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.

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:

\[ K \tan \theta = k \]  

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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 \( \theta \).

We arranged a transmitting diffraction grating in front of the cell to adjust the angle \( \theta \).\(^{21} \) The angle \( \theta \) is determined by the following equation using the spacing \( d \) and the order \( n \) of the diffraction grating.

\[
d \sin \theta = n \lambda
\]

where \( \lambda \) is the wavelength of the laser beam.

From eqs 1 and 2, we obtain the wavenumber \( k \) and the wavelength \( \Lambda \) of the observed capillary wave:

\[
k = 2\pi n d
\]

\[
\Lambda = d n
\]

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 beat 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 diffraction 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 \( \gamma \) is approximately expressed by Lamb’s equations,\(^{22} \)

\[
f = \left( \frac{\gamma}{2(\rho_w + \rho_o)} \right)^{1/2} k^{3/2}
\]

\[
\rho = \rho_w + \rho_o
\]

where \( \rho_o \) is the density of the aqueous phase, \( \rho_o \) is the density of the oil phase, and \( k \) is the wavenumber of the capillary wave. The relationship between the interfacial tension \( \gamma \) and the number density \( \Gamma \) of a monolayer is approximately expressed by the following equation, as we have reported previously.\(^{16,17} \)

\[
\gamma \propto 1/\Gamma
\]

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 \( \Gamma \) 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.

**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; 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.
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 by 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 interface to the NB phase. 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.

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 D2O/CCl4 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

\[
\ln C_{CTAB} = (E - \mu_{CTAB})/kT + \ln x/(1 - x) \quad (8)
\]

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, \( \mu_{CTAB} \) is the chemical potential of CTAB molecules in a 1 M solution, and \( x \) is the occupancy of the adsorption site.
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 $\Delta G_m^\circ(-\text{CH}_2-) = 0$ when 1 mol of methylene groups $(-\text{CH}_2-) \text{ move from an aqueous solution to a water/oil interface.}^{25}$

$$\Delta G_m^\circ(-\text{CH}_2-) = -RT \ln k$$

$$= -3.42 \text{ kJ/mol} \tag{9}$$

where $R$ is the gas constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$), $T$ 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 $-26.4 \text{ kJ/mol}$ using the following equation:

$$\Delta G_m^\circ = RT \ln X_{\text{CMC}} \tag{10}$$

$$X_{\text{CMC}} = 18.02 C_0/1000 \rho \tag{11}$$

where $C_0$ is the critical micelle concentration, and $\rho$ is the density of the solution. The theoretical adsorption energy of the CTAB micelles is estimated as $-25.0 \text{ kJ/mol}$ from the difference between the theoretical adsorption energy of the CTAB molecules ($-51.4 \text{ kJ/mol}$) and the formation energy of the CTAB micelles ($-26.4 \text{ kJ/mol}$).

The experimental adsorption energy ($-29.4 \text{ kJ/mol}$) calculated from the Langmuir isotherm is in agreement with the theoretical adsorption energy of the CTAB micelles ($-25.0 \text{ kJ/mol}$), and not with that of CTAB molecules ($-51.4 \text{ kJ/mol}$). 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 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.

**References and Notes**