

Amphiphilic molecules behaving as a surface-inactive agent in a mixture of water / acetonitrile

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1. Introduction

It is well-known that an amphiphilic molecule adsorbs at the interface between water and oil, and increases the mutual solubility of the mixture since the interfacial tension decreases. In this sense, an amphiphilic molecule is regarded as a surface-active agent. However, the effect of an amphiphilic molecule on a mixture containing miscible or semi-miscible solvents has not yet been studied in detail. Recently, we investigated the effect of ionic-surfactant (SDS) and non-ionic surfactant ($C_{12}E_5$) on a mixture composed of water and a semi-miscible organic solvent, 2,6-lutidine. As shown in Fig. 1(a), two-phase region (i.e., the region that the mixture shows macro-phase separation) shrinks by adding SDS, while expands by adding $C_{12}E_5$. In other words, $C_{12}E_5$ acts as a surface-inactive agent in contrast to the case of SDS. According to the theoretical consideration by Onuki [1], the mutual solubility of water and organic solvent increases when an amphiphilic molecules adsorbs at the interface between each solvent, while decreases when an amphiphilic molecule preferentially solvates solely in water or organic solvent. Therefore, it is suggested that SDS molecules adsorb at the interface between water-rich and 2,6-lutidine-rich domains, while $C_{12}E_5$ molecules preferentially solvate solely in water-rich or 2,6-lutidine-rich domains.

On the basis of this idea, we performed SANS measurements at 40m SANS (HANARO, Korea) to investigate how SDS or $C_{12}E_5$ molecules distribute in a mixture of water / 2,6-lutidine. As shown in Fig. 1(b), we found that the SANS profiles for D_2O / 2,6-lutidine / SDS could be explained by the model scattering function indicating the existence of the Charge-Density-Wave Structure (a kind of nm-sized ordered structure [2]), as

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

This result suggests that SDS molecules adsorb at the interface between D_2O and 2,6-lutidine, according to the theoretical speculation proposed by Onuki and Kitamura [1]. In addition, the SANS profiles under the condition of the contrast matching point (i.e., the film contrast) are considerably affected by the temperature change; the SANS intensity increases with increasing temperature.

On the other hand, the SANS profiles for D_2O / 2,6-lutidine / $C_{12}E_5$ could not be explained by Eq. (1) due to the shoulder around $Q = 0.1 \text{ \AA}^{-1}$ (see the data of the bulk contrast in Fig. 1(c)). Furthermore, the SANS intensity at the film contrast is almost independent of the temperature. These facts suggest that the nanostructure formed in

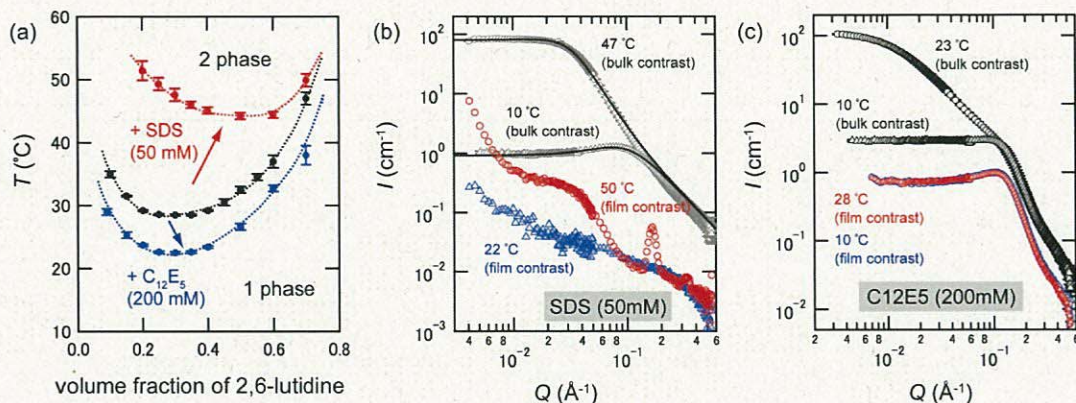


Figure 1: (a) Phase diagram of D_2O / 2,6-lutidine and D_2O / 2,6-lutidine / surfactants (50 mM of SDS or 200 mM of $C_{12}E_5$). (b) SANS profiles for water / 2,6-lutidine / SDS (50mM) both at the bulk contrast and the film contrast. Solid lines are the fit results given by Eq. (1). (c) SANS profiles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

$C_{12}E_5$ solution is quite different from that in SDS solution, i.e., the Charge-Density-Wave Structure. Most probably, the profiles for the $C_{12}E_5$ solution at film contrast reflect the sponge phase (L_3 phase).

2. Purpose of this research

In this manner, we confirmed that the some kind of nanostructure is formed in both water / 2,6-lutidine / SDS mixture (charge-density-wave structure) and water / 2,6-lutidine / $C_{12}E_5$ mixture (sponge structure). The interfacial tension between water / 2,6-lutidine decreases by charge-density wave structure, whereas increases by sponge structure. In order to clarify the generality of this nature, we investigated the structures of SDS and $C_{12}E_5$ in a mixture of water / acetonitrile by 18m SANS in HANARO. Recently, we confirmed that two-phase region of water / acetonitrile shrinks by adding SDS, whereas expands by adding $C_{12}E_5$. Therefore, it is expected that the charge-density-wave structure and the sponge structure are observed in water / acetonitrile / SDS and water / acetonitrile / $C_{12}E_5$ mixtures, respectively.

3. Experiments

D_2O (deuterium oxide, 99.9% purity, Merck) and acetonitrile (99.8% purity, Wako Pure Chemical) were mixed without further purification. The volume fraction of acetonitrile was set at 0.63, which corresponds to the critical composition. Then, 50 mmol/L of SDS (sodium n-dodecyl sulfate, 99% purity, Kanto Chemical Co., Inc.) or 50 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 18m SANS at HANARO. The wavelength of the incident neutron beam was set to 4.5 Å and 8.9 Å with resolutions of 12%, and the scattered neutrons were collected using a two-dimensional ^3He detector placed at specific distances from the sample position, i.e., 2 m and 9 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 ± 0.1 K. The momentum transfer, $Q = 4\pi\sin\theta/\lambda_w$, was covered in the range from $4.5 \times 10^{-3} \text{ \AA}^{-1}$ to $3.8 \times 10^{-1} \text{ \AA}^{-1}$, 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.

4. Results

Figure 2(a) shows the SANS profiles for water / acetonitrile / SDS. We confirmed that the charge-density-wave structure is formed in this mixture since the profiles at bulk contrast are explained by Eq. (1). On the other hand, the profiles for water / acetonitrile / C_{12}E_5 mixture at bulk contrast are just explained by Ornstein-Zernike equation:

$$I(Q) = \frac{I_0}{1 + \xi^2 Q^2}. \quad (2)$$

That is, the concentration fluctuation of water and acetonitrile is not affected by the addition of C_{12}E_5 . In addition, the profiles at film contrast represent that C_{12}E_5 molecules does not form sponge structure but micelle structure in contrast to our expectations. Thus, we concluded that the interfacial tension between water and semi-soluble organic solvent can be increased by the existence of the micelle structure as is the case with the sponge structure.

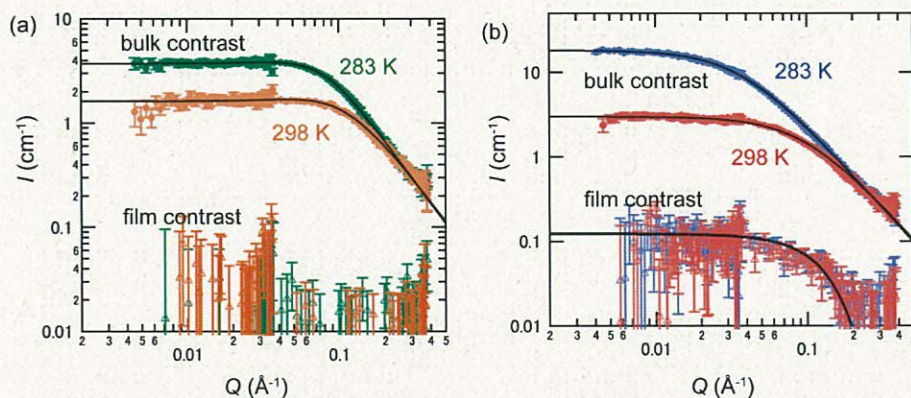


Figure 2: (a) SANS profiles for water / acetonitrile / SDS (50mM) both at the bulk contrast and the film contrast. Solid lines are the fit results given by Eq. (1). (b) SANS profiles for water / acetonitrile / C_{12}E_5 (50mM) both at the bulk contrast and the film contrast. Solid lines are the fit results given by Eq. (2) (for bulk contrast) and by the form factor of micelle structure (for film contrast).

References

- [1] A. Onuki, *JCP*, **128**, 224704 (2008).
- [2] A. Onuki and H. Kitamura, *JCP*, **121**, 3143 (2004).