

# Effect of Organic Phase on Dynamic and Collective Behavior of Surfactants at Liquid/Liquid Interfaces by a Time-Resolved Quasi-Elastic Laser-Scattering Method

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A time-resolved quasi-elastic laser-scattering method was applied to monitor the dynamic and collective behavior of molecules of an anionic surfactant, sodium dodecyl sulfate (SDS), around the critical micelle concentration (cmc) at several water/chlorinated hydrocarbon interfaces. The time courses of the capillary wave frequencies after injection of the SDS solutions into the water phase were investigated. We found that when the injected concentration is above the cmc, the relative number density of SDS molecules decreases with an increase in the bulk aqueous concentration at all the examined interfaces. We also found that the relative number density of SDS molecules adsorbed onto the interface increases with a decrease in the permittivity of the organic phase. Our results suggested that the adsorption of SDS molecules was affected by the permittivity of the organic phase.

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## Introduction

The study of liquid/liquid (L/L) interfaces is receiving growing attention, because the transport or reactions of molecules at L/L interfaces are fundamentally important for understanding many chemical processes in the fields of electrochemistry, biology, separation science, and environmental studies. The characterization of these chemical processes is often achieved by spectroscopically monitoring the adsorption, orientation, organization, and reactivity of submonolayer quantities of surfactant molecules adsorbed to the interface.<sup>1-22</sup> Second harmonic generation (SHG) and sum frequency generation (SFG) techniques have been used to probe L/L interfaces and have the potential to provide interface dynamic properties.<sup>5,11,16</sup> Neutron specular reflectivity measurements have been used to study the effect of surfactants on the roughness of L/L interfaces.<sup>6</sup> Many researchers have investigated liquid surfaces by measuring capillary waves.<sup>23-31</sup> Since capillary waves reflect the fundamental properties of the surface or interfacial region, much effort has been made to observe them and to analyze their spectra. The theoretical understanding of these waves is well estimated in hydrodynamics, and light scattering from the waves is also widely used to monitor the L/L interfaces.<sup>2</sup> In our previous papers,<sup>13,21,22</sup> we reported that a developed time-resolved quasi-elastic laser-scattering (QELS) method was a powerful tool for studying molecular dynamics at L/L interfaces. The QELS method monitors the change of the frequencies of the capillary waves, which are spontaneously generated by thermal fluctuation at L/L interfaces. The QELS

method has good interface selectivity for overcoming the problem of interference by bulk phases, because the capillary wave is a characteristic phenomenon at the interface.

Chemical processes, such as formation of monolayers or transformation of chemical species at the interface, cause changes of Gibbs free energy there.<sup>32,33</sup> In turn, these Gibbs free energy changes cause changes of interfacial tension. So it has been assumed that these chemical processes can be monitored by observing changes of interfacial tension. As we described previously,<sup>13,21</sup> 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; then the QELS method allows observation of the dynamic change of L/L interfaces such as the formation of a lipid monolayer,<sup>13</sup> or the adsorption of surfactant molecules.<sup>21,22</sup> Compared with conventional interfacial tension measurements, the QELS method has the obvious advantage of being able to probe interfaces between two bulk phases without any mechanical perturbation. It is suitable for *in situ* monitoring of interfaces. Furthermore, 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 L/L interfaces in a real environment. The simplicity of the measurement is also an advantage.

Using the QELS method, we have successfully monitored the dynamic and collective behavior of three kinds of surfactant molecules with different charges at the water/nitrobenzene (W/NB) interface, and found that the behavior of these molecules differs from each other.<sup>21,22</sup> Particularly for anionic sodium dodecyl sulfate (SDS) molecules, when the injected concentration is above the critical micelle concentration (cmc), the relative number density decreases with an increase in the

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bulk aqueous concentration, indicating that a possible local change in aggregation state of SDS molecules occurs, such as the formation of micelles or reversed micelles at the interface.<sup>22</sup> In the previous work,<sup>21,22</sup> we focused on the effect of the ionic nature of surfactants on the dynamic and collective behavior. In the present work, we focus on the effect of the organic phase, such as its dielectric constant, which is an important macroscopic property of a liquid at an interface. We can expect that the behavior of surfactant molecules will reflect the unique properties or structures of the interfaces. We look at how the interfacial behavior of SDS molecules changes around the cmc by monitoring the change in number density of SDS molecules at several water/chlorinated hydrocarbon interfaces, and at how the property of the organic phase affects the dynamic and collective behavior of SDS molecules.

## Experimental

The principle of the QELS measurement has been described in detail previously.<sup>13,21</sup> The experimental setup of the QELS method is shown in Fig. 1. The signal/noise ratio ( $S/N$ ) was improved by using a YAG laser (CrystaLaser, Model GCL-025s, 532 nm) with 20 mW power instead of the He-Ne laser we used previously. The noise that originates from the fluctuation of a gas laser was decreased. Furthermore, the YAG laser has a single longitudinal mode which is better suited to our measurement system; the multi longitudinal modes of the He-Ne laser resulted in a small  $S/N$  ratio in the measurement region. Owing to this improvement, we can apply the QELS method to not only the W/NB interface but to various other interfaces as well. The power of the incident laser beam was adjusted by using a neutral density filter positioned in front of the laser.

There exist capillary waves with different wavelengths at L/L interfaces, but one of them can be selected by a grating. In detail, we used a transmission diffraction grating having a spacing of 0.33 mm, the fifth order diffracted beam was selected for the measurement. Thus, the wavelength of the observed capillary wave in this work was 66  $\mu\text{m}$ .<sup>21</sup> As shown in Fig. 1, the beam is incident on the grating, and passes through the bottom of the sample cell. The cell is made of quartz glass and has an optically flat bottom. In this work, an optical heterodyne technique was used to detect the capillary wave frequency. The incident laser beam normal to the interface is quasi-elastically scattered by the capillary wave with a Doppler shift. The scattered beam is optically mixed with the diffracted beam from the grating to generate an optical beat in the mixed light. The beat frequency obtained here is the same as the Doppler shift, *i.e.* the capillary wave frequency. The optical beat of the mixed light is measured by the photodiode (Hamamatsu Photonics S1290). The signals are Fourier transformed and saved by a digital spectrum analyzer (Takeda Riken TR9404).

An L/L interface was prepared by slowly adding 10 mL of purified water (from a Millipore Milli-Q system) to 10 mL of organic solvent in the sample cell. To observe how the dynamic and collective behavior of surfactant molecules at the interface changes around the cmc, an SDS ( $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$ ) solution (0.5 mL; Kanto Chemical Co., Inc.; first grade) was injected into the water phase with a microsyringe. The concentrations of the injected SDS solution ( $C$ ) were in the range of 1 – 20 mM; the bulk aqueous concentrations were in the range of 0.05 – 1 mM. The cmc of an SDS solution above which surfactant molecules form micelles, is 8.1 mM at 20°C.<sup>14</sup> To observe the effect of the organic phase on the interfacial behavior of SDS molecules, three kinds of organic solvents: dichloromethane ( $\text{CH}_2\text{Cl}_2$ )

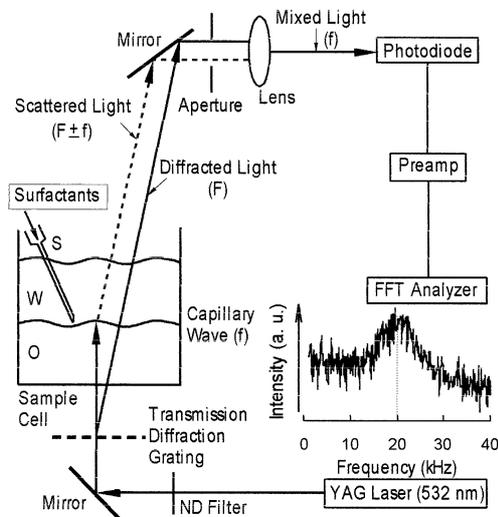


Fig. 1 Schematic diagram of the experimental setup for the QELS method: ND filter, neutral density filter; O, organic phase; W, water phase; S, microsyringe; F and f are light frequencies. Inset: A typical power spectrum for the capillary wave at the neat W/ $\text{CCl}_4$  interface at 20°C.

(Kanto Chemical Co., Inc.; special grade; 99.0% purity), chloroform ( $\text{CHCl}_3$ ) (Kanto Chemical Co., Inc.; special grade; 99.0% purity), and carbon tetrachloride ( $\text{CCl}_4$ ) (Kanto Chemical Co., Inc.; special grade; 99.5% purity) were chosen. We monitored the change of capillary wave frequencies at the W/ $\text{CH}_2\text{Cl}_2$ , the W/ $\text{CHCl}_3$ , and the W/ $\text{CCl}_4$  interfaces after the injection of SDS solution using the QELS method.

## Results and Discussion

To examine the dynamic behavior of SDS molecules at the interfaces, we investigated the time courses of the capillary wave frequencies after the injection of different amounts of SDS solution into the water phase. The time just prior to the injection is regarded as 0 s, a power spectrum like that shown in the inset of Fig. 1 was obtained every 3 s. The capillary wave frequencies at different interfaces are plotted as a function of time in Fig. 2. An anomalous temporary decrease in capillary wave frequency was observed at all the interfaces examined. The capillary wave frequency decreases on injection, and after attaining its minimum value, it increases gradually. As we have discussed previously,<sup>21</sup> the initial decrease in the capillary wave frequency means an increase in the molecular number density at the interface that can be attributed to the adsorption of surfactant molecules onto the interface from the water phase, whereas the later increase is due to the gradual decrease of the molecular number density by such phenomena as desorption from the interface to the organic phase. At the minimum frequency, we assume that a transient equilibrium between the water phase and the interface is approximately established. On the basis of this assumption, we estimated the relative molecular number density of the surfactants at the interface from the minimum values of the capillary wave frequencies. Experiments with equilibrated phases were performed, but the interfacial tension only decreased with the increase in concentration. From the measurement of the time course of capillary wave frequencies, further dynamical or structural information can be expected by the analysis of the minimum

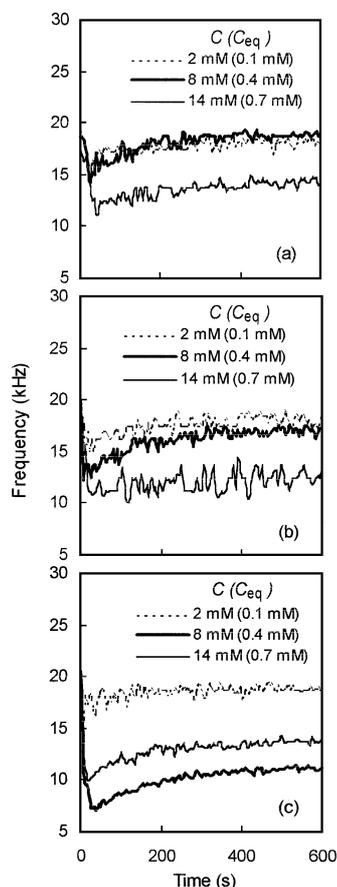


Fig. 2 Time courses of the capillary wave frequencies after injection of SDS solution into (a) W/CH<sub>2</sub>Cl<sub>2</sub>, (b) W/CHCl<sub>3</sub> and (c) W/CCl<sub>4</sub> interfaces. The concentrations of the injected solutions ( $C$ ) are shown, along with the bulk aqueous concentrations ( $C_{eq}$ ).

value, such as surfactant transport across the interface or possibly dynamic changes in state of molecular aggregation at the interface.

Relationships between the minimum values of the capillary wave frequencies and the bulk aqueous concentrations of SDS are shown in Fig. 3. We found that, when the injected concentration  $C$  is below the cmc, the frequency decreases with an increase in concentration. When the  $C$  is above the cmc, the frequency increases with an increase in concentration. From these results, we calculated the interfacial tension by using the Lamb's equation<sup>34</sup> (Eq. (1)), where  $f$  is the capillary wave frequency,  $\gamma$  is the interfacial tension,  $\rho_U$  is the density of the upper phase,  $\rho_L$  is the density of the lower phase, and  $k$  is the wavenumber of the capillary wave.

$$f = \frac{1}{2\pi} \left( \frac{\gamma}{\rho_U + \rho_L} \right)^{1/2} k^{3/2} \quad (1)$$

Although Eq. (1) neglects the effect of surface viscosity, it gives a good fit to the observed relationship between the frequency and wavenumber of capillary waves at a liquid surface.<sup>29,35-37</sup> In this work, we did not discuss the shape, or the width of the spectrum, because they are determined by the instrumental function as well as by the interfacial viscosity.<sup>24,38,39</sup> In our study, however, the instrumental function was undetermined because of the transmitting optical configuration employed for the observation of the interface, and

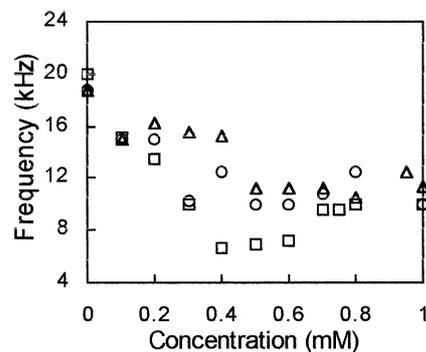


Fig. 3 Relationships between the minimum value of the capillary wave frequency and the bulk aqueous concentration. Experimental data are shown as  $\Delta$  for W/CH<sub>2</sub>Cl<sub>2</sub>,  $\square$  for W/CHCl<sub>3</sub> and  $\circ$  for W/CCl<sub>4</sub> interfaces.

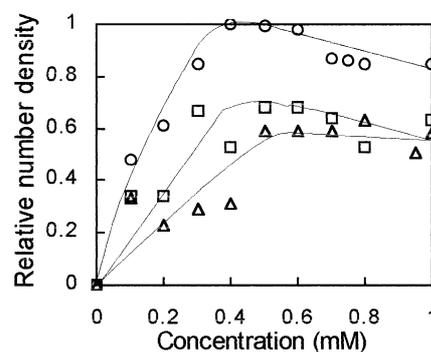


Fig. 4 Relationships between the relative number density of SDS and the bulk aqueous concentration. Experimental data are shown as  $\circ$  for W/CCl<sub>4</sub>,  $\square$  for W/CHCl<sub>3</sub> and  $\Delta$  for W/CH<sub>2</sub>Cl<sub>2</sub> interfaces. The solid lines are a guide to the eye.

the width could not be used for the analysis. In the present case, only the peak frequency is used for the analysis. Since the square 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,<sup>13,21</sup> details can be added to the above outline by estimating the molecular number density of surfactants at the interface.

The relationships between the relative molecular number densities and the bulk aqueous concentrations are shown in Fig. 4. Here, the relative number density is a ratio of the number density of SDS at the examined interfaces and the number density of SDS at the W/CCl<sub>4</sub> interface. It was found that, when the injected concentration  $C$  is below the cmc (8.1 mM at 20°C), the relative number densities of SDS increase with an increase in concentration at all the interfaces examined. This is due to the decrease in interfacial tension caused by the adsorption of SDS molecules onto the interface. When the  $C$  is above the cmc, it is interesting to note that the relative number densities of SDS decrease with an increase in concentration. Using the resonant TIR-SFG, Richmond and coworkers observed a reduction in ordering of the chain of the SDS at the D<sub>2</sub>O/CCl<sub>4</sub> interface at higher concentrations.<sup>14</sup> Here, we thought the decrease in the number density, *i.e.* the increase in the interfacial tension in our systems could be due to the local change in aggregation state or to the reorientation of SDS molecules at the interface caused by the electrostatic

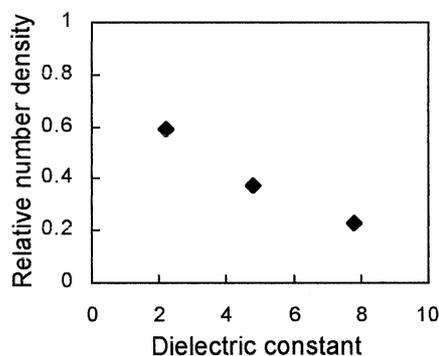


Fig. 5 Relationships between the relative number density of SDS and the dielectric constant of the organic phase. The dielectric constants are 2.2 for  $\text{CCl}_4$ , 4.8 for  $\text{CHCl}_3$ , and 7.8 for  $\text{CH}_2\text{Cl}_2$  at  $20^\circ\text{C}$ .

interactions of the head groups or the chain conformation.

To clarify the effect of the organic phase on the behavior of SDS molecules at the interface, we investigated the relationship between the relative number density of the SDS molecules at the interface and the dielectric constant of the organic phase by using the data when the  $C$  is 4 mM. As shown in Fig. 5, the relative number density increases with a decrease in the dielectric constant of the organic phase. This means that the adsorption of SDS molecules at the interface depends on some properties, such as the permittivity of the organic phase, that would affect the interaction between the hydrocarbon tails of surfactant molecules and the organic solvent molecules, and the tail-tail interaction of surfactant molecules as well. From comparison of our results with those reported by Grubb *et al.*,<sup>3</sup> we can consider that the increase in relative number density with a decrease in the dielectric constant of the organic phase reflects the increased orientation of the surfactant molecules that depends strongly on the property of the organic phase.

## Conclusions

We applied the time-resolved QELS method to study the dynamic and collective behavior of surfactant molecules at several water/chlorinated hydrocarbon interfaces. We found that the number density of SDS molecules adsorbed onto the interface increased with a decrease in the dielectric constant of the organic phase. For all the examined interfaces, when the injected concentration was above the cmc, the relative number density of SDS molecules decreased with an increase in the concentration. Our results suggested that SDS monomolecules coexisted with some molecular aggregates at the interface. This may reflect the electrostatic interaction of the headgroups of the SDS molecules.

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