Kinetic Studies on Double Relaxation of Surfactant Solutions Using a Capillary Wave Method

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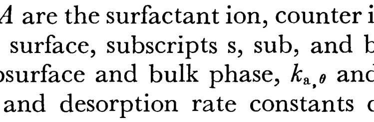
The frequency dependence of the damping coefficient of a capillary wave was measured in decylamine hydrochloride solutions. The observed relaxations were well expressed by the double-relaxation equations. From the concentration dependence of the relaxation parameters obtained, the relaxations at low and high frequencies were attributed to the adsorption-desorption and ion-pair formation reactions on the surface, respectively. Furthermore, the adsorption rate constants are related to the hydrophobic and hydrophilic properties of the surfactants.

Very recently, adsorption-desorption phenomena on the surface of sodium dodecyl sulfate (SDS), dodecylamine hydrochloride (DAC), and octylamine hydrochloride (OAC) solutions have been investigated theoretically and experimentally by means of the capillary wave method.[1,2] Similar studies on a homologous series of alkylamine hydrochloride solutions would give valuable information about the relationship between the dynamic behavior and the structure of the surfactant molecules.

The purpose of this paper is to study the adsorption-desorption phenomena by measuring the frequency dependence of the damping coefficient of the capillary wave on the surface of decylamine hydrochloride (DeAC) solutions as an extension of previous studies.

Theoretical

Let us consider the following scheme, which is a combination of adsorption-desorption and ion-pair formation reactions on the surface of a surfactant solution:[1]



where

$$K = \frac{k_2}{k_{-2}},$$

S, A, and SA are the surfactant ion, counter ion, and ion-pair on the surface, subscripts s, sub, and b refer to the surface, subsurface and bulk phase, $k_{a,\theta}$ and k_d are the adsorption and desorption rate constants defined in a previous paper,[1] k_2 and k_{-2} are the association and dissociation rate constants, D_S and D_A are the diffusion coefficients for S and A, respectively, and K is the equilibrium constant.

The following rate and diffusion equations are given for the two processes:[1]
For the diffusion processes ($y < -d_{sub}$),

$$\frac{dc_i}{dt} = D_i\left(\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2}\right)$$

$$(c_i = c_{S,b},\ c_{A,b} \text{ and } D_i = D_S,\ D_A), \tag{1}$$

and for the (Langmuir-type) adsorption-desorption and ion-pair formation processes ($0 \geq y \geq -d_{sub}$),

$$\frac{d\theta_1}{dt} = k_{a,\theta}(1-\theta_1-\theta_2)c_{S,sub} - k_d\theta_1 - k_2\theta_1 c_{A,sub} + k_{-2}\theta_2 \tag{2}$$

and

$$\frac{d\theta_2}{dt} = k_2\theta_1 c_{A,sub} - k_{-2}\theta_2,$$

where x and y are the rectangular coordinates normal and tangent to the surface at rest, $c_{S,sub}$, $c_{A,sub}$, $c_{S,b}$, and $c_{A,b}$ are the molar concentrations of S_{sub}, A_{sub}, S_b, and A_b, t is the time, d_{sub} is the thickness of the subsurface layer, and θ_1 and θ_2 are the fractions of sites occupied by S and SA, respectively. The changes in the concentrations are given by:

$$c_j = \bar{c}_j + \Delta c_j \exp\{i(\omega' t + \kappa x)\}$$

$$(c_j = c_i,\ c_{S,sub},\ c_{A,sub}) \tag{3}$$

and

$$\theta_k = \bar{\theta}_k + \Delta\theta_k \exp\{i(\omega' t + \kappa x)\} \quad (k=1,\ 2),$$

where

$$\omega' = 4\pi f, \quad \kappa = 2k,$$

with ω' and κ being the angular frequency and wavenumber of the perturbed variables, f and k the frequency and wavenumber, respectively, and with the bar denoting the equilibrium state. The solution of Eq. 1 gives:[1,3,4]

$$\Delta c_i = E_i \exp(n_i y)$$

$$(E_i = E_S,\ E_A \text{ and } n_i = n_S,\ n_A), \tag{4}$$

where

$$n_i = \left(\kappa^2 + \frac{i\omega'}{D_i}\right)^{1/2} = \beta_{i1} + i\omega'\beta_{i2},$$

E_i is a constant and n_i are the parameters related to the thickness of the bulk phase concerned with the diffusion process. On the other hand, the laws of conservation of mass give two independent relations for the concentration changes of the surfactant and counter ions:[1]

$$F(\Delta\theta_1 + \Delta\theta_2) + \int_{-\infty}^{-d_{sub}} E_S \exp(n_S y)\,dy = F(\Delta\theta_1 + \Delta\theta_2) + \frac{\Delta c_{S,sub}}{n_S} = 0 \tag{5}$$

and

$$F\Delta\theta_2 + \int_{-\infty}^{-d_{sub}} E_A \exp(n_A y)\,dy = F\Delta\theta_2 + \frac{\Delta c_{A,sub}}{n_A} = 0,$$

where

$$F = 10^3 \mathit{\Gamma}_{\max},$$

and $\mathit{\Gamma}_{\max}$ is the maximum value of the surface excess. A combination of Eqs. 2—5 gives:

$$\begin{aligned} i\omega'\{1+k_{\mathrm{a},\theta}(1-\bar{\theta}_1-\bar{\theta}_2)F\beta_{\mathrm{S2}}\}\Delta\theta_1 & \\ +i\omega' F\{k_{\mathrm{a},\theta}(1-\bar{\theta}_1-\bar{\theta}_2)\beta_{\mathrm{S2}}+k_2\bar{\theta}_1\beta_{\mathrm{A2}}\}\Delta\theta_2 & \\ = -[k_{\mathrm{a},\theta}\{\bar{c}_{\mathrm{S,sub}}+(1-\bar{\theta}_1-\bar{\theta}_2)F\beta_{\mathrm{S1}} & \\ +k_{\mathrm{d}}+k_2\bar{c}_{\mathrm{A,sub}}]\Delta\theta_1-[k_{\mathrm{a},\theta}\{\bar{c}_{\mathrm{S,sub}} & \\ +(1-\bar{\theta}_1-\bar{\theta}_2)F\beta_{\mathrm{S1}}\}+Fk_2\bar{\theta}_1\beta_{\mathrm{A1}}-k_{-2}]\Delta\theta_2 & \qquad (6) \end{aligned}$$

and

$$\begin{aligned} iw'(1+k_2F\bar{\theta}_1\beta_{\mathrm{A2}})\Delta\theta_2 & \\ = k_2\bar{c}_{\mathrm{A,sub}}\Delta\theta_1-(k_2F\bar{\theta}_1\beta_{\mathrm{A1}}+k_{-2})\Delta\theta_2. & \end{aligned}$$

For relatively concentrated surfactant solutions near the CMC, these equations are simplified in the cases of c_0 (the initial concentration)$>10^{-3}$ mol dm^{-3}, $k_2<5\times 10^4$ mol^{-1} dm^3 s^{-1}, and $K<10^4$ mol^{-1} dm^3 (with $D_{\mathrm{s}}\approx 10^{-6}$ cm^2 s^{-1}, $D_{\mathrm{A}}\approx 10^{-5}$ cm^2 s^{-1}, and $\bar{c}_{\mathrm{S,sub}},\approx\bar{c}_{\mathrm{A,sub}}\approx c_0$)[1] to

$$i\omega'\Delta\theta_1 = -a_{11}-a_{12}$$

and (7)

$$i\omega'\Delta\theta_2 = -a_{21}-a_{22},$$

where

$$a_{11} = k_{\mathrm{a},\theta}c_0+k_{\mathrm{d}}+k_2c_0, \quad a_{12} = k_{\mathrm{a},\theta}c_0-k_{-2},$$

$$a_{21} = -k_2c_0, \quad a_{22} = k_{-2}.$$

Solving Eq. 7, one obtains the following equation for the relaxation times, τ:[5]

$$\tau_{\mathrm{I,II}}^{-1} = \frac{1}{2}(a_{11}+a_{22})\left[1\pm\left\{1-\frac{4(a_{11}a_{22}-a_{12}a_{21})}{(a_{11}-a_{22})^2}\right\}^{1/2}\right]. \qquad (8)$$

This equation is easily simplified by the conditions $a_{11}\gg a_{22}$ and $a_{22}\gg a_{11}$ to the following forms:[5]
For $a_{11}\gg a_{22}$ $(\tau_{\mathrm{I}}^{-1}\gg\tau_{\mathrm{II}}^{-1})$,

$$\tau_{\mathrm{I}}^{-1} = a_{11} = k_{\mathrm{a},\theta}c_0 + k_{\mathrm{d}} + k_2c_0$$

and (9a)

$$\tau_{\mathrm{II}}^{-1} = a_{22} - \frac{a_{12}a_{21}}{a_{11}} = k_{-2} + \frac{k_2c_0(k_{\mathrm{a},\theta}c_0-k_{-2})}{k_{\mathrm{a},\theta}c_0+k_{\mathrm{d}}+k_2c_0},$$

and for $a_{22}\gg a_{11}$ $(\tau_{\mathrm{II}}^{-1}\gg\tau_{\mathrm{I}}^{-1})$,

$$\tau_{\mathrm{I}}^{-1} = a_{11} - \frac{a_{12}a_{21}}{a_{22}} = k_{\mathrm{a},\theta}(1+Kc_0)c_0 + k_{\mathrm{d}}$$

and (9b)

$$\tau_{\mathrm{II}}^{-1} = a_{22} = k_{-2}.$$

The apparent relaxation strengths, δ', for two-step reactions on the surface are given by the following equations on the basis of two-dimensional relaxation theory[1] and of the theory for ultrasonic absorption[5] at constant activity:

$$\delta_{\mathrm{I}}' = \frac{(W\Delta\gamma_1+X\Delta\gamma_2)^2}{\gamma RT}\left(W^2\Sigma\frac{{\nu_{\mathrm{i1}}}^2}{c_{\mathrm{i}}}+2XW\Sigma\frac{\nu_{\mathrm{i1}}\nu_{\mathrm{i2}}}{c_{\mathrm{i}}}+X^2\Sigma\frac{{\nu_{\mathrm{i2}}}^2}{c_{\mathrm{i}}}\right)^{-1}$$

and

$$\delta_{\mathrm{II}}' = \frac{(Y\Delta\gamma_1+Z\Delta\gamma_2)^2}{\gamma RT}\left(Y^2\Sigma\frac{{\nu_{\mathrm{i1}}}^2}{c_{\mathrm{i}}}+2YZ\Sigma\frac{\nu_{\mathrm{i1}}\nu_{\mathrm{i2}}}{c_{\mathrm{i}}}+Z^2\Sigma\frac{{\nu_{\mathrm{i2}}}^2}{c_{\mathrm{i}}}\right)^{-1},$$

where

$$\begin{pmatrix} W & Y \\ X & Z \end{pmatrix} = \begin{pmatrix} 1 & a_{12}/(a_{22}-\tau_{\mathrm{I}}^{-1}) \\ a_{21}/(a_{11}-\tau_{\mathrm{II}}^{-1}) & 1 \end{pmatrix},$$

γ is the surface tension, $\Delta\gamma$ is the standard surface tension change defined in a previous paper,[1] R is the universal gas constant, T is the temperature, ν is the stoichiometric coefficient, and subscripts 1 and 2 denote the adsorption-desorption and ion-pair formation processes, respectively. The conditions $a_{11}\gg a_{22}$ and $a_{22}\gg a_{11}$ then lead to:[1,5] for $a_{11}\gg a_{22}$:

$$\delta_{\mathrm{I}}' = \frac{(\Delta\gamma_1)^2}{\gamma RT}\left(\frac{1}{\mathit{\Gamma}_{\max}\bar{\theta}_1}+\frac{3}{2}\times 10^2 N^{1/3}{c_0}^{-2/3}\right)^{-1}$$

and (10a)

$$\begin{aligned} \delta_{\mathrm{II}}' = \frac{(Y\Delta\gamma_1+\Delta\gamma_2)^2}{\gamma RT}\left\{\frac{1-2Y-Y^2}{\mathit{\Gamma}_{\max}\bar{\theta}_2}+\frac{1}{\mathit{\Gamma}_{\max}\bar{\theta}_2}\right. & \\ \left.+\frac{3}{2}\times 10^2(1+Y^2)N^{1/3}{c_0}^{-2/3}\right\}^{-1}, & \end{aligned}$$

where

$$\begin{pmatrix} W & Y \\ X & Z \end{pmatrix} = \begin{pmatrix} 1 & -a_{12}/a_{11} \\ 0 & 1 \end{pmatrix},$$

and for $a_{22}\gg a_{11}$,

$$\begin{aligned} \delta_{\mathrm{I}}' = \frac{(\Delta\gamma_1+X\Delta\gamma_2)^2}{\gamma RT}\left\{\frac{1-2X+X^2}{\mathit{\Gamma}_{\max}\bar{\theta}_1}+\frac{X^2}{\mathit{\Gamma}_{\max}\bar{\theta}_2}\right. & \\ \left.+\frac{3}{2}\times 10^2(1+X^2)N^{1/3}{c_0}^{-2/3}\right\}^{-1} & \end{aligned}$$

and (10b)

$$\delta_{\mathrm{II}}' = \frac{(\Delta\gamma_2)^2}{\gamma RT}\left(\frac{1}{\mathit{\Gamma}_{\max}\bar{\theta}_1}+\frac{1}{\mathit{\Gamma}_{\max}\bar{\theta}_2}+\frac{3}{2}\times 10^2 N^{1/3}{c_0}^{-2/3}\right)^{-1},$$

where

$$\begin{pmatrix} W & Y \\ X & Z \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ -a_{21}/a_{22} & 1 \end{pmatrix}.$$

Experimental

The apparatus employed was the same as that reported in a previous paper.[2]

Decylamine (Schuchardt, purity; 90%) was distilled twice and the purity of the distillate was confirmed to be 99.8% using gas chromatography. Decylamine was neutralized by hydrochloric acid in a butanol solution and was then recrystallized four times from the butanol solution and finally washed with petroleum ether. The value of the CMC was determined to be 62.5 mM* using the electric conductivity method at 25 °C.

The measurements of the damping coefficient of the capillary wave were carried out from 40 to 700 Hz on the surface of concentrated DeAC solutions below the CMC at 25± 0.4 °C.

Results and Discussion

The frequency dependence of the damping coefficient, α, is shown in Fig. 1. As seen from this figure, the experimental values of α/f are greater than the theoretical results of α_{d}/f, where α_{d} refers to the damping coefficient resulting only from diffusion between the surface and the bulk phase.[1,3,4] This difference cannot be expressed by a single relaxation equation as was done in a previous paper.[2] In order to interpret the experimental results, let us consider multiple-step reactions on the surface. The equation for the damping coefficient derived in previously[2] is generalized to the mutiple relaxations, as follows:

$$\frac{3\rho c^3}{2\pi\gamma k}\left(\frac{\alpha}{f}-\frac{\alpha_{\mathrm{d}}}{f}\right) = \sum_{i=1}^{N}\frac{\omega'\tau_i\delta_i'}{1+\omega'^2{\tau_i}^2}, \qquad (11)$$

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* Throughout this paper, 1 M=1 mol dm^{-3}.

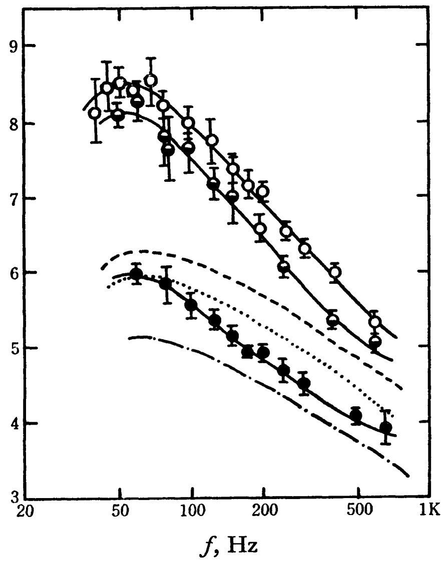

Fig. 1. The plots of α/f vs. f in the DeAC solutions. The theoretical curves of α_d/f are shown; ------: 50 mM, ······: 40 mM, —·—: 25 mM. ○: 50 mM, ◒: 40 mM, ●: 25 mM.

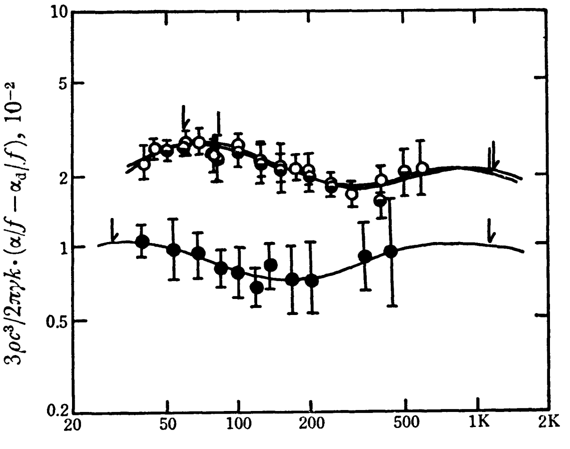

Fig. 2. The relaxation absorption spectra in the DeAC solutions. The solid lines show the theoretical curves calculated by right hand side of Eq. 11 with the relaxation parameters listed in Table 1. The arrows show the relaxation frequency $f_r = (4\pi\tau)^{-1}$.
○: 50 mM, ◒: 40 mM, ●: 25 mM.

TABLE 1. RELAXATION PARAMETERS IN DeAC AND OAC SOLUTIONS AT 25 °C

	c_0 (mM)	τ_1^{-1} ($10^2\,s^{-1}$)	τ_2^{-1} ($10^4\,s^{-1}$)	δ'_1 (10^{-2})	δ'_2 (10^{-2})
DeAC	25.0	5.6±0.4	1.5±0.2	2.0±0.5	1.9±0.5
	40.0	7.5±1.1	1.5±0.2	4.9±0.5	3.7±0.5
	50.0	10.5±0.6	1.5±0.5	4.8±1.0	2.7±0.5
	60.0	11.1±1.8	1.6±0.5	2.5±0.3	1.0±0.3
OAC	34.6	4.1±0.5	—	1.3±0.5	—
	46.1	3.6±0.5	—	2.5±0.3	—
	57.7	4.7±0.7	0.9±0.2	3.9±0.7	2.6±0.7
	76.9	6.1±0.8	1.1±0.3	5.2±0.7	2.9±0.7
	115.3	8.2±0.5	1.3±0.4	7.7±0.8	2.9±0.8

where ρ is the density, c is the propagation velocity, and N is the number of reaction steps. The frequency dependence of the left hand side of Eq. 11 is shown in Fig. 2. The experimental results can be satisfactorily represented by the right hand side of Eq. 11 in the case of $N=2$; thus, the existance of double relaxations was confirmed. The relaxation parameters obtained are listed in Table 1, where subscripts 1 and 2 refer to the relaxations at lower and higher frequencies, respectively.

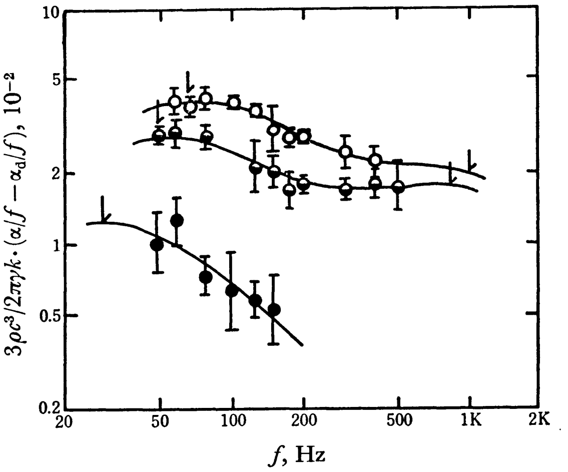

Fig. 3. The relaxation absorption spectra in the purified OAC solutions.
○: 115 mM, ◒: 76.9 mM, ●: 46.1 mM.

These facts lead to a new problem: why was only a single relaxation observed for the SDS, DAC, and OAC solutions reported in Ref. 2. Before this problem could be clarified, the experimental results for the OAC solutions stimulated a reexamination of the purified OAC solutions, since the OAC contained a minute amount of DeAC (content; 2.3%). The OAC was prepared by neutralizing octylamine (the purity of which was verified to be 99.9% using gas chromatography) with hydrochloric acid. The experimental results for the purified OAC solutions are shown in Fig. 3. As seen from this figure, double relaxations are observed and the relaxation parameters obtained are listed in Table 1 together with those for the DeAC solutions. The concentration dependence of the relaxation parameters is the same as that for the DeAC solutions. This suggests that the relaxation phenomena in both solutions are caused by perturbation of the same process. In a series of studies on relaxation phenomena on the surface of surfactant solutions,[2] double relaxations were observed in the DeAC and OAC solutions but were not observed in the SDS and DAC solutions. The concentration dependence of τ_1^{-1} for the former solutions differs from that of the reciprocal relaxation time for the latter solutions. Moreover, the τ_1^{-1} for the DeAC solution is larger than that for the OAC solution. Since the SDS and DAC hydrocarbon chain lengths are longer than those for DeAC and OAC, the abovementioned facts suggest that the relaxations at the higher frequency in the SDS and DAC solutions may be located outside the measured frequency range.

TABLE 2. KINETIC PARAMETERS IN VARIOUS SURFACTANT SOLUTIONS AT 25 °C

	purity (%)	CMC (mM)	$k_{a,\theta}$ (10^4 M^{-1} s^{-1})	k_a (10^5 s^{-1})	k_d (10^2 s^{-1})	k_2 (10^4 M^{-1} s^{-1})	k_{-2} (10^4 s^{-1})	K (M^{-1})
SDS[a]	99.5	8.3	11±5	4±2	9±1	—	—	—
DAC[a]	99.7	15.8	6±3	3±1	8±2	—	—	—
DeAC	99.8	62.5	1.3±0.4	0.5±0.2	3±1	6±1	1.5±0.3	4
OAC	97.7[a]	175	1.0±0.3	0.6±0.2	—	—	—	—
	99.9	180	0.32±0.09	0.2±0.05	2.5±0.5	7±1	1.1±0.2	5

a) Ref. 2.

TABLE 3. THERMODYNAMIC PARAMETERS IN VARIOUS SURFACTANT SOLUTIONS AT 25 °C

	ΔG ($-RT$)		$\Delta\gamma$ (10^{10} dyn cm mol^{-1})[d]	
SDS[a]	6.1	6.8[b]	10	6[c]
DAC[a]	5.9	6.3[b]	8	7[c]
DeAC	5.1	4.6[b]	2	7[c]
OAC	4.4	4.5[b]	2	7[c]

a) Ref. 2. b) These values were calculated using the Szyszkowski equation. c) These values were estimated using $(\gamma_{\rm water}-\gamma_{\rm CMC})/\Gamma_{\rm max}$. d) 1 dyn$=10^{-5}$ N.

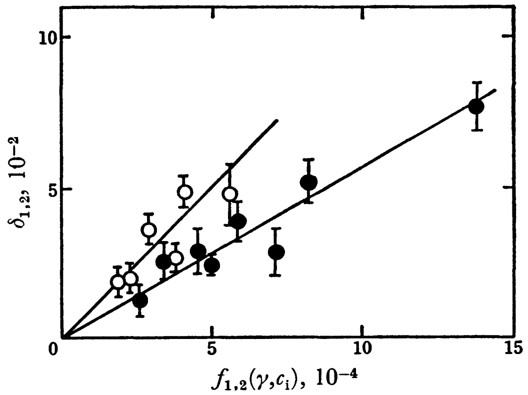

Fig. 4. The plots of $\delta'_{1,2}$ *vs.* $f_{1,2}$ (γ,c_i) in the DeAC (open circles) and OAC (closed circles) solutions. The values of $f_{1,2}$ (γ,c_i) were calculated using $K=4$ and 5 in the DeAC and OAC solutions, respectively.

The new experimental results described above prompted a modification of the adsorption-desorption mechanism model proposed in a previous paper.[1] The concentration dependence of $\tau_{\rm I}^{-1}$ listed in Table 1 is similar to that for the relaxation times reported previously.[2] This fact suggests that the relaxation at lower frequency may be due to the adsorption-desorption process of the surfactants. On the other hand, the τ_2^{-1} values were independent of the surfactant concentration as seen from Table 1. Various reactions on the surface are considered, *e.g.*, an ion-pair formation reaction, a monomer-dimer reaction, and a conformational change reaction. Of these, the ion-pair formation reactions between halide and dodecylpyridinium ions and between the various anions and polysoap on the surface have been studied under static conditions by Parreira[6] and Plaisance and Ter-Minassian-Saraga,[7] respectively. Thus, the model of the adsorption-desorption mechanism presented in a previous paper[1] was modified in the manner expressed by the scheme given in the theoretical section. Since the $\tau_{\rm I}^{-1}$ values are an order of magnitude smaller than the $\tau_{\rm II}^{-1}$ values, *i.e.*, $a_{22}\gg a_{11}$ (see Eq. 9b), the equations for the relaxation times and the apparent relaxation strengths are given by Eq. 9b ($\tau_{\rm I}=\tau_1$ and $\tau_{\rm II}=\tau_2$) and by the following equation, respectively:

$$\delta'_{1,2} = \frac{(\Delta\gamma)^2}{\gamma RT}\cdot f_{1,2}(\gamma,\ c_i), \tag{12}$$

where

$$f_1(\gamma,\ c_i) = (1+Kc_0)^2\left\{\frac{1-2Kc_0+K^2c_0{}^2}{\Gamma_{\rm max}\bar{\theta}_1}+\frac{K^2c_0{}^2}{\Gamma_{\rm max}\bar{\theta}_2}\right.$$
$$\left.+\frac{3}{2}\times 10^2(1+K^2c_0{}^2)N^{1/3}c_0{}^{-2/3}\right\}^{-1},$$
$$f_2(\gamma,\ c_i) = \left(\frac{1}{\Gamma_{\rm max}\bar{\theta}_1}+\frac{1}{\Gamma_{\rm max}\bar{\theta}_2}+\frac{3}{2}\times 10^2N^{1/3}c_0{}^{-2/3}\right)^{-1},$$

under the assumption that $\Delta\gamma_1$ in Eqs. 10a and 10b is approximately equal to $\Delta\gamma_2$, since the counter ion may associate in the immediate proximity of the surface.

The K values in Eq. 12 were determined so as to give straight lines for the plots of $\delta'_{1,2}$ *vs.* $f_{1,2}$ $(\gamma,\ c_i)$. As is shown in Fig. 4, the experimental values fall on the theoretical straight lines in the cases of $K=4$ and 5 for the DeAC and OAC solutions, respectively. With the K values obtained, the equations for the relaxation times were applied to the experimental results listed in Table 1. As seen from Figs. 5 and 6, the experimental values fall on the straight lines. The linearities of these plots confirm the validity of the scheme. The values of $\Delta\gamma$, $k_{a,\theta}$ k_d, and k_{-2} were obtained from the slopes and intercepts in Figs. 4, 5, and 6, respectively and are listed in Tables 2 and 3. The k_2 values listed in Table 2 were calculated using the values of K and k_{-2}. The values of the adsorption rate constant, k_a,[1] and the adsorption energy, ΔG,[2] were calculated and are also listed in Tables 2 and 3. The K and k_2 values listed in Table 2 satisfy the conditions for the simplification of Eq. 6. In the present work, other plausible processes, a monomer-dimer reaction and a conformational change reaction on the surface, were also examined, but no results were obtained.

Among the kinetic parameters concerned with the adsorption-desorption process listed in Table 2, $k_{a,\theta}$ and k_a are inversely proportional to the CMC, as seen in Fig. 7 but k_a is independent of the CMC. Since the logarithm of the CMC bears a linear relation to the hydrophile-liophile balance (HLB) value,[8,9] $k_{a,\theta}$ and k_a can be related to the HLB values as follows:

$$\log k_{a,\theta} = (0.30\pm0.06)HLB + (0.5\pm0.6)$$
and
$$\log k_a = (0.25\pm0.05)HLB + (1.8\pm0.6). \tag{14}$$

These relations indicate that the adsorption rate

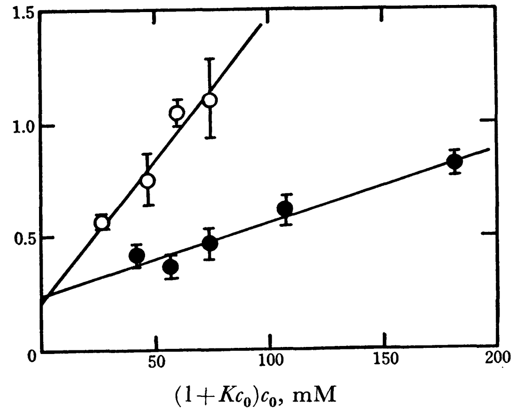

Fig. 5. The plots of τ_1^{-1} vs. $(1+Kc_0)c_0$ in the DeAC (open circles) and OAC (closed circles) solutions.

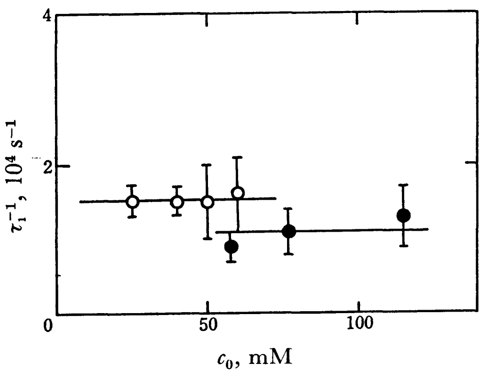

Fig. 6. The plots of τ_2^{-1} vs. c_0 in the DeAC (open circles) and OAC (closed circles) solutions.

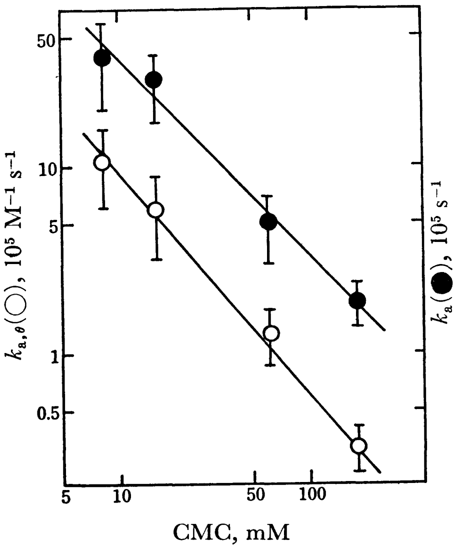

Fig. 7. The plots of $k_{a,\theta}$ (open circles) and k_a (closed circles) vs. CMC.

constants are influenced considerably by the instability of the surfactants in the bulk phase. In the alkylamine hydrochloride solutions, moreover, k_a also involves the number of $-CH_2-$ groups, n, as follows:

$$\ln k_a = (0.7\pm0.1)n + (4\pm1). \qquad (15)$$

This equation indicates that the activation adsorption energy per $-CH_2-$ group is 0.4 kcal at 25 °C. On the other hand, the ΔG values are in good agreement with the theoretical results calculated using the Szyszkowski equation, as can be seen from Table 3. The $\Delta\gamma$ values are also in orderly agreement with those estimated using $(\gamma_{\text{water}}-\gamma_{\text{CMC}})/\Gamma_{\text{max}}$.[2]

As seen in Table 2, the kinetic parameters involving the ion-pair formation process are appreciably independent of the hydrocarbon chain length. This suggests that the interaction between the surfactant and counter ions may be governed by that between a hydrophilic group and Cl^- ions. Since the interaction energy between Na^+ and the anionic surfactant is smaller than that between Cl^- and the cationic surfactant,[10] however, SDS will scarcely associate on the surface and the relaxation concerned with the ion-pair formation should not be observed even outside the measured frequency range.

The remarkable difference between the relaxations observed for the OAC solutions in the present work and those of previous work[2] implies that the relaxation phenomena on the surface of surfactant solutions are sensitive to impurities in the surfactants. In a subsequent paper, the experimental results for the effect of additives on the relaxation of DeAC solutions, which are homologous to the OAC solutions, will be reported.

Finally, it can now be asserted that the capillary wave method is a powerful tool for analyzing reactions at the gas-liquid interface.

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