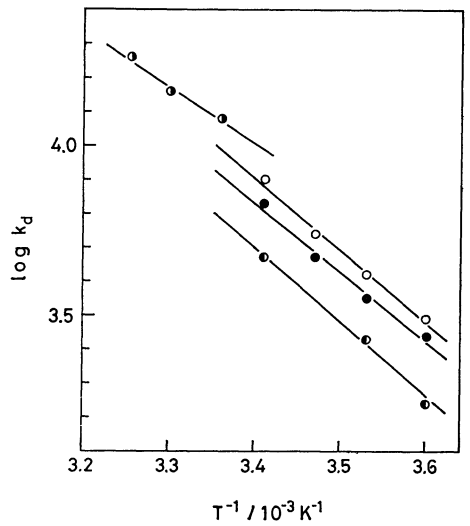


Fig. 3. Plot of log k_d *vs.* T^{-1} for different surfactant systems.
◑: STS, ○: TMTS, ●: TETS, ◐: TPTS. Straight lines represent the best fit of the data by least-squares method.

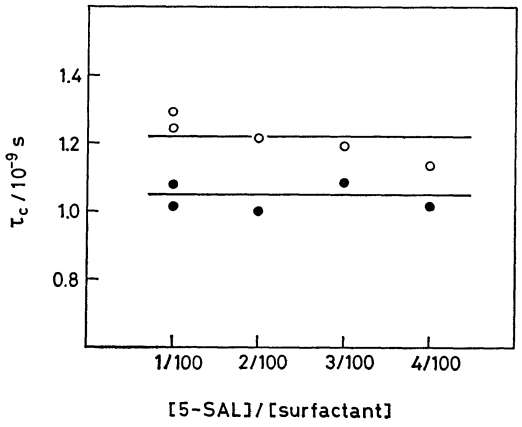


Fig. 4. Plot of τ_c against molar ratio of 5-SAL to surfactant.
●: TMTS, ○: TETS. Surfactant concentration: 1×10^{-2} mol dm^{-3}.

some scatter is seen for TPTS. This means that the micellar size distribution curve becomes narrower for micelles with hydrophobic counterions. The present results on the variation of k_d and σ^2/m are in agreement with those reported by Hoffmann *et al.*[5] for *N*-alkylpyridinium salts having hydrophobic counterion; however, opposite results are obtained for the variation of k_a.

In Fig. 3, the values of log k_d are plotted against $1/T$. The Arrhenius activation energies, E_d, for the dissociation process were determined from the slopes of the straight lines in this figure; these are also listed in Table 2. The E_d values for TMTS, TETS, and TPTS do not differ so significantly, but they are appreciably larger than that for STS.

ESR Study. The ESR spectra of the spin probe, 5-SAL, were analyzed in terms of an effective rotational correlation time, τ_c, which was calculated according to Eq. 3:

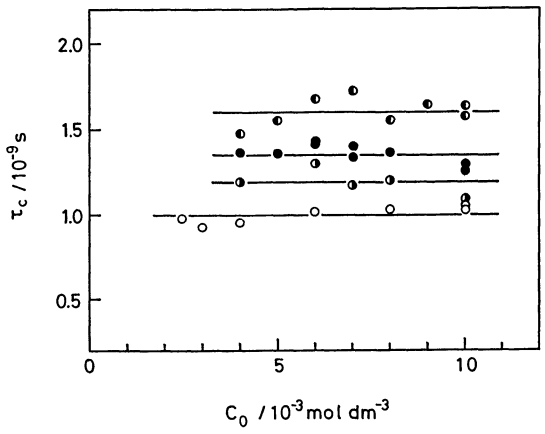


Fig. 5. Plot of τ_c against total surfactant concentration, C_0.
○: STS, ◑: TMTS, ●: TETS, ◐: TPTS. Molar ratio of 5-SAL to surfactant is 1/100.

TABLE 3. VALUES OF ROTATIONAL CORRELATION TIME, τ_c, HYPERFINE COUPLING CONSTANT, a_N, AND DEGREE OF COUNTERION ASSOCIATION

Surfactant	$\tau_c/10^{-9}$ s	a_N/G	Degree of counterion association
STS	1.00±0.04	15.17±0.04	0.73 (30 °C)
TMTS	1.19±0.07	14.90±0.04	0.79 (20 °C)
TETS	1.35±0.05	14.73±0.06	0.80 (20 °C)
TPTS	1.60±0.07	14.83±0.06	0.82 (20 °C)

$$\tau_c = 6.5 \times 10^{-10} W_0 \left[\left(\frac{h_0}{h_{-1}} \right)^{1/2} + \left(\frac{h_0}{h_{+1}} \right)^{1/2} - 2 \right], \quad (3)$$

where W_0 is the peak-to-peak width of the center line measured in Gauss, and h_0, h_{+1}, and h_{-1} are the heights of the center, low, and high field spectral lines respectively. This expression has frequently been used to evaluate the degree of motion of probes solubilized in the micelle.[11,12] It is known that Eq. 3 is applicable to a fast isotropic motion of small molecule. The spectra of the spin probe obtained in this study showed a high degree of fast motion, yielding the τ_c values of the order of 10^{-9} s when calculated according to Eq. 3. Furthermore, the patterns of these spectra were similar to those in isotropic media. Thus, it seems reasonable to use Eq. 3 for the present purpose.

Firstly, ESR measurements were carried out for TMTS and TETS by varying the molar ratio of 5-SAL to the surfactant in the range of 1/100 to 4/100 at the fixed total surfactant concentration of 6×10^{-3} mol dm^{-3} and 1×10^{-2} mol dm^{-3}. Under these conditions, the number of the probes solubilized in one micelle is estimated to be about 1 to 5, assuming that the aggregation number of the micelle is approximately 10^2 and that the 5-SAL dissolved in bulk phase is negligibly small compared with that solubilized in the micelle. Figure 4 shows τ_c values plotted against the ratio of the probe to the surfactant. τ_c is almost independent of the ratio. This shows that the state of the micellar interior is not appreciably perturbed by the uptake of the small amounts of the probe.

Secondly, the ESR spectra were measured varying the surfactant concentration at the range above the CMC, keeping the molar ratio of the probe to surfactant constant at 1/100. The values of τ_c obtained with various surfactant systems are shown in Fig. 5 as a function of the total surfactant concentration, C_0. No systematic variations of τ_c with C_0 are seen in Fig. 5. In Table 3 are listed the τ_c values which were averaged over the whole concentration range.

It is seen from Table 3 that τ_c increases with increasing hydrophobicity of the counterion. This means that the degree of motion of the probe in the micelle decreases in the same order. Two main factors may be considered to be responsible for the difference in the degree of motion of the probe; the fluidity of the environment around the probe, and the electrostatic interaction between the negatively charged head group of the probe and the micellar surface charge which is affected by the degree of counterion association. The degree of counterion association was estimated from the counterion concentration dependence of the CMC, and is listed in Table 3. These values are not so different, although a slight regular increase with the hydrophobicity of the counterion is seen. Hence, the difference in τ_c may be mainly attributed to the difference in the fluidity around the solubilized probe.

In Table 3 are also listed the values of the hyperfine coupling constant, a_N, which were determined from the separation between the lines at low and center field in the spectra; these give information about the polarity of the environment around the spin labelled portion. The a_N values for each system were almost independent of both the probe/surfactant ratio and the surfactant concentration. Comparison of STS with other surfactants shows that a_N values for the latter are smaller than that for STS. This indicates that the polarity of the environment around the paramagnetic site becomes smaller for the surfactant with a hydrophobic counterion. For a series of surfactant micelles studied here, the region probed by 5-SAL is considered to be nearly identical, since all the micelle interiors consist of the same long-chain ion, *i.e.*, tetradecyl sulfate ion. Furthermore, the probe used here are considered to be sensing the region relatively close to the surface in the micellar interior, because the probe is the stearic acid derivative spin-labelled at the fifth carbon atom from the carboxyl carbon. Thus, the a_N values in Table 3 show that the tetradecyl sulfate micelles with hydrophobic counterions have fewer water molecules penetrated at the near surface of the micelle interior than STS has; this would be a consequence of the exclusion of water molecules due to the attachment of the hydrophobic counterion. This difference in the extent of water penetration plays a role in the difference in the fluidity at the region probed by 5-SAL.

Discussion

Aniansson *et al.*[1] have treated the dissociation of a monomer from a micelle as a diffusion process of a monomer perpendicular to the micellar surface.

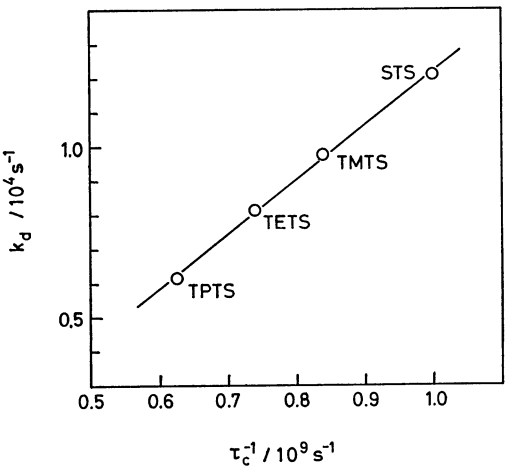


Fig. 6. Relation between dissociation rate constant, k_d, and τ_c^{-1}.
The values of k_d are at 25 °C.

According to their treatment, the dissociation rate constant, k_d, is approximately expressed by Eq. 4:

$$k_d = \frac{D_m}{l^2}\exp(-\Delta G^*/RT), \quad (4)$$

where ΔG^* is the height of the potential barrier corresponding to the activation free energy for the dissociation process, D_m is the diffusion coefficient of a monomer at the potential maximum, and l is the width of the potential maximum region. The main contribution to ΔG^* may arise from the hydrophobic energy, and also from the electrostatic interaction for a charged micelle. Equation 4 can be understood intuitively by noting that D_m/l^2 corresponds to the specific rate constant for the diffusion through the potential maximum, *i.e.*, the number of the molecules transferred through the distance l per unit time, and that $\exp(-\Delta G^*/RT)$ is the probability finding a monomer at an activated state. According to the model postulated by Aniansson *et al.*, the dissociation rate is governed by both ΔG^* and the rate at which a dissociating monomer passes through the potential maximum region.

The diffusion coefficient is proportional to the reciprocal of the viscosity. The viscosity is also reflected in the rotational correlation time of the spin probe, and is proportional to τ_c. Thus, according to the model described above, k_d may be related to τ_c^{-1} through the viscosity, assuming that τ_c well reflects the local viscosity at the region of potential maximum. When k_d was plotted against τ_c^{-1} for the series of surfactant systems studied here, a definite linear relationship was obtained, as is shown in Fig. 6. This indicates that in the series of surfactants the activation free energies, ΔG^*, are almost identical and that the difference in k_d is mainly attributed to the difference in D_m.

For a spherical particle of radius r_1 in a viscous fluid, the value of τ_c is related to the viscosity η by[13]

$$\tau_c = 4\pi\eta r_1^3/3kT. \quad (5)$$

The translational diffusion coefficient of a spherical particle of radius r_2 is related to the viscosity of the

Table 4. Values of D_m and activation parameters for the dissociation of a monomer from a micelle estimated from Eqs. 4—6.

Surfactant	D_m / 10^{-7} cm^2 s^{-1}	ΔG^* / kJ mol^{-1}	ΔH^* / kJ mol^{-1}	ΔS^* / J K mol^{-1}
STS	5.6	32.5	11.3	−71
TMTS	4.7	32.6	20.7	−40
TETS	4.1	32.7	18.5	−48
TPTS	3.5	33.0	21.8	−38

medium by the Stokes-Einstein equation, *i.e.*,

$$D = kT/6\pi\eta r_2. \quad (6)$$

Assuming that 5-SAL and tetradecyl sulfate ion are spheres of radius 5 Å (*i.e.*, $r_1=r_2\approx 5$ Å), the values of D_m were estimated from Eqs. 5 and 6 for the present systems. Furthermore, using these D_m values and $l\approx 1$ Å,[1] the value of ΔG^* were estimated from Eq. 4. These values are listed in Table 4. In spite of the rather crude numerical values adopted here, D_m values are in agreement to the order of magnitude with the diffusion coefficient of a different type of spin probe in SDS micelle.[14]

ΔG^* is expressed as

$$\Delta G^* = \Delta H^* - T\Delta S^*, \quad (7)$$

where ΔH^* and ΔS^* are the activation enthalpy and entropy for the dissociation process of a monomer from a micelle. On the other hand, D_m is expressed as Eq. 8, taking into account the temperature dependence of η in Eq. 6, *i.e.*, η=constant$\cdot\exp(\Delta H_v/RT)$:[15]

$$D_m = TC\exp(-\Delta H_v/RT), \quad (8)$$

where ΔH_v is the viscous enthalpy and C a constant independent of the temperature. Then, from Eqs. 4, 7, and 8, one obtains

$$k_d = \frac{TC}{l^2}\exp(\Delta S^*/R)\exp[-(\Delta H_v+\Delta H^*)/RT]. \quad (9)$$

According to Eq. 9, $\Delta H_v+\Delta H^*$ can be evaluated from the temperature dependence of k_d. The values of $\Delta H_v+\Delta H^*$ for the present surfactant systems were determined from the slope of the $\log k_d$ *vs.* $1/T$ plot in Fig. 3. The values of ΔH^* were evaluated assuming $\Delta H_v\approx 17.6$ kJ mol^{-1} for STS.[1] Furthermore, ΔS^* values were evaluated from Eq. 7. These values of activation parameters are listed in Table 4.

The numerical values in Table 4 might not be good enough for a quantitative discussion, since they were evaluated using rather crude approximations. However, the qualitative discussion given below is reasonable.

As seen in Table 4, the values of ΔS^* are negative for all cases. This implies that the degree of freedom of the system becomes smaller through the activation process. The activated state may be described as a state where the hydrocarbon chain of the dissociating monomer partially leaves the hydrocarbon core of the micelle, while the tail end still remains in this core. Since the freedom of the dissociating monomer chain itself may increase, the observed overall decrease of the freedom may be attributed to the decrease in freedom of water molecules resulting from the formation of an ordered structure around the nonpolar portion of the dissociating monomer. Thus, the negative values of ΔS^* may be interpreted as due to an "iceberg" structure formation of water around the exposed hydrocarbon tail of the escaping monomer.

The absolute values of ΔS^* for TMTS, TETS, and TPTS do not differ significantly, although that for STS is considerably larger than the others. This means that the degree of hydration of the monomer (or degree of "iceberg" formation) at an activated state is larger for STS. This difference in hydration may be interpreted as follows. The properties of water molecules in the vicinity of the micellar surface may be altered from that of the bulk free water by the influence of the counterion present at fairly high concentration. If one assumes that only free water molecules could participate in the formation of the "iceberg" structure, one expects the existence of a water layer which is non-effective for the "iceberg" formation just outside the micellar surface. The thickness of this "non-effective" layer is expected to be larger for a bulky tetraalkylammonium ion than for the sodium ion. Thus, if one assumes, at the activated state, the hydration or "iceberg" formation around the exposed hydrocarbon chain, and also the presence of a thicker water layer which is ineffective for hydration on a micellar surface covered with bulky counterions, then the larger negative ΔS^* for STS could be qualitatively explained.

On the other hand, the values of ΔH^* are positive. This corresponds to the situation in which the energy to break the hydrocarbon contact in the micellar interior is required for activation. This energy may be partly compensated by the heat of hydration which is liberated by the attachment of water molecules to the hydrocarbon chain. Therefore, the ΔH^* value may become smaller when more hydration proceeds through the activation process. Thus, the smaller value of ΔH^* for STS system, compared with those for the others, is also understood on the basis of the difference in the degree of hydration in the activated states.

The contributions from ΔS^* and ΔH^* to the activation free energy are reverse and compensate each other; hence, nearly identical values of ΔG^* are obtained for different surfactant systems. It is considered from the values of ΔS^* and ΔH^* that the water molecules play an important role in the activated state. Furthermore, from the relation between τ_c and a_N, the water molecules present in the probed near-surface region of the micelle may also be responsible for the difference in the fluidity, which is the main factor governing the dissociation rate.

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