Structural Evolution from Vesicles to Lamellar Domains and Liquid Crystals in Aqueous Solutions of Multi-Branched Amino Acid–Sugar Hybrid Surfactant

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We have previously synthesized linear amino acid–sugar hybrid surfactants incorporating naturally derived amino acids and sugars as hydrophilic groups, and investigated their aggregation behavior in aqueous solutions. Depending on the combinations of amino acids and sugars, these surfactants formed various aggregates, including ellipsoidal micelles, rod-like micelles, worm-like micelles, and vesicles. However, the aggregation behavior of surfactants is strongly influenced not only by the molecular structures of the hydrophilic groups but also by the molecular structures of the hydrophobic groups. Branched hydrophobic chains are known to alter molecular packing and interfacial curvature compared with linear chains, thereby significantly affecting aggregate morphology. In this study, we synthesized a novel amino acid–sugar hybrid surfactant with a highly branched hydrophobic chain (*b*C_{15}GlyMal) and investigated the concentration-dependent structural evolution of the aggregates in aqueous solution mainly by small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS).

The concentration dependence of the SAXS and SANS profiles of *b*C_{15}GlyMal aqueous solutions is shown in Fig. 1. The SAXS profiles at 1–10 mmol dm^{-3} and the SANS profile at 10 mmol dm^{-3} exhibited q^{-2} dependence in the low-q region, indicating the formation of vesicles. Fitting analyses of the SAXS and SANS profiles using a unilamellar vesicle model showed good agreement with the experimental data, confirming the vesicular structure. Cryogenic transmission electron microscopy (cryo-TEM) observations at 5 mmol dm^{-3} also supported the formation of vesicles (Fig. 2). At 25–100 mmol dm^{-3}, the SAXS profiles retained the q^{-2} dependence in the low-q region, while diffraction peaks corresponding to lamellar interlayer spacing ratios and features originating from the bilayer form factor were observed, suggesting the coexistence of vesicles and lamellar domains. At 250 and 500 mmol dm^{-3}, the SAXS profiles indicated the formation of lamellar domains. Furthermore, at 750 and 1000 mmol dm^{-3}, polarized optical microscopy revealed textures characteristic of lamellar liquid crystals, indicating the formation of a lamellar liquid crystalline phase. These results demonstrate that the multi-branched amino acid–sugar hybrid surfactant exhibits a unique concentration-dependent structural evolution from vesicles to lamellar domains and further to lamellar liquid crystals with increasing surfactant concentration. The highly branched hydrophobic chains are considered to reduce interfacial curvature and promote the formation of bilayer-based assemblies.

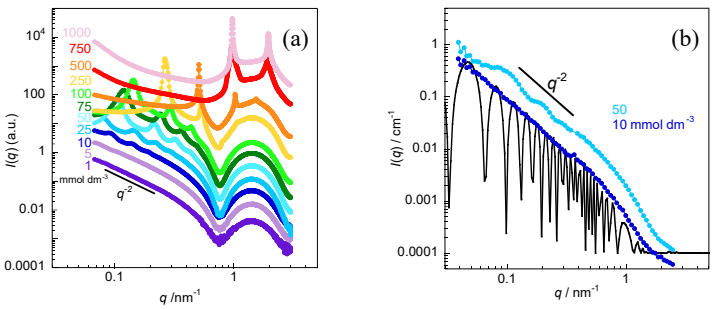

Fig. 1. Concentration dependence of (a) SAXS (1–1000 mmol dm^{-3}) and (b) SANS (10, 50 mmol dm^{-3}) profiles of *b*C_{15}GlyMal aqueous solutions at 25 ºC.

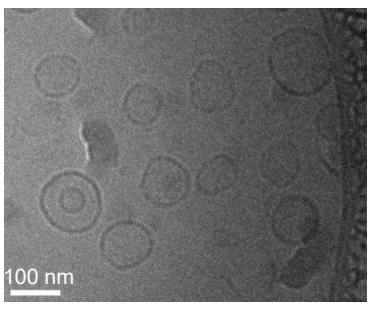

Fig. 2. Cryo-TEM image of *b*C_{15}GlyMal aqueous solution at 5 mmol dm^{-3} at 25 ºC.