

Structures of molecular assembly formed by sugar-based surfactants having branched alkyl chains in water

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Introduction

In recent years, much attention has been paid to the sugar-based surfactants such as alkyl glucoside from the ecological and industrial viewpoints. However, the Kraft temperature (T_K) of them is usually higher than room temperature, which seriously limits the usefulness of them in many technological applications and also make it difficult to study the structures of micellar and liquid crystal phases. Recently, Hato et al. [1] have synthesized novel alkylglycosides, that consist of an isoprenoid-type hydrophobic chain, the 3,7,11,15-tetramethylhexadecyl (phytanyl) group. It has been shown that T_K of these surfactants are significantly lower than room temperature and that they exhibit interesting phase behaviors. In the present study, we have measured small angle x-ray scattering on aqueous solutions of 1- α -3,7-dimethyloctyl-*D*-glucopyranoside (abbreviated as Glu(Ger)) as well as aqueous mixtures of Glu(Ger) and 1- α -3,7-dimethyloctyl-*D*-maltoside (Mal(Ger)). To investigate effects of branching of alkyl chains, the same measurements have been made for aqueous solutions of 1- α -decyl-*D*-glucopyranoside (Glu(C10)) and 1- α -decyl-*D*-maltoside (Mal(C10)).

Experimental

Measurements were performed using SAXS spectrometer installed at the BL-10C instrument at the Photon Factory of the National Laboratory. We used a sample cell made of copper with Kapton windows (sample thickness = 1mm) whose temperature is controlled by using the DTA/SAXS instrument reported before.

Analyses

Observed scattering intensity curves were analyzed by the following procedure. For monodispersed system of ellipsoidal micelles, the scattering intensity can be expressed as

$$I(q) = AN_p \left[\langle F(q)^2 \rangle + \langle F(q) \rangle^2 (S(q) - 1) \right] \quad (1)$$

where N_p is the number density of micelles, $F(q)$ is the single particle form factor, and $S(q)$ is the structure factor depending on intermicellar interactions. The form factor $F(q)$ can be expressed as:

$$\begin{aligned} \langle F(q)^2 \rangle &\equiv \int |F(q,x)|^2 dx & \langle F(q) \rangle^2 &\equiv \left| \int F(q,x) dx \right|^2 \\ F(q,x) &= (B_C - B_S)V_C [3j(u_C)/u_C] \\ &\quad + (B_S - B_W)V [3j(u)/u] \\ u_C &\equiv qR_C \sqrt{x^2 + a_C^2(1-x)} \\ u &\equiv qR \sqrt{x^2 + a^2(1-x)} \end{aligned}$$

where B_C , B_S , and B_W are the scattering length densities of the micellar core, micellar shell including hydrated water, and solvent, respectively, j is the first order spherical Bessel function, R_C and R are the semiminor axes of the micellar core and whole micelle, respectively, V_C and V are volumes of the micellar core and whole micelle, respectively, and a_C and a are the axial ratios of the micellar core and whole micelle, respectively. All the parameters needed to calculate $I(q)$ are functions of R_C , a_C , and the thickness of the micellar shell, which are used as free-fitting parameters in the nonlinear least-squares analysis of the data. In addition to them, a scaling parameter, A , was used as a free-fitting parameter due to uncertainty in calibration for absolute intensity.

Results

First, we have analyzed the scattering intensity for single-component micelles formed by Mal(C10) or Mal(Ger) (5 % by weight at 30°C). The observed scattering curves can be fitted by prolate ellipsoid better than oblate ellipsoid. The obtained axial ratios of the micellar core are about 1.8 and 2.1 for Mal(C10) or Mal(Ger), respectively. The thickness of the micellar shell is about 1.0 nm for both micelles, as expected. Then the mole fraction of Glu(C10) and Glu(Ger) in the total mixed solute (the total weight concentration was fixed to 5wt%) is increased up to 0.9 and 0.55, respectively. As the mole fraction of glucoside increases, the axial ration increases up to about 2.5 for both systems.

References

[1] M. Hato, H. Minamikawa, R. A. Salkar, and S. Matsutani, *Langmuir* **18**, 3425 (2002).

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