Amphiphilic molecules behaving as a surface-inactive agent

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1. Introduction

It is well-known that surfactant molecules adsorb at the interface between water and oil, and the mutual solubility of water and oil increases since the interfacial tension decreases. However, the feature of surfactant molecules in a mixture of water / miscible organic solvent has not yet been studied in detail. Recently, we examined the effect of ionic-surfactant (SDS) and non-ionic surfactant ($C_{12}E_5$) on a mixture of water / 2,6-lutidine.. As shown in Fig. 1(a), two-phase region shrinks by adding SDS into the mixture of D_2O / 2,6-lutidine; that is, the mutual solubility of D_2O and 2,6-lutidine increases by adding SDS. On the other hand, the mutual solubility of D_2O and 2,6-lutidine decreases by adding $C_{12}E_5$, which indicates that $C_{12}E_5$ acts as "surface-inactive" agent in a mixture of water / miscible organic solvent.

According to the theoretical consideration by Onuki, the mutual solubility of water and organic solvent increases when surfactant molecules adsorb at the interface between each solvent, whereas the mutual solubility decreases when surfactant molecules preferentially dissolve solely in water or organic solvent [1]. Therefore, it is expected that SDS molecules adsorb at the interface between water-rich and 2,6-lutidine-rich domains, whereas $C_{12}E_5$ molecules preferentially dissolve solely in water-rich or 2,6-lutidine-rich domains.

Based on this idea, we performed SANS measurements to investigate how SDS or $C_{12}E_5$ molecules dissolve in a mixture of water / 2,6-lutidine.

2. Experiments

D_2O (deuterium oxide, 99.9% purity, Merck) and 2,6-lutidine (99.9% purity, Kanto Chemical Co., Inc.) was mixed without further purification. The volume fraction of 2,6-lutidine was set at 0.3, which corresponds to the critical composition. Then, 50 mmol/L of SDS (sodium n-dodecyl sulfate, 99% purity, Kanto Chemical Co., Inc.) or 200 mmol/L of $C_{12}E_5$ (Pentaethylene Glycol Monododecyl Ether, 98.0% purity, Tokyo Chemical Industry Co., Ltd.) were dissolved into the mixture.

The SANS measurements were performed using the 40m SANS at HANARO. The wavelength of the incident neutron beam was 6 Å with resolutions of 12%, and the scattered neutrons were collected using a two-dimensional ^3He detector placed at specific destances from the sample position, i.e., 1.16 m, 11 m, and 15 m. The samples were kept in titanium cells with quartz windows. The sample thickness was 1 mm or 2 mm. A Temperature controlled chamber was used to regulate the sample temperature T with an accuracy of $\pm$ 0.1 K. The momentum transfer, $Q = 4\pi\sin\theta/\lambda_w$, was covered in the range from 5.2×10^{-3} Å^{-1} to 5.5×10^{-1} Å^{-1}, where λ_w and 2θ are the incident neutron wavelength and scattering angle, respectively. The observed two-dimensional data

were azimuthally averaged and then corrected for transmission, background scattering, and the sample thickness to obtain absolute intensities in the unit of cm^{-1}. The estimated incoherent scattering intensity was subtracted from the absolute intensity data.

3. Results

Figure 1(b) shows the SANS profiles from D_2O / 2,6-lutidine / SDS. Here, we found that the SANS profiles can be expressed by the model function proposed by Onuki and Kitamura [2], which represents that surfactant molecules adsorb at the interface between water and organic solvent, as

$$I(Q) = \frac{I_0}{1 + \left[1 - \gamma_p^2/\left(1 + \lambda^2 Q^2\right)\right]\xi^2 Q^2},$$ (1)

where I_0 denotes the forward scattering, ξ the correlation length of concentration fluctuation, λ the Debye screening length, and γ_p ($\gamma_p > 0$) the dimensionless parameter related to the difference in solubilities between cations and anions for polar solvents, i.e., water (see the solid lines of Fig. 1(b)).

On the other hand, the profiles from D_2O / 2,6-lutidine / $C_{12}E_5$ cannot be explained by Eq. (1) due to the shoulder around $Q = 0.1$ $Å^{-1}$. That is, it is confirmed that $C_{12}E_5$ molecules does not adsorb at the interface between each solvent unlike SDS. At present, we speculate that $C_{12}E_5$ molecules dissolve solely in water-rich or 2,6-lutidine rich domains with forming some kind of nanostructures.

Here, it is noted that we were also planning to measure the mixture of water / 2,6-lutidine-d9 / $C_{12}E_5$ at film contrast condition with changing temperature in order to clarify the detailed nanostructures. However, we failed them because we had to stay in the guesthouse without setting the samples due to heavy snow from Dec 5th (evening) to Dec 6th (afternoon). Therefore, additional beam-time is necessary to complete this research.
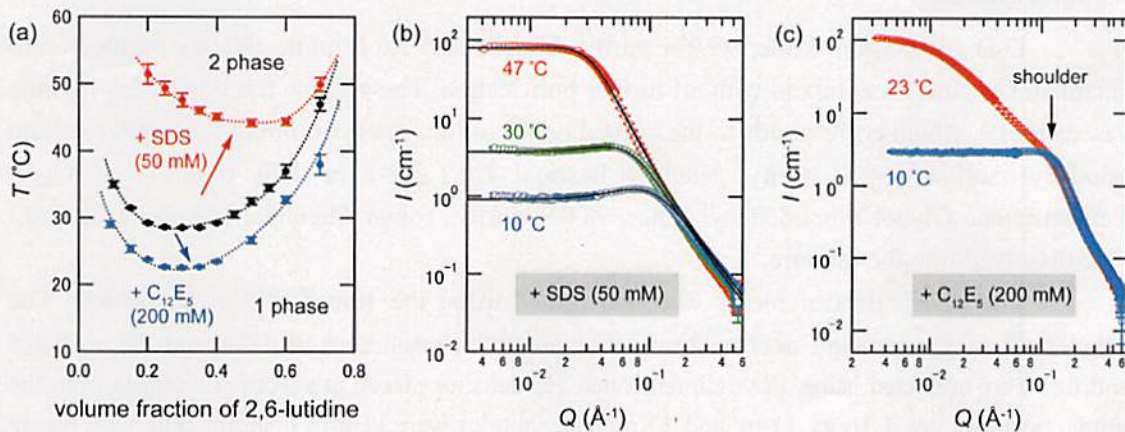

Figure 1: (a) Phase diagram of D_2O / 2,6-lutidine and D_2O / 2,6-lutidine / surfactants (50 mM of SDS or 200 mM of $C_{12}E_5$). (b) SANS profiles for D_2O / 2,6-lutidine / SDS (50mM). Solid lines are the fit results given by Eq. (1). (c) SANS profiles for D_2O / 2,6-lutidine / $C_{12}E_5$ (200mM).

References

[1] A. Onuki, *JCP*, **128**, 224704 (2008).

[2] A. Onuki and H. Kitamura, *JCP*, **121**, 3143 (2004).