

Observation of the Dynamic and Collective Behavior of Surfactant Molecules at a Water/Nitrobenzene Interface by a Time-Resolved Quasi-Elastic Laser-Scattering Method

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A spectroscopic technique of time-resolved quasi-elastic laser-scattering measurement was applied to monitor the dynamic and collective behavior of anionic surfactant sodium dodecyl sulfate (SDS) and neutral surfactant Triton X-100 molecules around their critical micelle concentrations (cmc's) at a water/nitrobenzene liquid/liquid interface. The time courses of the capillary-wave frequencies after the injection of the surfactant solutions into the water phase were investigated. We found that the dynamic and collective behavior of these two kinds of surfactant molecules at the interface differ from that of the cationic surfactant cetyltrimethylammonium bromide we reported previously. Our results suggested that for SDS the monomolecules at the interface coexist with some molecular aggregates such as micelles at the interface; for Triton X-100, the monolayer at the interface was disrupted and some molecular aggregates, such as micelles, were formed at the interface.

Introduction

Amphiphilic surfactant molecules which contain both a hydrophilic and a hydrophobic group can be used as a unique kind of probe molecule at liquid/liquid interfaces and thus are meaningful for the study of interface properties. Moreover, interest in the behavior of surfactants is growing because they play an increasingly important role in various chemical and biological areas.^{1–4}

Although linear and nonlinear spectroscopic and spectrochemical studies of surfactants at liquid/liquid interfaces have been performed,^{5–25} little has been reported on the dynamic and collective behavior of surfactants at the interface. Without a doubt, the observation of the dynamics of collective behavior is one of the most important experiments which can be undertaken to understand interfaces and surfactants.

We have developed a time-resolved quasi-elastic laser-scattering (QELS) method and have reported that it is a powerful tool for studying the dynamics at liquid/liquid interfaces.^{26,27} The QELS method monitors the frequencies of capillary waves, which are spontaneously generated by thermal fluctuation at liquid/liquid interfaces. The interfacial tension acts as a restoring force on the fluctuation, and it excites an interfacial wave, which is called a capillary wave or ripplon. The relationship between the capillary-wave frequency and the interfacial tension follows Lamb's equation as we have described it in our previous paper.²⁷ Because the capillary-wave frequency is a function of interfacial tension and the change in the interfacial tension depends on the change in the number density of surfactant molecules at the interface, we can obtain various kinds of information on the dynamic change of liquid/liquid interfaces such as the formation of a lipid monolayer,²⁶ the change in number density of surfactant molecules,²⁷ and the evaluation of interfacial density profiles.²⁸ Compared with conventional interfacial tension measurements, the QELS method has the advantage of probing interfaces between two bulk phases without any mechanical disturbance. It is suitable for in situ monitoring of

interfaces. In our work, the in situ, noncontact monitoring of the interface is of great importance, because the observation of collective and dynamic behavior of surfactant molecules would be affected by mechanical disturbance. Owing to its improved time resolution, each power spectrum can be obtained in 1 ms to 1 s, so the method can be used to monitor the dynamic change in number density of surfactants at liquid/liquid interfaces in a real environment. Furthermore, this method has good interface selectivity for overcoming the problem of interference by bulk phases, because the capillary wave is a characteristic phenomenon at interfaces and the frequency of this wave can be detected by an optical heterodyne technique. The purpose of this work is to monitor the change in number densities of two kinds of surfactant molecules at a water/nitrobenzene (W/NB) interface and to study how the interfacial molecular behavior of these surfactants changes around the critical micelle concentration (cmc) using the QELS method we have developed.

Experimental Section

The principle and experimental setup of the QELS measurements has been described previously.^{26,27} In this work, a liquid/liquid interface was prepared by slowly adding 10 mL of purified water (from a Millipore Milli-Q system) to 10 mL of nitrobenzene (Kanto Chemical Co., Inc.; special grade; 99.5% purity) in a sample cell. The cell is made of quartz glass and has an optical flat bottom, which is indispensable to maintaining good reproducibility of the experimental results. To observe the dynamic and collective behavior of surfactant molecules with different charges, an anionic surfactant sodium dodecyl sulfate (SDS) solution (0.5 mL; Kanto Chemical Co., Inc.; first grade) or a neutral surfactant Triton X-100 solution (0.5 mL; Kanto Chemical Co., Inc.; first grade) was injected into the water phase with a microsyringe. The injected concentrations (*C*) of the SDS and Triton X-100 solutions were in the ranges of 1–20 and 0.075–1.5 mM, respectively; the bulk aqueous concentrations (*C*_{eq}) were in the ranges of 0.05–1 and 0.00375–0.075 mM. The cmc's of an SDS solution and a Triton X-100 solution above which surfactant molecules form micelles are 9.8 and 0.2 mM

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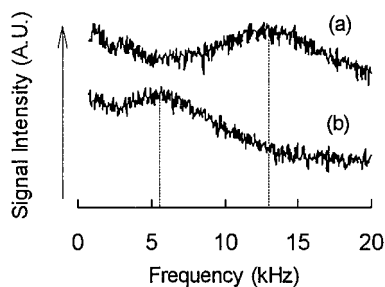


Figure 1. Typical power spectra for capillary waves at the W/NB interface (a) without SDS molecules and (b) 10 s after injection of a SDS solution (0.5 mL, 10 mM) into the water phase.

at 25 °C. All experiments were performed at room temperature. We intended to study how the dynamic and collective behavior of the surfactant molecules changes around the cmc's.

Results and Discussion

Typical power spectra for capillary waves at the W/NB interface are shown in Figure 1a without SDS molecules and in Figure 1b 10 s after the injection of an SDS solution (0.5 mL, 10 mM) into the water phase. As we discussed previously,^{26,27} the peaks appearing around 5–13 kHz are the beat frequencies, i.e., the capillary-wave frequencies. In Figure 1, the peak of the capillary-wave frequency shifts from 13 to 5.5 kHz on the injection of an SDS solution. This is due to the decrease in interfacial tension caused by the increased number density of surfactant molecules at the interface.

To examine the dynamic change in the number densities of surfactant molecules at the interface in detail, we investigated the time courses of the capillary-wave frequencies after the injection of the SDS and Triton X-100 solutions into the water phase. The time just prior to the injection was regarded as 0 s, and a power spectrum was obtained every 3 s. The capillary-wave frequencies after the injection of the SDS and Triton X-100 solutions are plotted as a function of time in Figure 2. From Figures 1 and 2, it is apparent that the time resolution (3 s) of the present QELS method is sufficiently high to detect the change in the number density of surfactant molecules at the interface. In Figure 2, an anomalous temporary decrease in capillary-wave frequency is observed at almost all of the concentrations of SDS and Triton X-100 we used. The capillary-wave frequency decreases rapidly on injection, and after attaining its minimum value, it increases gradually. The initial sudden decrease in the frequency means an abrupt increase in the molecular number density at the interface that can be attributed to the rapid adsorption of surfactant molecules onto the W/NB interface from the W phase whereas the later gradual increase is due to the gradual decrease of the molecular number density by such phenomena as desorption from the W/NB interface to the NB phase. It is clear from the figure that the adsorption rate onto the W/NB interface from the W phase is much higher than the desorption rate from the W/NB interface to the NB phase. Thus, at the minimum frequency, it is reasonable to assume that the equilibrium between the W phase and the W/NB interface is approximately established and that the mass transfer from the W/NB interface to the NB phase is negligible. On the basis of this assumption, we estimated the relative molecular number densities of SDS and Triton X-100 at the interface from the minimum value of the capillary-wave frequencies in Figure 2.

The relationship between the minimum values of the capillary-wave frequencies and the bulk aqueous concentrations of SDS and Triton X-100 is shown in Figure 3. Because the square

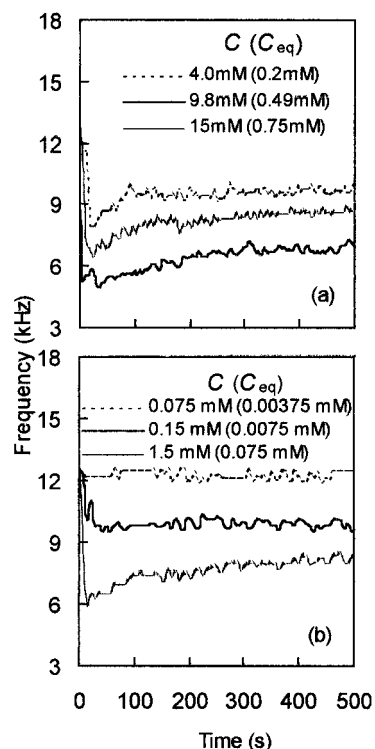


Figure 2. Time courses of the capillary-wave frequencies after injection of (a) SDS and (b) Triton X-100 solutions into the interface. The concentrations of the injected solutions (C) are shown along with the bulk aqueous concentrations (C_{eq}).

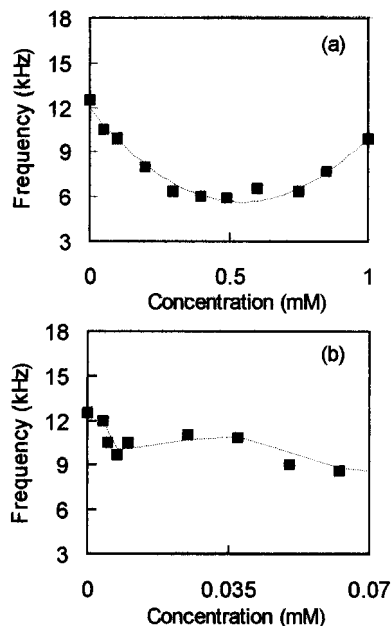


Figure 3. Relationship between the minimum value of the capillary-wave frequency and the bulk aqueous concentration for (a) SDS and (b) Triton X-100.

of the capillary-wave frequency is proportional to the interfacial tension, which is approximately inversely proportional to the number density of surfactant molecules at the interface,^{26,27} details can be added to the above outline by estimating the molecular number density of surfactants at the interface.

The relationship between the relative number density of SDS molecules and the bulk aqueous concentration is shown in Figure 4a. We found that when the C is below the cmc (9.8 mM at 25 °C), the number density increases with an increase in concentration. The experimental data are in agreement with the Langmuir

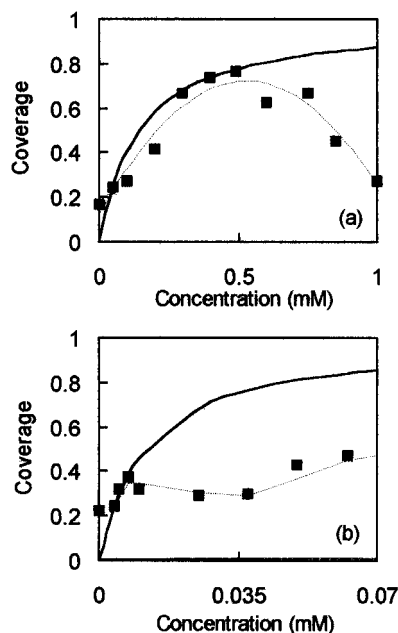


Figure 4. Relative interface coverage of (a) SDS and (b) Triton X-100 at the W/NB interface as a function of bulk aqueous concentration. Experimental data are shown as squares, the solid lines are the calculated Langmuir adsorption isotherms, and the dotted lines are a guide to the eye.

adsorption isotherm, suggesting that the SDS molecules are adsorbed onto the interface as a monolayer. The adsorption energy of the SDS molecules onto the interface is estimated at ca. -21.9 kJ/mol from the experimental data. The free-energy change, ΔG , when 1 mol of methylene groups ($-\text{CH}_2-$) moves from an aqueous solution to a water/oil interface is estimated at -3.4 kJ/mol using Troube's rule.²⁹ Thus, the free-energy change of SDS molecules when they move from the W phase to the interface should be higher than -37.6 kJ/mol. However, the experimental value, -21.9 kJ/mol, is lower than this. This discrepancy suggests that about 60% of the methylene groups in SDS molecules is transported to the NB phase. This may be a reflection of molecular orientation, because the SDS does not form a well-ordered monolayer at the W/NB interface.

When the C is above the cmc, it is interesting to note that the number density of SDS molecules at the interface decreases with an increase in the concentration. This may be due to the local change in aggregation state at the interface from monolayer to molecular aggregates. The molecular aggregates observed here are assumed to be micelles or reversed micelles, but further investigation is necessary to verify this. Furthermore, this gradual decrease above the cmc suggests that the equilibrium between interfacial molecules and the molecular aggregates is established and the change in the concentration causes the shift of the equilibrium. It could be thought that the interfacial concentration of SDS is higher than the bulk aqueous concentration, so it is possible for SDS molecules to form molecular aggregates at the interface while the bulk aqueous concentration is below the cmc. We also find that when the C is above the cmc, the collective behavior of SDS at the W/NB interface is very different from that of cationic surfactant cetyltrimethylammonium bromide (CTAB) which we reported previously.²⁷ CTAB forms an oriented monolayer whereas SDS does not form well-ordered layers ($C > \text{cmc}$). Using the resonant TIR-SFG, Richmond and co-workers observed a reduction in ordering of the chain of the SDS at the $\text{D}_2\text{O}/\text{CCl}_4$ interface at higher concentrations,¹³ and they also reported that the alkyl chains of the cationic surfactants DTAC and DAC possess the fewest

gauche defects whereas the anionic surfactants SDS and DDS display more disorder in the hydrocarbon chains at similar surface concentrations.²³ Similar results were reported by others^{30,31} for SDS adsorption onto hydrophobic substrates from water. On the basis of our experimental results and those of the others, we thought that when the C of SDS is above the cmc, the increase in capillary-wave frequency, i.e., the decrease in number density, may be due to the change in aggregation state of SDS molecules caused by the chain conformation or the electrostatic interactions of the headgroups. It is generally said that the formation of reversed micelles in the bulk NB phase is quite unlikely because of the high polarity of NB molecules. However, it is reasonable to consider that the behavior of SDS molecules at the interface differs from that in the bulk NB phase because W and NB molecules can mix at the interfacial region and because the properties of the interface differ from those of the bulk liquid.

By estimating the relative molecular number density of Triton X-100 at the interface, we find that when the C is below the cmc (0.2 mM at 25 °C), the experimental data in Figure 4b are in good agreement with the calculated Langmuir adsorption isotherm. This indicates that the adsorbed Triton X-100 molecules are confined to a monolayer. When the C is above the cmc, a slight decrease in the number density was observed. It is reasonable to consider that the slight decrease is due to the change in aggregation state at the interface such as the formation of micelles whereas the latter slow increase is due to the increase of molecular aggregates at the interface. This result suggests that the phase transition from a monolayer to molecular aggregates occurs at a certain concentration unlike the case with SDS.

The molecular behavior at the interface may be affected by the ionic nature, ion pair formation, solvent polarity, or the chain conformation of surfactants. Through comparison of the measurements of the behavior of different kinds of surfactants at the liquid/liquid interface, the interfacial structure is also expected to be deduced.

Conclusions

In summary, we observed the dynamic and collective behavior of SDS and Triton X-100 at a W/NB interface by monitoring the time courses of the capillary-wave frequency using the QELS method. These results suggested that below the cmc SDS molecules were adsorbed onto the interface, forming a monolayer; above the cmc, the monolayer was disrupted and some molecular aggregates such as micelles or reversed micelles were formed. It could also be thought that below the cmc Triton X-100 molecules were adsorbed onto the interface, forming a monolayer; above the cmc, the monolayer was disrupted and some molecular aggregates such as micelles were formed, and with further increases in concentration, the number of micelles increased. The behavior of surfactant molecules described above may be affected by the ionic nature, ion pair formation, solvent polarity, or the chain conformation of surfactants. Through comparison of the measurements of the behavior of different kinds of surfactants at the liquid/liquid interface, the interfacial structure is also expected to be deduced.

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