Monitoring of Molecular Collective Behavior at a Liquid/Liquid Interface by a Time-Resolved Quasi-Elastic Laser Scattering Method

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We monitored the change in the number density of cetyltrimethylammonium bromide (CTAB) molecules at a water/nitrobenzene (W/NB) liquid/liquid interface by a newly developed time-resolved quasi-elastic laser scattering (QELS) method. The results are used to discuss the molecular collective behavior there. From the time-courses after the injection of a CTAB solution beyond its critical micelle concentration (cmc), we found an anomalous temporary increase of the number density of CTAB molecules at the interface, which cannot be explained by a simple diffusion model. This suggests that the transfer of CTAB micelles across the interface occurs in the following process: the collapse of micelles at the interface region; the oriented adsorption of CTAB molecules onto the interface, forming a monolayer; and the desorption from the interface. Thermodynamic evaluation results also support this model; that is, the equilibrium number density of CTAB molecules at the interface follows the Langmuir adsorption isotherm obtained from our measurement, and the adsorption energy calculated from the isotherm agrees well with the theoretical value of the micelles.

Introduction

The interface between two immiscible liquids is one of the most interesting and important areas of study, since transport phenomena across the interface are fundamental to understanding solvent extraction, chromatography, phase transfer catalysis, biological membranes, etc. Although numerous experimental studies and theoretical modelings have been done,[1−3] there are still some basic points to be clarified, e.g., the nature of the barrier in mass transfer across the interface and the molecular interface structure.

Experimental probes of structure have been done mainly by spectroscopic techniques, which are advantageous for monitoring the interface between two bulk phases because their measurements result in no mechanical perturbation. Second harmonic generation (SHG) and sum frequency generation (SFG) techniques have been used to probe liquid/liquid interfaces and have the potential to provide interface dynamic properties.[4−13] These techniques are suitable for the measurement of the orientation of adsorbed molecules at liquid/liquid interfaces, but they cannot provide information on the behavior of the molecules in a disordered orientation. Neutron specular reflectivity measurements have been used to study the effect of surfactants on the roughness of oil/water interfaces.[14] This method, however, requires too much time to allow its use in elucidating molecular dynamic behavior. Therefore, these spectroscopic techniques are not appropriate for the dynamic properties of the interfaces, because they require too much time for measurement.

We have developed a quasi-elastic laser scattering (QELS) method for monitoring the dynamics of liquid/liquid interfaces.[15−17] The QELS method has an advantage over other spectroscopic methods, owing to its improved time-resolution, that each power spectrum can be obtained in 1−3 s. The method monitors the frequencies of capillary waves, which are spontaneously generated by thermal fluctuation at liquid/liquid interfaces. Since the capillary wave frequency is a function of interfacial tension, and the change in the interfacial tension reflects the change in the number density of surfactant molecules at the interface, the QELS method enables us to observe the dynamic change of liquid/liquid interfaces such as the formation of a lipid monolayer[17] and the change in number density of surfactant molecules.

In this study, we focus on the molecular collective behavior of surfactant molecules at a liquid/liquid interface. Since amphiphilic surfactant molecules contain both a hydrophilic head and a hydrophobic tail, they are expected to exhibit meaningful behavior of the investigation of dynamic properties of liquid/liquid interfaces. Moreover, interest in the behavior of surfactants is growing because they play an increasingly important role in various chemical and biological areas such as the synthesis of inorganic materials, pharmaceuticals, and detergents.[18−20] Then we focus on elucidating the molecular collective behavior in transfer across a liquid/liquid interface by using the QELS method.

Here we present the results from monitoring the capillary wave frequency at a liquid/liquid (W/NB: water/nitrobenzene) interface by the QELS method when a cationic surfactant (CTAB: cetyltrimethylammonium bromide) solution was injected into the aqueous phase. An anomalous change of the capillary wave frequency was observed when a CTAB solution beyond the critical micelle concentration (cmc) was injected, and we discuss a model for mass transfer dynamics across the interface.

Experimental Section

Principle. The principle of the quasi-elastic laser scattering method was described previously.[15−17] A brief outline follows here based on Figure 1. A thermally generated spontaneous density fluctuation occurs at the liquid/liquid interface. The interfacial tension acts as a restoring force on the fluctuation, and it excites an interfacial tension wave, which is called a capillary wave or ripplon. The incident beam normal to the interface is quasi-elastically scattered by the capillary wave with a Doppler shift at an angle determined by the following equation:

$$K \tan \theta = k \quad (1)$$

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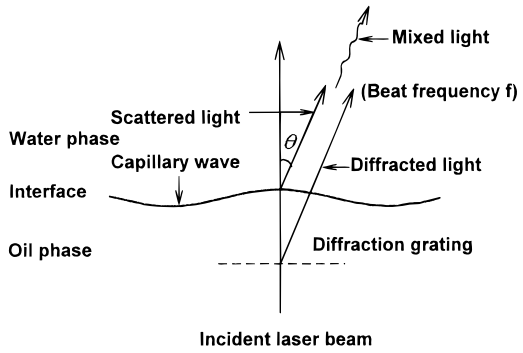

Figure 1. Principle of the quasi-elastic laser scattering method.

where K and k are the wavenumbers of the incident beam and the capillary wave, respectively. Thus, the wavenumber k of the capillary wave is obtained by giving θ.

We arranged a transmitting diffraction grating in front of the cell to adjust the angle θ.[21] The angle θ is determined by the following equation using the spacing d and the order n of the diffraction grating,

$$d \sin \theta = n\lambda \tag{2}$$

where λ is the wavelength of the laser beam.

From eqs 1 and 2, we obtain the wavenumber k and the wavelength Λ of the observed capillary wave:

$$k = 2\pi n/d \tag{3}$$

$$\Lambda = d/n \tag{4}$$

The capillary wave frequency is detected by an optical heterodyne technique. The laser beam quasi-elastically scattered by the capillary wave at the liquid/liquid interface is accompanied by a Doppler shift. The scattered beam is optically mixed with the diffracted beam from the diffraction grating to generate an optical heat in the mixed light. The beat frequency obtained here is the same as the Doppler shift, i.e., the capillary wave frequency. By selecting the order of the mixed diffracted beam, we can change the wavelength of the observed capillary wave according to eq 4.

The relationship between the capillary wave frequency f and the interfacial tension γ is approximately expressed by Lamb's equations,[22]

$$f = \frac{1}{2\pi}\left(\frac{\gamma}{\rho_w + \rho_o}\right)^{1/2} k^{3/2} \tag{5}$$

$$\rho = \rho_w + \rho_o \tag{6}$$

where ρ_w is the density of the aqueous phase, ρ_o is the density of the oil phase, and k is the wavenumber of the capillary wave. The relationship between the interfacial tension γ and the number density Γ of a monolayer is approximately expressed by the following equation, as we have reported previously:[16,17]

$$\gamma \propto 1/\Gamma \tag{7}$$

We employed this experimental relation instead of the conventional Gibbs equation because it is actually more suitable for our liquid/liquid interfacial system. Therefore, the number density Γ of surfactant molecules can be monitored by measuring the capillary wave frequency f. Since the time-resolution of the QELS method is 1−3 s, the method can provide great insight into the collective motion of surfactant molecules at the interface.

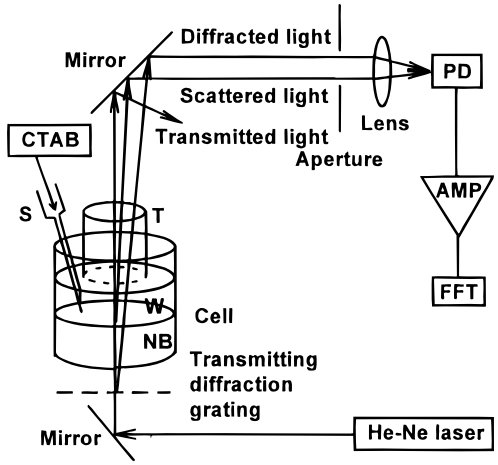

Figure 2. Schematic diagram of the experimental setup: NB, nitrobenzene phase; W, water phase; S, microsyringe; T, glass tube; PD, photodiode; AMP, preamplifier; FFT, FFT analyzer.

Apparatus. A schematic diagram of the experimental setup is shown in Figure 2. The beam from a He−Ne laser with 10 mW power (Uniphase 1135P) is incident on the transmitting diffraction grating having a spacing of 3.3×10^{-2} cm and passes through the bottom of the sample cell. The cell is made of quartz glass and has an optically flat bottom, which is indispensable to maintaining good reproducibility of the experimental results. After passing through the sample, the diffracted beams are mixed with the scattered light from the capillary wave, and one of them is selected by an aperture (1 mm ϕ) positioned in front of a photodiode. 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). In the present study, the fifth-order diffracted beam was selected for the measurement. Thus, the wavelength of the observed capillary wave was 6.6×10^{-3} cm according to eq 4.

Sample Preparation. 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 the quartz cell. To observe the collective motion of surfactant molecules, the injection of a CTAB solution (0.5 mL; Kanto Chemical Co., Inc.; first grade) to the aqueous phase was carried out with a microsyringe. The concentrations of the injected CTAB solution were in the range 2−30 mM; the average concentrations of CTAB in the aqueous phase after injection were in the range 0.1−1.5 mM. The cmc of a CTAB solution, beyond which surfactant molecules form micelles, is 1.3 mM at 25 °C. We intended to study how the behavior of surfactant molecules changes around the cmc.

Results and Discussion

Typical power spectra for capillary waves excited at the W/NB interface are shown in Figure 3: (a) without CTAB molecules and (b) 10 s after the injection of a CTAB solution (0.5 mL, 10 mM) to the aqueous phase. The detected signals are somewhat noisy, but the beats of the local beam and the scattered beam due to the capillary wave are seen in the spectra. The peaks appearing around 10−13 kHz are the beat frequencies, i.e., the capillary wave frequencies, as we discussed previously.[16,17] The peak of the capillary wave frequency shifts from 12.5 to 10.0 kHz on the injection of CTAB solution. This is due to the decrease in interfacial tension caused by the increased number density of surfactant molecules at the interface.

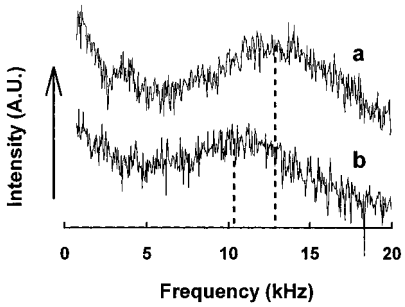

Figure 3. Power spectra for capillary waves excited at the W/NB interface (a) without CTAB molecules and (b) 10 s after injection of a CTAB solution (0.5 mL, 10 mM) into the water phase.

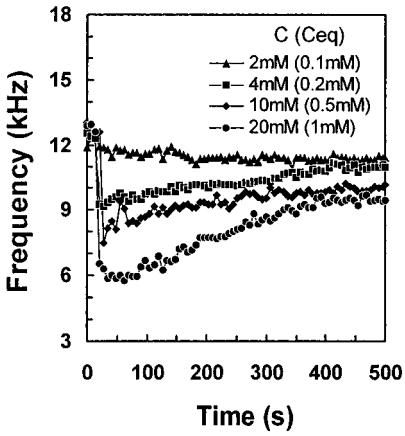

Figure 4. Capillary wave frequency vs time after injection of the CTAB solutions (0.5 mL, 2−30 mM). The concentrations of the injected solution (*C*) are shown, along with the average concentrations (C_{eq}) in the aqueous phase.

In order to examine the change in the number density of surfactant molecules at the interface in detail, we investigated the time-course of the capillary wave frequency after the injection of the CTAB solution into the aqueous phase. The power spectrum was obtained every 3 s, and the capillary wave frequencies after the injection of the CTAB solution (0.5 mL, 2−30 mM) are plotted as a function of time in Figure 4. From Figures 3 and 4, 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 CTAB molecules at the interface. In Figure 4, an anomalous temporary decrease in capillary wave frequency is observed when the CTAB solution beyond the cmc was injected. The capillary wave frequency decreases rapidly on injection, and after attaining its minimum value, it increases gradually, as shown in Figure 4. The initial sudden change means an abrupt increase in the molecular number density at the interface.

When the injected concentration of CTAB is below the cmc, the capillary wave frequencies gradually decrease, in other words, the molecular number density gradually increases. We have explained this gradual change of molecular number density using a diffusion model.[23] The theoretical time-course of the number density of the surfactant molecules at the interface calculated by assuming that surfactant molecules are transferred only by diffusion from one phase to the other is in good agreement with the observed one below the cmc. This diffusion model, however, cannot explain the anomalous behavior beyond the cmc. Therefore, it seemed natural to us to consider the adsorption of surfactant molecules onto the W/NB interface. In short, the abrupt decrease in the capillary wave frequency can be attributed to the adsorption of surfactant molecules onto the W/NB interface from the W phase, while the gradual increase is due to the desorption from the W/NB interface to the NB phase.

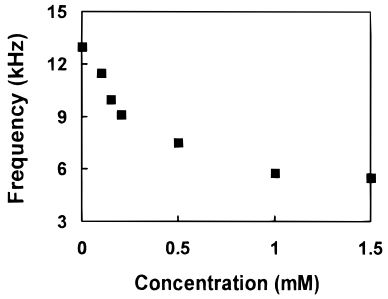

Figure 5. Capillary wave frequency vs CTAB average concentration in the water phase.

Details can be added to the above outline by estimating the molecular number density of CTAB at the interface from Figure 4. Around the minimum frequency, both adsorption onto the W/NB interface from the W phase and the desorption from the interface to the NB phase are taking place as competing processes. It is clear from Figure 4 that the former process is much faster than the latter one. Thus, at the minimum frequency, it is reasonable to assume that the adsorption equilibrium between the W phase and the W/NB interface is 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 molecular number density of CTAB at the interface from the minimum value of the capillary wave frequency in Figure 4.

The minimum value of the capillary wave frequency changes with the average concentration of CTAB as shown in Figure 5. Since the square of the capillary wave frequency is proportional to the interfacial tension (eq 5), which is approximately inversely proportional to the number density of surfactant molecules (eq 7), the relationship between the number density of CTAB molecules adsorbed onto the interface and the average concentration of CTAB in the W phase was obtained as shown in Figure 6. The experimental data are in good agreement with the calculated Langmuir adsorption isotherm, indicating that the adsorbed surfactant molecules are confined to a monomolecular layer, and the affinity of each binding site for surfactant molecules is the same. It is apparent from this result that the CTAB molecules are adsorbed onto the interface as an oriented monolayer. This is consistent with the experimental results by the SFG measurements, which indicated that SDS (sodium dodecyl sulfate) molecules are ordered at the D_2O/CCl_4 interface as a monolayer.[10] Therefore, we thought Figure 4 suggested that the transfer of CTAB molecules across the interface occurs via the following process (Figure 7): the collapse of micelles at the interface region; the oriented adsorption of CTAB molecules onto the interface, forming a monolayer; and the desorption from the interface.

Then, to confirm this model, we made a thermodynamic evaluation. The adsorption energy of the CTAB micelles onto the interface is estimated at ca. −29.4 kJ/mol from the experimental data in Figure 6 using the following equation,[24]

$$\ln C_{CTAB} = (E - \mu_{CTAB}^{\circ})/kT + \ln x/(1 - x) \qquad (8)$$

where C_{CTAB} is the concentration of the CTAB (here, it is reasonable to use concentration instead of activity because the concentration of CTAB is low enough), E is the adsorption energy, μ_{CTAB}° is the chemical potential of CTAB molecules in a 1 M solution, and x is the occupancy of the adsorption site.

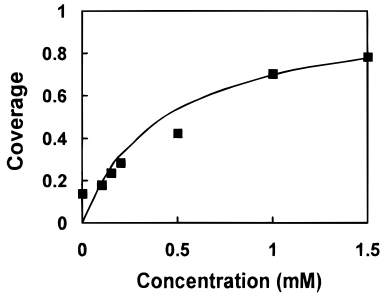

Figure 6. Interface coverage by CTAB molecules vs CTAB average concentration in the water phase. Experimental data are shown as squares, and the calculated Langmuir adsorption isotherm is the solid line.

The theoretical adsorption energy of the CTAB micelles is calculated as the difference between the adsorption energy of CTAB molecules and the micelle formation energy. The adsorption energy of the CTAB molecules from an aqueous solution onto the interface is estimated at −51.4 kJ/mol from the free energy change $\Delta G_m^\circ(-CH_2-)$ when 1 mol of methylene groups ($-CH_2-$) move from an aqueous solution to a water/oil interface,[25]

$$\Delta G_m^\circ(-CH_2-) = -RT \ln k$$
$$= -3.42 \text{ kJ/mol} \qquad (9)$$

where R is the gas constant (8.31 J K^{-1} mol^{-1}), T is the temperature, and k is the adsorption parameter that appears in Troube's rule.

The formation energy of the micelles is roughly estimated as −26.4 kJ/mol using the following equation:

$$\Delta G_m^\circ = RT \ln X_{CMC} \qquad (10)$$

$$X_{CMC} = 18.02 C_0/1000\rho \qquad (11)$$

where C_0 is the critical micelle concentration, and ρ is the density of the solution.[26] The theoretical adsorption energy of the CTAB micelles is estimated as −25.0 kJ/mol from the difference between the theoretical adsorption energy of the CTAB molecules (−51.4 kJ/mol) and the formation energy of the CTAB micelles (−26.4 kJ/mol).

The experimental adsorption energy (−29.4 kJ/mol) calculated from the Langmuir isotherm is in agreement with the theoretical adsorption energy of the CTAB micelles (−25.0 kJ/mol), and not with that of CTAB molecules (−51.4 kJ/mol). This indicates that the CTAB micelles are in equilibrium with the adsorbed CTAB molecules, and consequently, the CTAB micelles collapse to molecules immediately before the adsorption onto the interface. Therefore, we concluded that the above thermodynamic investigation strongly supports the collective behavior of the CTAB molecules described in Figure 7.

The dynamics of mass transfer across the liquid/liquid interface can be observed by the time-resolved QELS method, providing a picture of both mass transfer dynamics and the role of the interface in the mass transfer process of surfactant

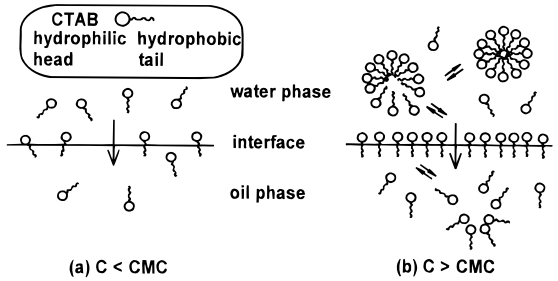

Figure 7. Schematic illustration of the collective motion of CTAB molecules at the liquid/liquid interface and its vicinity: (a) $C <$ cmc; (b) $C >$ cmc.

molecules. On the other hand, new fundamental questions arise from the present model. For example, what triggers the collapse of micelles? In what part of the interface region do the micelles collapse? It is apparent that the micelles are affected by some of the properties of the interface before they collapse, and these special interface properties must be closely associated with behavior. The QELS method is a powerful tool for studying molecular dynamics at liquid/liquid interfaces, and we can expect it to be turned to answering these questions.

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