Orientation of Hydrophobic Polyoxyethylene Chain on Aggregate Structure for Homogeneous Polyoxyethylene-Polyoxypropylene-type Nonionic Amphiphilic Compounds using Small-Angle Neutron Scattering

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1. Introduction

Polyoxyethylene (EO) alkyl ether type nonionic surfactants (C_nEO_x; *n* and *x* represent alkyl and EO chain length, respectively), comprising an EO chain as the hydrophilic group, are generally safe, non-toxic, and non-irritant. Because their hydrophilic/lipophilic balance (HLB, degree of surfactant affinity for water/oil) can be easily changed by altering both the alkyl and EO chain length, these surfactants have been employed in a wide range of fields (e.g., detergents and cosmetics). Thus, much research has been dedicated towards the design, development, and analyses of novel surfactant structures with improved properties and greater functionality. The EO chain length distribution as well as the lengths of the alkyl and EO chains must also be taken into account when investigating the surface-active and aggregation properties of these surfactants in aqueous solution. Consequently, interpretation of these surfactant properties has proven to be difficult. In contrast, because C_nEO_x surfactants with a single chain length have a homogeneous chain length distribution, their properties can be determined precisely. Thus, in recent years, the development of homogeneous surfactants has been a prime objective. PO-EO alkyl ether type nonionic surfactants ($C_nEO_xPO_y$, *y* represents PO chain length), synthesized from propylene oxide and C_nEO_x species with a distribution of chain lengths have also been investigated. Narrowing the chain length distributions of both the EO and PO chains afforded excellent foaming and antifoaming properties. $C_nEO_xPO_y$ surfactants with single EO and PO chain lengths have not been investigated to date. The analyses of these surfactants would allow the precise determination of their physicochemical properties. The small-angle X-ray scattering (SAXS) showed that the C_nEO_x species formed small micelles in solution at low concentrations and the structures transformed to hexagonal liquid crystals as the surfactant concentration increased, conversely, $C_nEO_xPO_y$ maintained a micellar structure even at high concentrations. Notably, the introduction of a PO chain into the C_nEO_x surfactant controlled the formation of aggregates with a higher-order structure (hexagonal liquid crystals). However, it is not clear the orientation of the PO chain in the surfactant micelles. We want to know the detail information about the orientation of PO chain using SANS measurements.

The aim of this study is to evidence the detail nano-structure of aggregates formed by novel nonionic surfactants in aqueous solution. Our final goal is to discuss the effects of alkyl chain length, oxyethylene and oxypropylene chain lengths, and distribution of polymerization degree of the nonionic surfactants on the aggregate formation. Because this is the first trial for TAIKAN measurements, we will measure some more steels with typical microstructure and check reproducibility of profile shape and intensity by comparing SAXS measurement in the future.

2. Experiment

The SANS measurement of the polyoxyethylene-polyoxypropylene-type novel nonionic surfactants with

identical chain lengths in D_2O was performed at room temperature by changing the alkyl chain length (10, 12, 14, 16), oxyethylene chain length (4, 6, 8), oxypropylene chain length (3, 6), and the concentration (5 points per 1 sample).

3. Results

Fig.1 shows the best-fitted theoretical scattering curves with experimental SANS profiles for $C_{12}EO_8PO_y$ (y = 0, 3) at 100 mmol dm^{-3} in D_2O. We tried to reproduce for SANS profile from the results of analysis of the model-fitting obtained by SAXS; y = 0 showed good agreement, however, y = 3 did not. This is considered that micelle size obtained by SAXS estimated to be smaller than the actual micelle structure because the PO chain was not visible, since the scattering length density of the PO chain for X-ray almost agrees with that of water. On the other hand, in SANS, it is possible to evaluate accurately, because D_2O has sufficient contrast. The SANS results suggested that the size of micelle became slightly small and the thickness of shell decreased, as the PO chain length increased. This is considered that $C_{12}EO_8PO_y$ form ellipsoidal micelles with the EO chain folded by the interaction between the alkyl chain and the PO chain by the introduction of PO chain to the EO surfactant. The aggregation number of the ellipsoidal micelles formed by the surfactants was calculated by using radius of core part, axial ratio of core, and volume of the core per a molecule obtained from the scattering length density. The aggregation numbers decreased by the introduction of the PO chain (PO_1, PO_2, and PO_3). This is resulted that the curvature of molecule became large due to form the micelle with the EO chain folded by the introduction of PO chain.

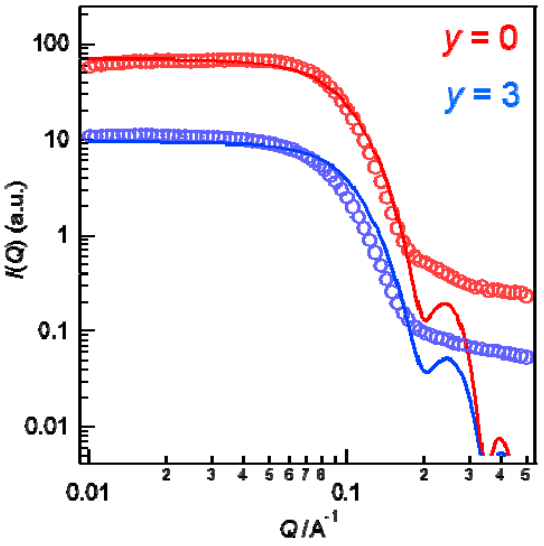

Fig.1 SANS profiles, and fitting curves for $C_{12}EO_8PO_y$ (y = 0, 3).

We are currently studying by model analysis using both SANS and SAXS.

4. Conclusion

It was clear that the homogeneous polyoxyethylene-polyoxypropylene-type novel nonionic surfactants with identical chain lengths formed ellipsoidal micelles in D_2O, and the EO chain was folded in the micelle. This micelle formation was differed with those by the EO surfactants.

In the future, further detailed structure of the micelle will be clarified by model analysis.