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Characteristic Behavior of Damping Coefficient of Capillary Wave on Surfactant Solution

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Synopsis. The damping coefficient of a capillary wave on decylamine hydrochloride and octylamine hydrochloride solutions decreased abruptly in the vicinity of a critical micelle concentration. The phenomenon observed was well interpreted by an equation derived on the basis of a surface mechanical impedance.

The dynamic properties of surfactants existing on a surface have been studied by means of capillary wave technique.[1–4)] Most of the experimental studies have been carried out on the surfactant solutions below a critical micelle concentration (CMC) and the phenomena observed have been attributed to the diffusion and adsorption-desorption of surfactants between the surface and the bulk phase.

Preliminary measurements on decylamine hydrochloride (DeAC) solution above the CMC revealed that the damping coefficient of the wave decreases abruptly in the vicinity of the CMC. The purpose of this paper is to study the above phenomenon on the DeAC and octylamine hydrochloride (OAC) solutions above the CMC.

Experimental

The apparatus employed was the same as that reported previously.[1)] The frequency range of measurement was 45 to 600 Hz at 25±0.4 °C.

The DeAC and OAC were prepared from decylamine (purity, 99.8%) and octylamine (purity, 99.9%) according to the previous procedure,[4)] respectively. The CMC values of the DeAC and OAC solutions were determined to be 62 and 180 mM*, respectively.

Results and Discussion

The frequency dependence of the damping coefficient, α, was measured in the DeAC and OAC solutions above the CMC. The results are shown in Figs. 1 and 2, together with the data on the solutions below the CMC.[4)] As can be seen from these figures, the α/f values on the solutions above the CMC are considerably smaller than those below the CMC, where f is the frequency. If the phenomenon is related to some chemical relaxation, the α/f value should be greater than that based on only the diffusion of surfactants between surface and bulk phase. This prediction, however, contradicts the present result.

One next considers the effect of a bending viscosity which has been observed on a highly condensed insoluble monolayer.[5)] The theoretical curve of α/f based on the bending viscosity is shown by the curve 3 in Fig. 1. As can be seen from this figure, the tendency of this curve differs from that of the experimental curve.

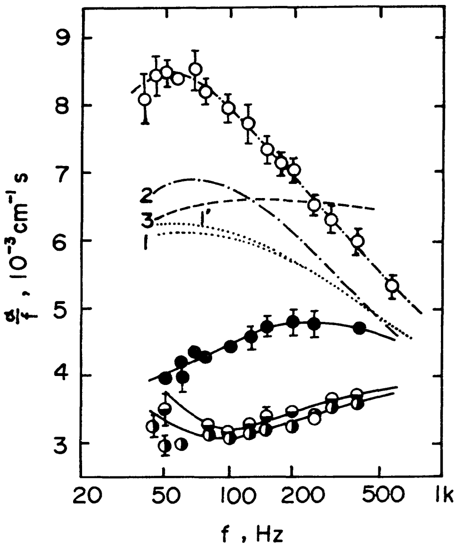

Fig. 1. Frequency dependence of α/f on the DeAC solutions. curves 1(C>CMC) and 1′(C<CMC): theoretical curves based on only the diffusion, curve 2: theoretical curve based on the relaxation, curve 3: theoretical curve based on the bending viscosity.[5)] The solid lines shown the theoretical curves calculated by Eq. 3.
○: 50 mM (below the CMC), ●: 62.5 mM ($G^\sigma = 1.8$ dyn cm^{-1}, $\eta^\sigma = 3.9 \times 10^{-3}$ dyn cm^{-1} s), ◒: 70 mM ($G^\sigma = 3.1$ dyn cm^{-1}, $\eta^\sigma = 3.5 \times 10^{-3}$ dyn cm^{-1} s), ◑: 80 mM ($G^\sigma = 3.0$ dyn cm^{-1}, $\eta^\sigma = 4.3 \times 10^{-3}$ dyn cm^{-1} s).

Let us introduce a surface mechanical impedance, Z, concerned with the normal stress which is proportional to the rate of change in the curvature of the surface, ζ. The boundary condition for the balance of the normal stress at the gas-liquid interface is represented by the following relation:[6)]

$$\gamma\zeta + p - 2\eta\frac{\partial v}{\partial y} - Z\frac{\partial \zeta}{\partial t} = 0, \qquad (1)$$

where y is a rectangular coordinate tangent to the surface at rest, v the component in the y direction, γ the surface tension, p the hydrostatic pressure, η the viscosity, and t the time. Furthermore, one assumes that Z is given by the linear combination of the elasticity, G^σ, and the viscosity, η^σ, as follows:

$$(2i\pi fZ)^{-1} = \{G^{\sigma-1} + (2i\pi\eta^\sigma f)^{-1}\}^{-1}. \qquad (2)$$

According to the previous treatment,[6)] a combination of Eqs. 1 and 2 gives the following equation for α:

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* Throughout this paper, 1 mM$=10^{-3}$ mol dm^{-3}.

$$\frac{\alpha}{f}=\frac{4\pi}{3c}(\varepsilon_{\mathrm{ela}}+\varepsilon_{\mathrm{r}})_{\mathrm{im}}-\frac{4\pi^2kG^{\sigma 2}\eta^{\sigma}f}{3\rho c^3\{G^{\sigma 2}+(2\pi\eta^{\sigma}f)^2\}},\tag{3}$$

where $\varepsilon_{\mathrm{ela}}$ and ε_{r} are the parameters concerned with the surface viscoelaticity and the relaxation,⁽6⁾ respectively; ρ is the density, k the wave number, c the propagation velocity, and the subscript im indicates the imaginary part. In the present case, ε_{r} was ignored because of the absence of the relaxation. The theoretical curves calculated by Eq. 3 are shown by the solid lines in Figs. 1 and 2. Here, the values of the parameters G^{σ} and η^{σ} in Eq. 3 were determined so as to reduce the residual variance about the regression line. As can be seen from these figures, the experimental values fall on the theoretical curves. This fact suggests the validity of the present theory.

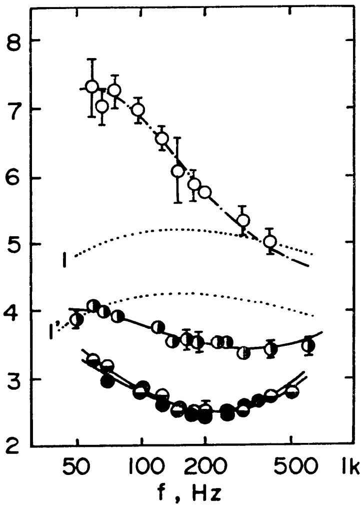

Fig. 2. Frequency dependence of α/f on the OAC solutions. curves 1(C>CMC) and 1′(C<CMC): theoretical curves based on only the diffusion. The solid lines show the theoretical curves calculated by Eq. 3.
○: 114 mM (below the CMC), ◑: 250 mM ($G^{\sigma}=2.4$ dyn cm^{-1}, $\eta^{\sigma}=1.0\times10^{-3}$ dyn cm^{-1} s), ⊖: 280 mM ($G^{\sigma}=3.7$ dyn cm^{-1}, $\eta^{\sigma}=1.4\times10^{-3}$ dyn cm^{-1} s), ●: 351 mM ($G^{\sigma}=3.8$ dyn cm^{-1}, $\eta^{\sigma}=2.0\times10^{-3}$ dyn cm^{-1} s).

Since we have no direct measure of G^{σ} and η^{σ}, we infer their validity from the following consideration. According to the present idea, the dynamic surface tension in the case of $f\gg\eta^{\sigma}/G^{\sigma}$ is expressed by a sum of γ and G^{σ}. From the data of the dynamic surface tension in sodium dodecyl sulfate solution above the CMC,⁽7⁾ the G^{σ} value was obtained to be *ca.* 3 dyn cm^{-1} (1 dyn $=10^{-5}$ N). This value is of the same order as that obtained in the present work (3.8 dyn cm^{-1} in the 351 mM OAC solution). This agreement in the order of magnitude gives further evidence of the validity of the present theory. No consideration for η' was made.

Further clarification for G^{σ} and η^{σ} will be reported in a subsequent paper.

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