Amphiphilic molecules behaving as a surface-inactive agent

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1 Introduction

Generally, oil mixes with water when surfactants are added. In other words, surfactants act as a "surface-active" agent in a mixture. However, we recently discovered that surfactants can also behave as a "surfact-inactive" agent in some cases. For example, two-phase region of water / acetonitrile shrinks by adding SDS, whereas expands by adding $C_{12}E_5$. In other words, the mutual solubility of water and acetonitrile decreases in the presence of $C_{12}E_5$ 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 acetonitrile-rich domains, while $C_{12}E_5$ molecules preferentially solvate solely in water-rich or acetonitrile-rich domains. On the basis of this assumption, we recently performed SANS measurements at 40m SANS at HANARO (from Dec 3rd to 6th 2012) to investigate how SDS or $C_{12}E_5$ molecules dissolve in a mixture of water / acetonitrile. Then, we found that the SANS profiles from D_2O / acetonitrile / SDS could be explained by the model scattering function proposed by Onuki [2]:

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

which shows that surfactant molecules adsorb at the interface between water and organic solvent.

On the other hand, the profiles from water / acetonitrile / $C_{12}E_5$ could not 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 consider that $C_{12}E_5$ molecules dissolve solely in water-rich or acetonitrile rich domains with forming some kind of nanostructures.

2 The aim of this study

In order to clarify the detailed structures in the mixture of water / acetonitrile / $C_{12}E_5$, we further performed SANS measurements by applying contrast variation techniques. Especially, we expected that nanostructures formed by $C_{12}E_5$ molecules and concentration fluctuation of water and acetonitrile are observed with changing temperature.

3 Results

The SANS profiles for D_2O / acetonitrile / $C_{12}E_5$ at bulk contrast are well explained by Ornstein-Zernike function,

$$I_{\mathrm{OZ}}(Q) = \frac{I_0}{1 + \xi^2 Q^2}\,, \tag{2}$$

and no charge-density-wave structure is confirmed. On the other hand, the SANS profiles for D_2O / acetonitrile / $C_{12}E_5$ at film contrast are well explaned by the form factor of a spherical micelle, as

$$I_{\mathrm{sp}}(Q) = C \int_0^\infty f(R)\,|F(Q,R)|^2\,dR\,, \tag{3}$$

$$f(R) = \left(\frac{Z+1}{R_{\mathrm{m}}}\right)^{Z+1} R^Z \exp\left[-\left(\frac{Z+1}{R_{\mathrm{m}}}\right) R\right] / \Gamma(Z+1)\,, \tag{4}$$

$$F(Q,R) = \frac{\sin(QR) - QR\cos(QR)}{(QR)^3}\,. \tag{5}$$

Thus, it is shown that a spherical micell composed of $C_{12}E_5$ is formed in acetonitrile solution. Here, the hydrophilic part of $C_{12}E_5$ may preferentially attract water molecules around themselves, and this decrease the mutual solubility of water and acetonitrile.

Furthermore, we also discovered that sponge-like structures are generaged in acetonitrile solution when $C_{12}E_5$ above 300 mmol/L is added (Fig. 1 (a)). In this case, $C_{12}E_5$ forms a bilayer structure, and the hydrophilic part preferentially attracts water molecules around themselves (see Fig. 1 (b)).

In this manner, we concluded that a hydrophilic part of a micelle or a bilayer preferentially attracts water molecules, and this results in the decrease of the mutual solubility of water and acetonitrile.

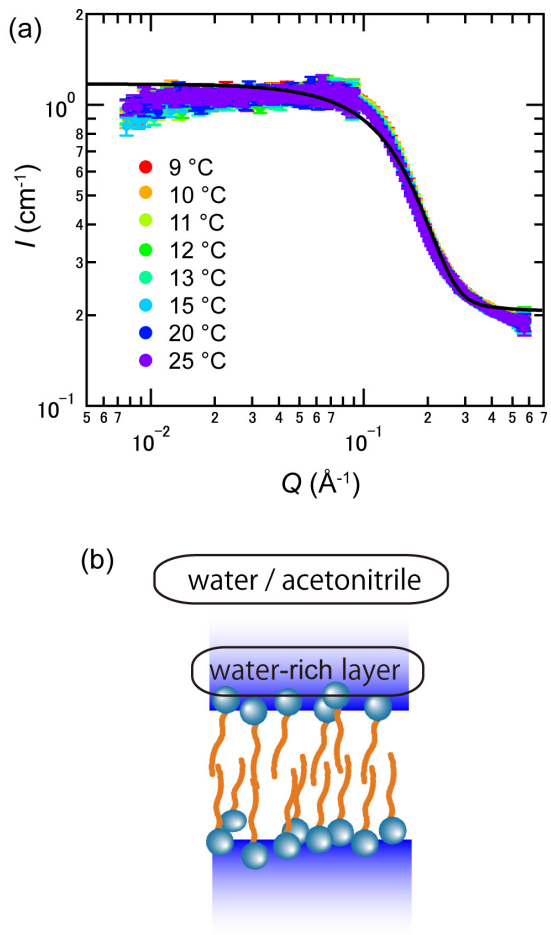

Fig. 1. (a) SANS profiles for acetonitrile solution with C12E5 (300 mmol/L). (b) The schemetic illustration of water molecules around the bilayer.

References

[1] A. Onuki, J. Chem. Phys, **128**, 224704 (2008).

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