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Very slow relaxation observed in the surface tension of surfactant solutions

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A light scattering study was made on ripplons generated over the surface of C_nTAB (*n*-cetyltrimethyl ammonium bromide) solutions (in the present case $n=14$ and 16). After preparing the sample solution we measured its surface tension for 3 h and confirmed that the tension did decrease with time exponentially but very slowly. The relaxation time depended on the surfactant concentration of solutions and increased sensitively with the progress of dilution, e.g., 3 min at 10^{-2} mol/l to 80 min at 10^{-4} mol/l for C_{16}TAB. The results obtained were correlated with surface adsorption densities estimated from the observed surface pressure vs concentration curves using Langmuir's adsorption equation. Two mechanisms were proposed to interpret such a slow relaxation process: One is a model in which reorientation or redistribution of the surfactant molecules adsorbed on the solution is considered, while the other is a two-state model that assumes the existence of a high energy barrier for surfactant molecules between those on the surface and those in the subsurface. A question still remains as to which of the two is more probable.

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INTRODUCTION

In the early part of the last century Adam and Shute experimentally studied surface tension of a dilute solution of cetyltrimethyl bromide and noticed a very slow decrease in the tension, a decrease which lasted for hours or days [1]. Their results, however, have not been fully confirmed because of a lack of successive studies.

Previously we studied the surface elasticity of SDS (sodium dodecyl sulfate) aqueous solutions and found a relaxation effect associated with two-dimensional viscoelasticity [2]. In the present study we aimed to confirm such a slow relaxation process on liquid surfaces as Adam and Shute observed and, if verified, to clarify its mechanism. To achieve this purpose we principally employed a technique termed "ripplon light scattering," a technique which permits a precise determination of the wavelength of ripplons, i.e., thermally excited surface tension waves propagating on a liquid surface, in a perfectly noncontact manner. For producing and measuring surface tension waves at frequencies below 10 kHz, we used another technique [3,4].

It is the significant feature of surfactant molecules that they have two kinds of molecular terminations with conflicting natures, i.e., hydrophilic and hydrophobic. When a surfactant is dissolved in a solvent, this feature usually helps to reduce the surface tension of the solution. The reduction must be greatly influenced by the solution temperature and the concentration of the surfactant. In the present study, hence, we measured the surface tension of surfactant solutions as a function of time, temperature, and surfactant concentration. We chose tetradechyl trimethyl ammonium bromide (C_{14}TAB) and hexadecyl trimethyl ammonium bromide (C_{16}TAB) as surfactants.

Our results clearly indicate that very slow relaxations do occur in the surface tension of surfactant solutions with relaxation times extending from several tens of minutes to hours. This is to be discussed.

THEORETICAL BASIS OF EXPERIMENT

A liquid is never perfectly flat and smooth but always microscopically rough because of the thermally generated density fluctuation of bulk liquid. This surface roughness forms ripplons, the vertical disturbance waves which propagate and attenuate in accord with a dispersion relation depending on the intrinsic surface properties. For the waves with wave number k, frequency ω and the temporal attenuation constant G, the relation is written as

$$\omega^2=\frac{\sigma}{\rho}k^3 \quad \text{and} \quad G=\frac{\eta}{\rho}k^2, \tag{1}$$

where σ is the surface tension, ρ the liquid density, and η the liquid viscosity. These equations have been derived from a strict and somewhat complicated dispersion relation under the approximation of $G \ll \omega$. Fortunately this simplification holds well at frequencies below 10 MHz. In Eq. (1) only the surface tension is considered as a restoring force of the waves, while the gravity term that is significant for waves with wavelength longer than 10 mm is ignored; it should be noted that the ripplons we studied had wavelength shorter than 1 mm. From Eq. (1) one can see that the ripplon measurement enables us to determine the dynamic values of σ and η of the liquid on which ripplons with a frequency of ω are propagating.

Since the principle of the rippon light scattering technique has been described elsewhere [4], a brief explanation is given here: When a light beam irradiates a liquid surface, it is scattered diffusively by the ripplons traveling on the surface. The momentum conservation law holds among three kinds of waves concerned, i.e., the incident light, the scattered light and the ripplons. The wave number of ripplons k can be determined from optical wave numbers and the light scattering angle. (The angle was fixed at about 1.5° throughout our experiment, because the value corresponded to ripplons with

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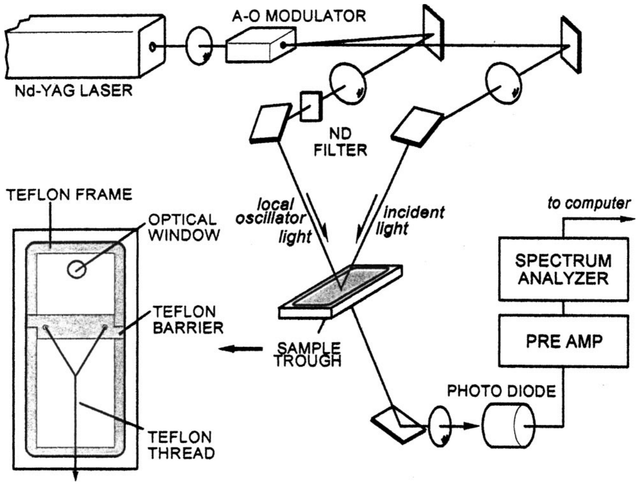

FIG. 1. Block diagram of the ripplon light scattering system used in this study. The inset shows detail of the sample trough with a movable barrier.

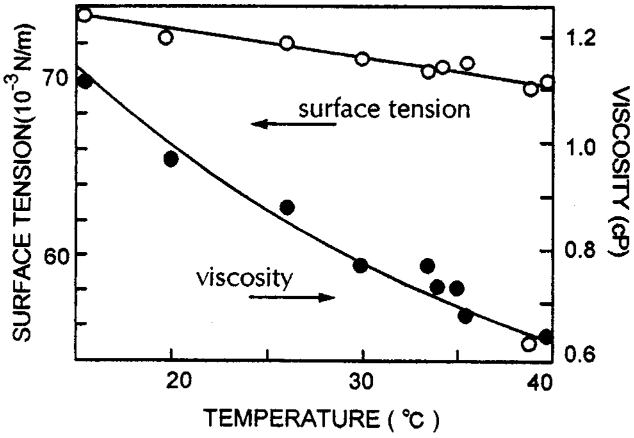

FIG. 2. Surface tension and viscosity of pure water observed by the ripplon light scattering technique over a temperature range from 20 °C to 40 °C. The experimental points are in good agreement with the literature values [5] represented by the solid lines, showing reliability of the experimental system.

a frequency of 120 kHz, i.e., a frequency in the optimum range of our system for accuracy.)

The light scattered by ripplons is naturally subjected to Doppler shifts and exhibits a doublet spectrum consisting from Stokes and anti-Stokes components. This frequency shift of the scattered light is equal to ω, the ripplon frequency. The scattered light is detected as successive peaks of spectrum and the line broadening of each peak leads to determine G. From the values of k, ω, and G thus obtained, we can estimate σ and η of the surfactant solution using Eq. (1).

To achieve a very high spectroscopic resolution and sensitivity, we employed an optical heterodyne system schematically shown as the block diagram of Fig. 1. The light source is an Nd-YAG (yttrium aluminum garnet) laser with a 100 mW output at 532 nm in the second harmonic generation. The laser beam is divided into two paths with an acousto-optic modulator driven at 80 MHz. One, 95% in power, is used as an intensive incident light, while the rest as a local oscillator light for optical heterodyning. The two beams cross each other on the liquid surface. This intersection determines the scattering area. The local oscillator light and the light scattered in the same direction as the former enter into a photodiode. The output current of this photodetector carries an optical beat signal having the doublet power spectrum symmetric with respect to the central frequency of 80 MHz. The peak and width of the spectrum are processed with a spectrum analyzer so as to give ω and G, respectively. Because of frequency sweep and data accumulation it requires about 1 sec to determine a value of σ or of η. It should be noted that this delay time is negligibly short in the observation of slow phenomena lasting for several tens of minutes or more.

The metal trough used in the present study for keeping a sample solution is shown in the inset of Fig. 1. It has a rectangular $220\times100\ \mathrm{mm}^2$ shape with a pool depth of 20 mm. Since the prevention of sample contamination was essential in the present experiment, we covered the trough with a Teflon film completely. A frame made of a 50 μm thick Teflon sheet was placed on the sample surface. A Teflon barrier of the frame slid sidewise in a pistonlike manner and swept the surface so as to produce a clean controlled area on the sample surface. The trough had a clear transparent canopy which served to prevent the sample from both evaporation and contamination. The sample temperature was controlled to $\pm0.1\,°\mathrm{C}$.

In order to check on the performance of the whole experimental system, we made a preliminary measurement of viscosity and surface tension of pure water, changing water temperature from 15 °C to 40 °C. The observed values of σ and η are shown by the closed and the open circles, respectively, in Fig. 2. These data agree well with the previously reported values represented by the solid lines in Fig. 2 [5]. This agreement, particularly with respect to σ, seems to guarantee the reliability of the light scattering system used in the present study.

VERY SLOW RELAXATION OF SURFACE TENSION

Before measurement we prepared C_nTAB aqueous solutions ($n=14$ and 16 in our case) which had concentrations varying from 0.008 to 4 mM (10^{-3} mol/l). The critical micelle concentration (CMC) was included in this range. It seems noteworthy here that the carbon chain length is an important factor for making C_nTAB molecules either hydrophobic or hydrophilic: the affinity to water is markedly reduced with an increase in n.

After filling the trough with a sample solution, we sealed up the trough except for two very tiny holes, through which thin Teflon threads for pulling the barrier passed. Just before measurement we pulled the barrier very carefully so that a clean sample surface with no adsorbed surfactant molecules could be produced. Then we started measurement immediately. Whether the sweeped surface area of a sample solution was clean or not at the beginning of measurement could be easily checked from the value of surface tension initially obtained: If the value was close to that of pure water, i.e., $\sigma=72.75\times10^{-3}$ N/m at 20 °C, the sweeped area was re-

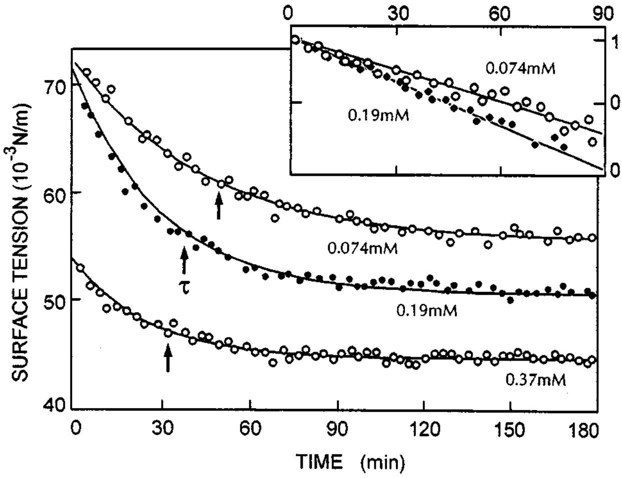

FIG. 3. The slow decrease observed in the surface tension of C_{14}TAB solutions with different concentrations. The temperature is at 20 °C. The inset figure shows the results in a logarithmic ordinate. The solid lines in both figures represent the exponential decay, of which the time constant is indicated with the arrows.

garded as initially clean. Otherwise, some of the surfactant molecules adsorbed on the dirty surface area were thought to have leaked out to the sweeped area before measurement.

Figure 3 shows slow changes in the surface tension of C_{14}TAB solutions of different concentration at 20 °C. It should be pointed out that these curves represent a real-time observation of equilibrium achievement in the surfactant solutions used. Let the surface tension at time t be denoted by $\sigma(t)$. Then it is apparent that all of these observed data can be fitted well with an exponential decay function written as

$$\sigma(t)=\sigma_{\infty}+(\sigma_0-\sigma_{\infty})\exp(-t/\tau), \tag{2}$$

where τ is the characteristic relaxation time, while σ_0 and σ_{∞} are the initial and the final value of surface tension, respectively. In the case of dilute solutions (0.074 and 0.19 mM) the values of σ_0 obtained from graph fitting seem to be in good agreement with the one for pure water. In the case of a more concentrated solution (0.37 mM), however, the estimated value of σ_0 is 54×10^{-3} N/m, which is 20% lower than that of pure water. This indicates that a considerable amount of surfactant molecules had leaked out to the cleaned area through the barrier when the barrier sweeped the surface of the concentrated solution and hence the sweeped surface area was not free from surfactant contamination even at the time of starting measurements.

The characteristic relaxation time τ is particularly important in the present study. This can be determined from logarithmic plots of surface tension change with time such as shown in the inset of Fig. 3. Figure 3 suggests also that τ is affected by the surfactant concentration. Figure 4 shows the concentration dependence of τ obtained for C_{14}TAB and C_{16}TAB solutions. In both cases τ increases markedly with dilution, i.e., with a reduction of concentration. No peculiarity is found at or near a point corresponding to CMC, though the concentration dependence of τ seems to be considerably lessened at concentrations above CMC.

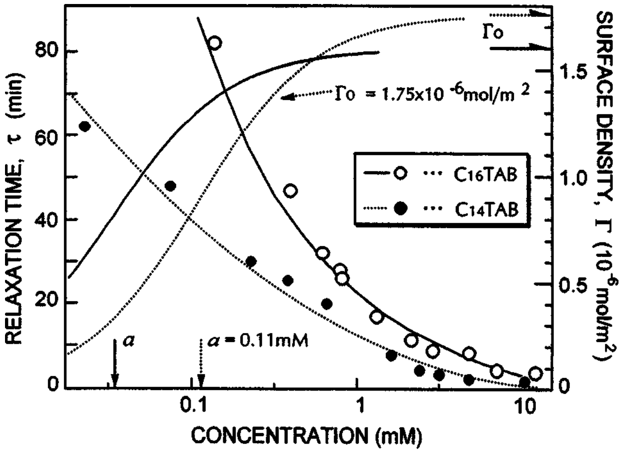

FIG. 4. Dependence of the relaxation time on the concentration. All the open circles and the solid lines in this figure represent the results for C_{16}TAB solutions; and the closed circles and the dotted lines, for C_{14}TAB. The left-hand curves represent the surface density estimated with the Langmuir's equation of adsorption fitted to the experimental data of π-c curves shown in Fig. 5. The arrows indicate the Langmuir parameters whose values for C_{14}TAB and C_{16}TAB are given in Figs. 4 and 5, respectively.

Examining the results shown in Fig. 4, one may realize a subtle contradiction: The longer carbon chain of C_{16}TAB implies a more hydrophobic nature of this molecule. Nevertheless, τ of C_{16}TAB solutions is longer than that of C_{14}TAB solutions. C_{16}TAB molecules seem to be more reluctant to float up on the sample surface. This paradoxical result has provided us with a hint in considering the mechanism of slow relaxation observed in the present study. The other curves in Fig. 4 showing the surface density vs concentration relation will be mentioned in the next section.

ADSORPTION DENSITY

In the case of two-dimensional physics on liquid surface, surface pressure π is defined as a difference in surface tension, i.e., $\pi=\sigma_0-\sigma$ in our case. This pressure is known to be tightly associated with a quantity Γ, defined as the number or mol of the molecules adsorbed on a unit surface area. When the molecules are insoluble, Γ is readily determined; the total amount of adsorbed molecules divided by the total surface area.

Since C_{14}TAB and C_{16}TAB molecules are soluble, Γ cannot be determined in a straightforward manner. To estimate Γ for a given concentration of the solution used, we adopted an idea that, for molecular adsorption on a solution, equilibrium should be attained between the surface molecular density and the concentration on the solution underneath. In other words, Γ should be determined so that a decrease in surface free energy (here in σ) can be compensated for by an increase in chemical potential of the solute in the surface region. Based on this idea we reached the following Gibbs equation of adsorption:

$$\Gamma=\frac{c\,d\pi}{k_B\vartheta\,dc}, \tag{3}$$

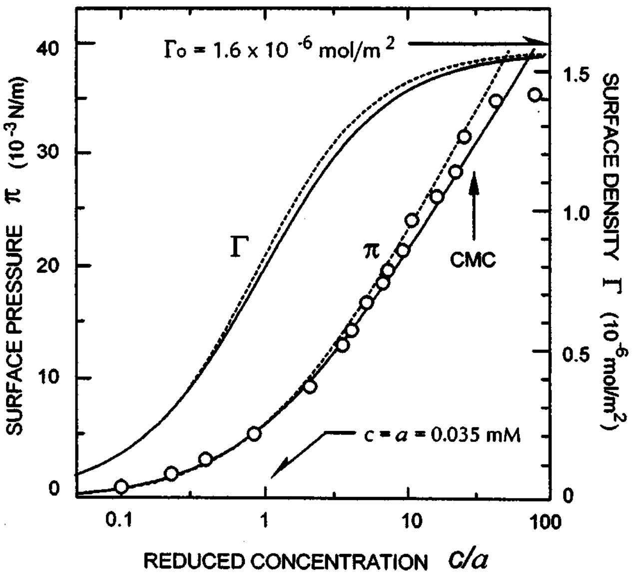

FIG. 5. Dependence of the surface pressure on the concentration observed in C_{16}TAB solutions, and fitted curve of Langmuir's equation of adsorption (solid line). The abscissa is reduced with respect to a, one of the Langmuir parameters. Also shown are the curves of surface density calculated by the Langmuir's equation with the parameters given in the figure. The dashed lines represent the curves of π and Γ obtained by the fitting of Frumkin's equation with the third parameter $b=0.2kT$.

where c is the concentration of the solution, θ the solution temperature, and k_B the Boltzmann constant. Equation (3) holds only in a very dilute region, where Γ is small enough for adsorbed molecules to be far separated from each other. Because the number of adsorption sites is rather limited, adsorption saturation can occur in a region where c is not rather low. Taking this effect into account, Langmuir formerly presented his equation of adsorption written as

$$\pi=-k_B\theta\Gamma_0 \log\{1-(\Gamma/\Gamma_0)\} \tag{4}$$

and

$$\frac{\Gamma/\Gamma_0}{1-\Gamma/\Gamma_0}=\frac{c}{a}, \tag{5}$$

where Γ_0 is the saturation value of Γ and a is a constant determined from the adsorption and desorption rates at a concentration corresponding to $\Gamma=\Gamma_0/2$.

Figure 5 shows the π-c relation we obtained for C_{16}TAB solutions. Here π represents a decrease in surface tension from the initial to the final value at each concentration, i.e., $\pi=\sigma_0-\sigma$. It should be noted that in Fig. 5 a logarithmic scale is used for the abscissa which represents the reduced concentration c/a. It appears possible from Eq. (3) to estimate Γ using the gradient of the π-c curve, at least in a very dilute region, since $(1/c)dc=2.303d(\log c)$. The broken Γ curve in Fig. 5 shows the Γ values thus estimated.

We have, however, realized from a simple analysis that more than one surfactant molecule must be present on the surface area of a 4-nm square even in the most dilute sample solution used. This implies that the premise of Eq. (3) does not hold well in the present study and the above-stated direct estimation of Γ should be abandoned. We therefore fitted Eqs. (4) and (5) to the experimental points of π as shown by the lower solid curve in Fig. 5, estimating Γ_0 at 1.6×10^{-6} mol/m^2 and $a=0.11$ mM. Since the carbon chain of C_{14}TAB is shorter than that of C_{16}TAB, it is very plausible that a C_{14}TAB molecule occupies a smaller area when adsorbed on the surface, leading to a larger value of Γ_0. The larger value of a for C_{14}TAB can be ascribed to the more hydrophilic nature of the molecule. The adsorption curves, which were obtained using all parameters regarding C_{14}TAB and C_{16}TAB, are shown also in Fig. 4.

RELAXATION MECHANISM

To account for the slow relaxation of surface tension observed in the present study, we first considered a model rather commonly employed, i.e., a molecular diffusion process in the sample solution. However, the model has proved unsuccessful in our case because of the reason stated as follows:

According to the model, excess surfactant molecules on the sample surface should sink into the solution as deep as their diffusion length L within a characteristic time T of the system concerned. Note here that L is given by $L=(DT)^{1/2}$, where D is a diffusion constant, and T is defined as the ripplon period obtained from the spectroscopic studies of ripplon relaxation. In a phase when the surface is short of surfactant molecules, they should be supplied to the surface from the upper layer of solution with a depth of L. This diffusion model suggests that an equilibrium state of surface tension should be attained through an exchange of surfactant molecules between the surface and the solution layer underneath. However, we have realized that this is impossible because the estimated relaxation time τ is orders of magnitude shorter than the observed relaxation time of surface tension and the estimated thickness of the diffusion layer L is too small to accommodate molecules enough to fill up the surface. In the case of a 0.1 mM C_{14}TAB solution, for instance, we roughly estimated τ and L to be 0.8 ms and 5 nm, respectively, using a value of $D=6\times10^{-6}$ cm^2/s which is commonly used for surfactant molecules of this kind.

Such a slow relaxation as observed here seems to be interpreted by taking a simultaneous collective motion of many molecules into consideration. A good example can be found in the case of the critical slowing-down of a liquid crystal at an isotropic phase: When its transition point to a nematic phase is approached, the correlation length of collective motion is increased and the time constant of reorientation relaxation is prolonged almost to infinity. Hence our first assumption is that a quasi-two-dimentional group of surfactant molecules in a subsurface layer makes a collective motion toward a surface to be adsorbed, though the existence of such a layer has not been experimentally verified. According to this assumption, a group of fewer molecules in a dilute solution should move faster and so should have a shorter relaxation time than that of a larger number of molecules in a concentrated solution. Therefore, this assumption apparently contradicts the results shown in Fig. 4.

Our second assumption is that there exists a secondary stage of surface adsorption: The surfactant molecules, after once adsorbed on the surface, form a monolayer that requires a considerable time to reach its equilibrium state. The adsorbed molecules are thought to experience a reorientation or redistribution process over a macroscopic surface area, until equilibrium is reached. It seems natural that this process may lead to such a long relaxation time as observed. As is suggested from Frumkin's equation of adsorption, this process should be accompanied by energy exchange among the adsorbed molecules or, in practice, between the nearest neighbors. According to this model, a longer relaxation time is expected for a smaller surface density or a solution of lower concentration, which has been in fact observed in the present study. A double relaxation phenomenon is assumed in this model, an initial fast adsorption followed by a slow reorientation or redistribution of adsorbed molecules. The first fast step is likely to be missed in our measurement, whose experimental system had a time resolution too poor to follow phenomena with relaxation times shorter than 1 min. To settle this open question, a careful study of ripplon spectroscopy at a kHz or MHz range will be required. This second assumption is, however, not excluded at present.

The very slow relaxation of surface tension can be elucidated from a completely different viewpoint. It is known that, when surfactant molecules are stably present in a water solution, a caplike structure of water association forms to cover the hydrocarbon chain of the surfactant molecules [6]: The hydrophobic tail of the molecule tends to avoid the direct contact with water monomers so much that the energy for pushing back the surrounding water may surpass the excess energy required to build the caplike structure. We consider that a surfactant molecule partially covered with associated water molecules will behave as a single hydrophilic compound. Before the stable state of adsorption is achieved, such compounds in the subsurface region have to remove their water cap and expose their hydrophobic tail to the surrounding water monomers transiently. At this transition the surfactant molecules have to overcome a great energy barrier between a stable state of solution and that of adsorption. This two-state model associated with an energy barrier seems to be consistent with the observed very long relaxation time of surface tension, if the barrier is much higher than $k_B\theta$.

In view of this two-state model it seems natural that the longer hydrophobic tail of C_{16}TAB yields a higher energy barrier, causing a longer relaxation time, than that of C_{14}TAB. In the solution with higher concentration, say near CMC, separated surfactant molecules in the solution are more closely crowded, which may lower the activation energy for overcoming the barrier by the elevation of the energy bottom of the solution state; the relaxation time decreases with an increase in concentration. The two-state model is, thus, in agreement with the results of the present study in a qualitative sense.

For a quantitative analysis the activation energy should be determined through experiments made at different temperatures and the results should be discussed in terms of the molecular tail length and the concentration of sample solutions. We are planning a study in this direction.

SUMMARY

We applied the ''ripplon light scattering'' technique for determining the surface tension of surfactant solutions, and successfully observed very slow relaxations in the tension after preparation of sample solutions. The mechanism of the relaxation was discussed in association with the surface adsorption density, a value estimated from Langmuir's equation of adsorption and from the π-c curves experimentally obtained. Two possible mechanisms were proposed: One is that reorientation or redistribution of the surfactant molecules once adsorbed occurs on the surface in a macroscopic scale. The other is that the surfactant molecules on the surface and those in the layer of solution just beneath the surface exchange their positions with each other in spite of a high activation energy required. The energy is thought to arise from the transient exposure of the hydrophobic part of the surfactant molecules to the surrounding water monomers. However, it has not been settled in the present study which of the two mechanisms is more probable. To clear up the problem, we feel it necessary to carry out more quantitative studies on the relaxation time of surfactant molecules with different hydrocarbon lengths over a wide temperature and concentration range.

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[1] N. K. Adam and H. L. Shute, Trans. Faraday Soc. **34**, 758 (1938).
[2] A. Ozawa and A. Minamisawa, Jpn. J. Appl. Phys., Part 1 **33**, 1468 (1994).
[3] K. Sakai, H. Kikuti, and K. Takagi, Rev. Sci. Instrum. **63**, 5377 (1992).
[4] A. Ozawa and A. Minamisawa, Jpn. J. Appl. Phys., Part 1 **36**, 2951 (1997).
[5] Andreas P. Froba, Stefan Will, and Alfred Leipertz, Appl. Opt. **36**, 7615 (1997).
[6] A. Ben-Naim, J. Chem. Phys. **67**, 4884 (1977).