# Relaxation Studies of the Adsorption-Desorption Equilibrium of Surfactants on the Gas-Liquid Interface. II. Experimental Studies

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The propagation characteristics of the capillary wave were studied in aqueous solutions of sodium dodecyl sulfate, octylamine hydrochloride, and dodecylamine hydrochloride. In most of the solutions, relaxation was observed both in the propagation velocity and the damping coefficient; it could be well interpreted by means of the theory for the propagation characteristics derived in Part I.[1] The obtained relaxation parameters reveal the dynamic behavior of the adsorption-desorption of surfactants on the gas-liquid interface.

The dynamic physicochemical properties of the gas-liquid interface have been studied by many investigators[2-5] by means of the capillary wave method. Davies and Vose[2] have found relaxation on the surface of the surfactant solutions and have attributed it to the adsorption-desorption process of surfactants on the surface. However, questions still remain concerning the definition of the relaxation frequency and the rate equation.[6]

The purpose of the present investigation is to explore the validity of the theory[1] which supports to solve the above problems. Since the experimental values of the damping coefficient reported by Davies and Vose[2] were not precise enough to apply the theoretical equations, the experimental studies were newly carried out in the surfactant solutions.

## Experimental

The apparatus used was a modification of that described by Davies and Vose;[2] the schematic diagram is shown in Fig. 1. The capillary wave was generated by a vibrator attached to a drive-unit of the trumpet speaker. The vibrator was made of Teflon, which has a weak affinity to all solutions. The flash of the stroboscope was synchronized with the signal of the oscillator, and the stationary image of focus was observed with a microscope. The propagation velocity and the damping coefficient were obtained as has been described in Brown's paper.[7] The frequency range of the apparatus was from 25 Hz to 4 kHz.

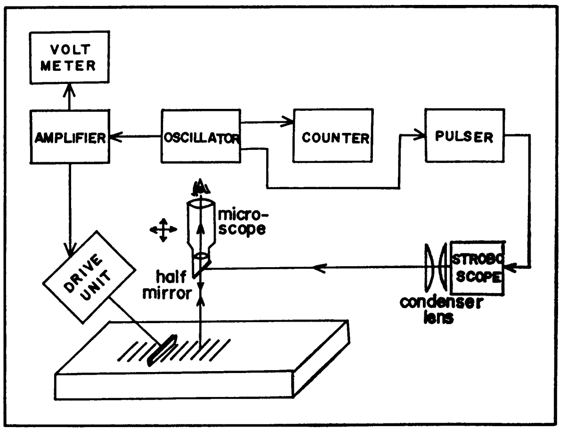

Fig. 1. Schematic diagram of the apparatus for measurements of the propagation characteristics of the capillary wave.

Sodium dodecyl sulfate (SDS) was prepared from Tokyo Kasei reagent-grade dodecyl alcohol (purity; 99.5%) according to the procedure of Dreger *et al.*[8] Octylamine hydrochloride (OAC) and dodecylamine hydrochloride (DAC) were prepared as follows. Octylamine and dodecylamine (Tokyo Kasei reagent-grade; Purities; 97.7 and 99.7% respectively) were neutralized by HCl in benzene solutions and were then recrystallized three times from benzene solutions and finally washed with petroleum ether. The values of the CMC were determined to be 8.3, 15.8, and 175 mM* for the SDS, DAC, and OAC solutions respectively by the electric conductivity method at 25 °C.

## Results and Discussion

The propagation velocity, $c$, and the damping coefficient, $\alpha$, of water were measured at various frequencies; they are shown in Figs. 2 and 3. The theoretical values

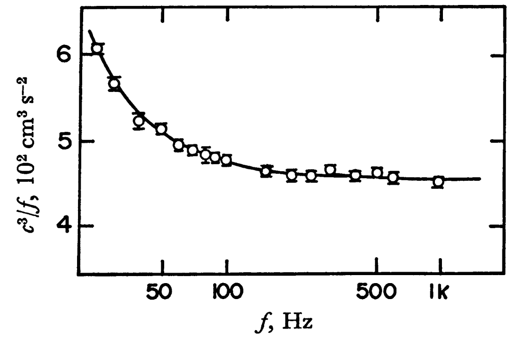

Fig. 2. The plots of $c^3/f$ *vs.* $f$ in water. The solid line shows the theoretical curve of $c^3/f$ calculated by Eq. 1.

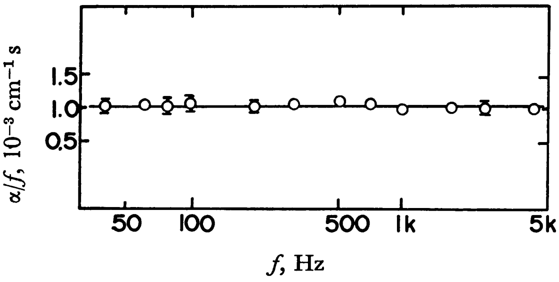

Fig. 3. The plots of $\alpha/f$ *vs.* $f$ in water. The solid line shows the theoretical curve of $\alpha/f$ calculated by Eq. 2.

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

of $c$ and $\alpha$ were calculated by means of the following equations for a clean (fully mobile) surface,[2)] using the literature values of $\rho$, $\nu$, and $\gamma$:[9)]

$$\frac{c^3}{f} = \frac{g\lambda^2}{2\pi} + \frac{2\pi\gamma}{\rho}, \tag{1}$$

$$\frac{\alpha}{f} = \frac{8\pi\rho\nu}{3\gamma}, \tag{2}$$

where $f$ is the frequency, and $\lambda$, the wavenumber. The observed values of $c^3/f$ and $\alpha/f$ fell on those curves within ±0.7 and ±4% respectively in the frequency range studied. These facts confirm that the present apparatus can be applied to the measurements of $c$ and $\alpha$ in the frequency range from 25 Hz to 4 kHz.

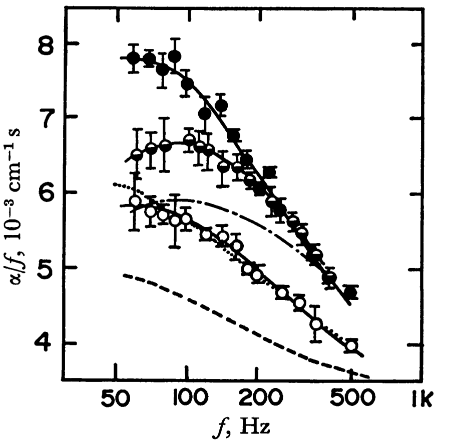


Fig. 4. The plots of $\alpha/f$ *vs.* $f$ in SDS, DAC, and OAC solutions.
The theoretical curves of $\alpha_d/f$ are shown; ----: 8 mM SDS, ······: 15 mM DAC, —·—: 121 mM OAC.
○: 8 mM SDS, ●: 15 mM DAC, ⊖: 121 mM OAC.

The measurements were carried out on the surfaces of the SDS, DAC, and OAC solutions; the frequency depences of $\alpha/f$ are shown in Fig. 4. As seen from this figure, the experimental values of $\alpha/f$ are greater than the theoretical ones of $\alpha_d/f$, where $\alpha_d$ refers to the damping coefficient based on only the diffusion process between the surface and the bulk phase. According to the theory presented in the previous paper,[1)] the equations for the frequency dependences of $c$ and $\alpha$ on the surface of relatively concentrated surfactant solutions are given by

$$c^2 = \left(\frac{g}{k}+\frac{\gamma k}{\rho}\right)\left(1+2\varepsilon_{\mathrm{ela,re}}+\frac{\gamma k}{\rho c^2}\,\frac{\omega'^2\tau^2\delta'}{1+\omega'^2\tau^2}\right), \tag{3}$$

$$\frac{\alpha}{f} = \frac{\alpha_d}{f} + \frac{2\pi\gamma k}{3\rho c^3}\,\frac{\omega'\tau\delta'}{1+\omega'^2\tau^2}. \tag{4}$$

Equation 4 is, then, rearranged as follows:

$$\frac{3\rho c^3}{2\pi\gamma k}\left(\frac{\alpha}{f}-\frac{\alpha_d}{f}\right) = \frac{\omega'\tau\delta'}{1+\omega'^2\tau^2}. \tag{5}$$

The frequency dependences of the l. h. s. of this equation are shown in Fig. 5. This figure shows that the excess damping can be expressed by a single relaxation equation. The relaxation phenomena were also observed in all the other solutions except the 60 mM OAC solution, where the apparent relaxation strength was negligibly small. Nonlinear least-squares routines employing a computer were used to calculate the relaxation parameters; the values of $\tau$ and $\delta'$ obtained are listed in Table 1.

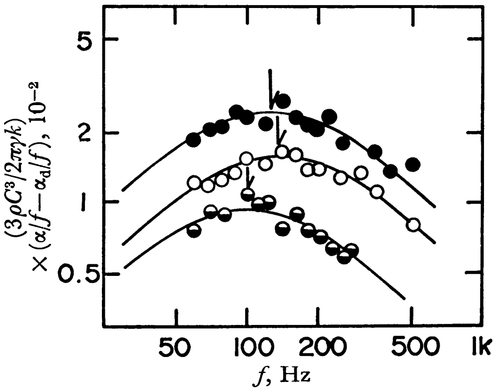


Fig. 5. The plots of $(3\rho c^3/2\pi\gamma k)\cdot(\alpha/f-\alpha_d/f)$ *vs.* $f$ in SDS, DAC, and OAC solutions. The solid lines show the theoretical curves calculated by r. h. s. of Eq. 5 with the relaxation parameters listed in Table 1. The arrows show the relaxation frequency $f_r = (4\pi\tau)^{-1}$.
○: 8 mM SDS, ●: 15 mM DAC, ⊖: 121 mM OAC.

Table 1. Relaxation parameters in SDS, DAC, and OAC solutions at 25 °C

| | CMC (mM) | $c_0$ (mM) | $\tau^{-1}$ ($10^3$ s$^{-1}$) | $\delta'$ ($10^{-2}$) |
|---|---|---|---|---|
| SDS | 8.3 | 4 | 1.3±0.2 | 2.2±0.5 |
| | | 6 | 1.6±0.2 | 2.7±0.3 |
| | | 8 | 1.7±0.2 | 3.0±0.4 |
| | | 10 | 1.8±0.2 | 2.2±0.3 |
| DAC | 15.8 | 5 | 1.0±0.2 | 1.0±0.6 |
| | | 8 | 1.4±0.4 | 1.2±0.3 |
| | | 10 | 1.6±0.3 | 2.2±0.2 |
| | | 12 | 1.4±0.2 | 3.4±0.3 |
| | | 15 | 1.6±0.3 | 5.0±0.4 |
| | | 20 | 1.9±0.2 | 4.3±0.3 |
| OAC | 175 | 60 | — | 0 |
| | | 80 | 0.8±0.2 | 1.5±0.4 |
| | | 100 | 1.0±0.3 | 1.4±0.4 |
| | | 121 | 1.3±0.1 | 1.8±0.5 |

The relaxation parameters can also be obtained from the frequency dispersion of $c$, which was expressed by the following equation with the assumption that $\gamma k/\rho \gg g/k$:

$$\frac{c^3}{f} - \frac{g\lambda^2}{2\pi} = \frac{2\pi\gamma}{\rho}\left(1+2\varepsilon_{\mathrm{ela,re}}+\frac{\gamma k}{\rho c^2}\,\frac{\omega'^2\tau^2\delta'}{1+\omega'^2\tau^2}\right). \tag{6}$$

The theoretical curves in Fig. 6 were calculated by means of this equation, using the values of the relaxation parameters in Table 1. Unfortunately, the apparent relaxation strength was so small that the experimental results of the propagation velocity were not precise enough to give the relaxation parameters, only to refine the validity of those obtained from the damping coefficient.

If the observed relaxation phenomena are based on the adsorption-desorption process of the surfactants, the concentration dependence of the relaxation time is

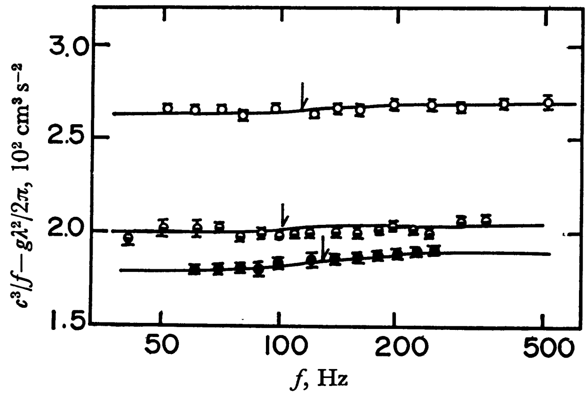


Fig. 6. The frequency dispersion of $(c^3/f-g\lambda^2/2\pi)$ in SDS, DAC, and OAC solutions. The solid lines show the theoretical curves calculated by Eq. 6 with the relaxation parameters listed in Table 1. The arrows show the relaxation frequency obtained from the experimental results of the damping coefficient.

expressed by[1]

$$\tau^{-1} = \frac{d_s k_a c_m \exp\left(-\dfrac{Ze\psi_{sub}}{k_B T}\right)}{10^3 \Gamma_{max}} + k_d, \tag{7}$$

where $c_m$ is the monomer concentration of the surfactants. In the concentrated surface concentration of ionic surfactants, most of the adsorbed surfactants are neutralized by the counter ions and the Stern layer is formed at the surface. Then, $\psi_{sub}$ may be much smaller than $k_B T/e$. Under this condition, Eq. 7 is simplified to

$$\tau^{-1} = \frac{d_s k_a}{10^3 \Gamma_{max}} c_m + k_d = k_{a,\theta} c_m + k_d. \tag{8}$$

The plots of $\tau^{-1}$ *vs.* $c_m$ are on the straight lines, as is shown in Fig. 7. The linearity of these plots suggests that the relaxation phenomena are based on the adsorption-desorption process of the surfactants. The values of $k_{a,\theta}$ and $k_d$ were calculated from the straight lines in Fig. 7; they are listed in Table 2. The values of $k_a$ were calculated from $k_{a,\theta}$ with the literature values of $d_s$[10] and $\Gamma_{max}$;[11] they are also listed in Table 2.

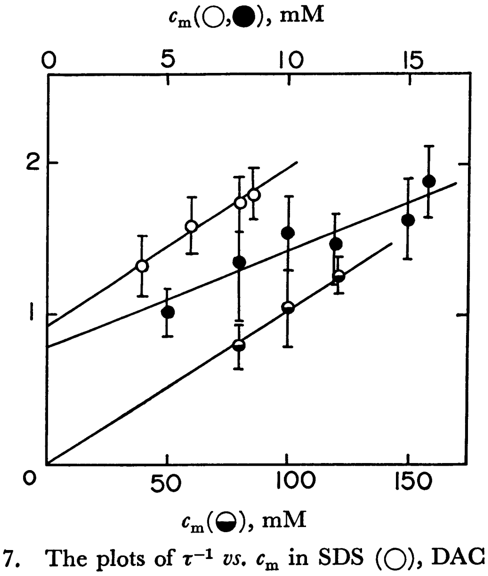
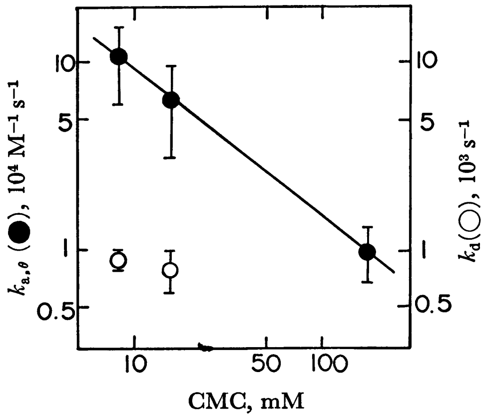


Fig. 7. The plots of $\tau^{-1}$ *vs.* $c_m$ in SDS (○), DAC (●), and OAC (◒) solutions.

TABLE 2. KINETIC PARAMETERS IN SDS, DAC, AND OAC SOLUTIONS AT 25 °C

| | $k_{a,\theta}$ ($10^5$ M$^{-1}$ s$^{-1}$) | $k_a$ ($10^5$ s$^{-1}$) | $k_d$ ($10^2$ s$^{-1}$) | $\Delta G$ ($-RT$) | | $\Delta\gamma$ ($10^{10}$ dyn·cm mol$^{-1}$)[c] | |
|---|---|---|---|---|---|---|---|
| SDS | 1.1±0.5 | 4±2 | 9±1 | 6.1[a] | 6.8 | 10[b] | 6 |
| DAC | 0.6±0.3 | 3±1 | 8±2 | 5.9[a] | 6.3 | 8[b] | 7 |
| OAC | 0.1±0.03 | 0.6±0.2 | — | — | | 3[b] | 7 |

a) The values were calculated by means of Szyszkowski's equation. b) The values were calculated by means of $\Delta\gamma \approx (\gamma_{water}-\gamma_{CMC})/\Gamma_{max}$. c) 1 dyn$=10^{-5}$ N.



CMC, mM

Fig. 8. The plots of $k_{a,\theta}$ (closed circles) and $k_d$ (open circles) *vs.* CMC.

Among the values in Table 2, $k_{a,\theta}$ is fairly dependent on the CMC, but $k_d$ is appreciably independent of the CMC, as is seen from Fig. 8. As a result, the following relation was obtained:

$$\log k_{a,\theta} = (3.4\pm0.3) - (0.8\pm0.3) \log \mathrm{CMC}. \tag{9}$$

On the other hand, the values of $k_d$ were evaluated as follows. Since the state of surfactants on an adsorbed layer is similar to that in a micelle in a surfactant solution, the desorption rate constant can be reasonably compared with the dissociation rate constant of the monomer from the micelle. In an SDS solution, the value of the former falls in the same order of magnitude as that of the latter, $7.5\times10^2$ s$^{-1}$, obtained by means of the pressure-jump method.[12] These facts support the idea that the adsorption-desorption mechanism proposed is reasonable.

The adsorption-desorption energies, $\Delta G$, were calculated by means of $k_a$ and $k_d$; $\Delta G = -RT\ln(k_a/k_d)$. They are listed in Table 2. The obtained values, however, cannot be referred to the literature ones by the static methods,[6] since the surface excess near the CMC increases appreciably with $c_m$. Then, the effective adsorption-desorption energy near the CMC was computed by means of Szyszkowski's equation; it is listed in Table 2. The values of $\Delta G$ obtained are in good agreement with the calculated ones. This also suggests that the proposed mechanism is reasonable.

The concentration dependences of the apparent relaxation strength obtained must also be interpreted by means of the following equation:[1]

$$\delta' = \frac{2(\Delta\gamma)^2 N^{-1/3} c_m^{2/3}}{3\times10^2 RT\gamma}. \tag{10}$$

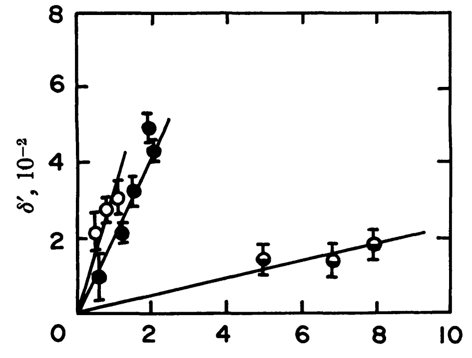


Fig. 9. The plots of $\delta'$ *vs.* $c_m^{2/3}/\gamma$ in SDS (○), DAC (●). and OAC (◒) solutions.

The plots of $\delta'$ *vs.* $c_m^{2/3}/\gamma$ are on the straight lines, as is shown in Fig. 9. The values of $\Delta\gamma$ calculated from the slopes of these straight lines are in good agreement with those of $\delta\gamma/\delta\Gamma \approx (\gamma_{\text{water}} - \gamma_{\text{CMC}})/\Gamma_{\text{max}}$ listed in Table 2, where $\gamma_{\text{water}}$ and $\gamma_{\text{CMC}}$ are the surface tensions in water and the surfactant solution at the CMC respectively.

A preliminary kinetic investigation of the adsorption-desorption on the surfaces of other surfactant solutions by means of the capillary-wave method has shown that similar relaxation phenomena exist in these systems. Further studies of these systems will lead to a quantitative clarification of the adsorption-desorption phenomena.

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