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論文の内容の要旨

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Structural Study of Self-Assembled Aggregates Formed by Ionic Oligomeric Surfactants

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(多鎖型界面活性剤が形成する自己組織化会合体の構造特性)

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In this theses, the structure of oligomeric surfactant aggregates was investigated for the purpose to elucidate the unique property of oligomeric surfactants.

Oligomeric surfactants are surfactants with multiple hydrophobic groups and multiple hydrophilic groups in a molecule. Normal surfactant is a monomeric surfactant that has only one hydrophilic head group and one hydrophobic carbonchain. Oligomeric surfactants show higher efficiency for lowering surface tension and lower critical micelle concentration (CMC). Additionally, it is reported by many researchers that they can form various aggregates without any additives in an aqueous solution due to their higher hydrophobic interaction.

Applications of surfactant aggregates depend on the structure of them, and there are many studies to elucidate the relationship between the aggregation structure and the chemical structure of the surfactant. However, there are few studies about the aggregation behavior of oligomeric surfactants because they are difficult to synthesize. Investigations of the aggregation structure of oligomeric surfactants are important for enabling their application. Therefore, I investigated the aggregation behavior of oligomeric surfactants by using scattering techniques.

In chapter 2, novel star-type trimeric surfactants of quaternary ammonium bromide ($3C_n$trisQ), which comprised three hydrocarbon chains and three hydrophilic groups connected by three ethylene spacer chains and a nitrogen atom, were investigated because they are easier to synthesize than previous ones (Fig.1). The $3C_n$trisQ molecule exhibited unique physicochemical properties, including lower CMC and a higher efficiency for lowering surface tension when compared with monomeric and gemini surfactants. The aggregation behaviors of these tris(*N*-alkyl-*N*,*N*-dimethyl-2-ammoniumethyl)amine bromides ($3C_n$trisQ, where *n* is the

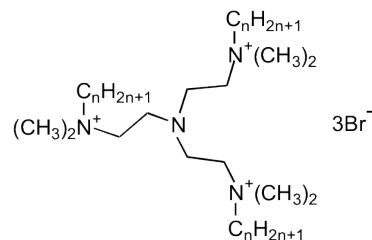**Fig.1** Structure of $3C_n$trisQ

number of carbon atoms in the alkyl chain) were investigated using rheological, SANS, and cryoTEM techniques. The results indicated that $3C_{10}trisQ$ formed ellipsoidal micelles and $3C_{12}trisQ$ underwent a sphere-to-rod transition with increasing surfactant concentration (C_D). On the other hand, the aggregation structure of $3C_{14}trisQ$ was rodlike micelles and was independent of the surfactant concentration because of its high packing parameter and high hydrophobicity. Furthermore, growth mechanisms of wormlike micelles formed in an aqueous solution by the star-type trimeric surfactant $3C_{12}trisQ$ were investigated. According to the model-fitting analysis of small-angle neutron scattering (SANS), $3C_{12}trisQ$ exhibited sphere-to-rod transition without salts (Fig.2). The end-cap energies of trimeric, gemini, and monomeric surfactants were also evaluated from rheological measurements. It waa found that wormlike micelles formed by $3C_{12}trisQ$ exhibited higher end-cap energy than gemini surfactant.

In chapter 3, the aggregation behavior of star-type trimeric surfactants ($3C_n trisQ$) in the presence of sodium salicylate (NaSal) was investigated. Using small-angle X-ray scattering (SAXS) and rheological measurements, a structural phase diagram of solutions of $3C_n trisQ$ with various hydrocarbon chain lengths ($n = 10, 12, 14$) and various NaSal concentrations (C_S) was constructed. NaSal was observed to induce a structural transition of $3C_n trisQ$
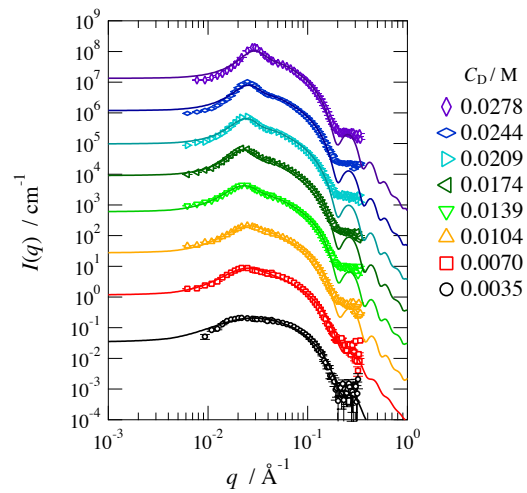

Fig.2 Comparisons of experimental scattering profiles (symbols) and the best-fit scattering curves (solid lines).

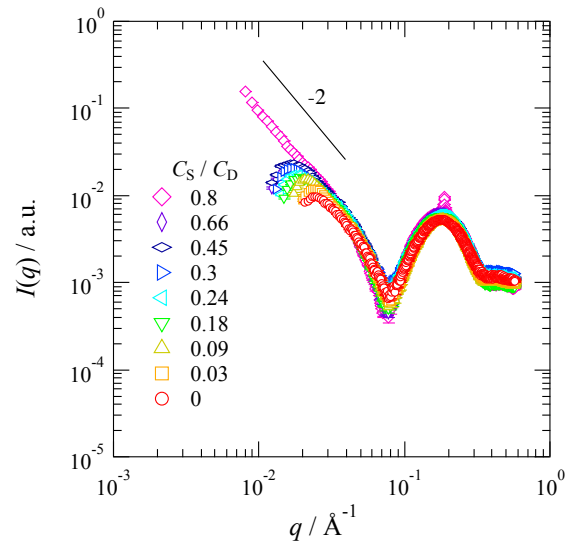**Fig.3** SAXS profiles for $3C_{12}trisQ$ systems in salt solution

that significantly depended on the hydrocarbon chain length. $3C_{10}trisQ$ formed ellipsoidal micelles in solution, independent of C_S. On the other hand, Fig.3 shows the SAXS profiles for $3C_{12}trisQ$ solutions. SAXS profiles depended on the salt concentration, which indicates that $3C_{12}trisQ$ shows structural transition with increasing C_S. In the case of $3C_{12}trisQ$ solutions, the micellar structures changed from ellipsoidal micelles to rodlike micelles with increasing C_S. In addition, at higher C_S levels, the SAXS profiles of $3C_{12}trisQ$ exhibited q^{-2} behavior in low-q region, and sharp peak in high-q region, which indicates the formation of multilamellar vesicles in solution. $3C_{12}trisQ$ solutions exhibited structural transitions from ellipsoidal micelles, though rodlike or wormlike micelles, to vesicles as the C_S was increased. Aggregate structures of $3C_{14}trisQ$ were rodlike or wormlike micelles at lower

C_S levels and unilamellar vesicles at higher concentrations, respectively. 3C$_{14}$trisQ also exhibited a structural transition from rodlike micelles to vesicles with increasing C_S. The surfactant concentration (C_D) dependence of the aggregation behavior of 3C$_{12}$trisQ in a solution was also investigated (Fig.4). At higher C_D levels, 3C$_{12}$trisQ did not form vesicles in the solution. The structural transition of 3C$_{12}$trisQ aggregates strongly depended on not only C_S but also C_D in solution.

In chapter 4, water-in-ionic liquid type reverse micelles (RMs) can be prepared in the absence of organic solvent by using aprotic / protic ionic liquid mixture (aIL/pIL mixture) and gemini surfactant AOT (Fig. 5). Fig. 6 shows the variation of the radius of water droplets as a function of water concentration, C_W, determined by SAXS and DLS. The RM radius increases rather linearly with C_W. This result is in good accordance with that previously reported in RM systems. This result indicates that water-in-IL RMs are formed due to the presence of AOT even without organic solvent. Fig. 7 shows the R_h values observed for the aIL/pIL mixtures with alkyl chain length of pIL, n = 4 and 8. The dashed lines are guides for the eye. In the case of the [C$_8$mIm$^+$][TFSA$^-$] / [C$_8$ImH$^+$][TFSA$^-$] mixture system, i.e., the case where the alkyl-chain lengths are the same for aIL and pIL, the R_h increases with x_{pIL}. By replacing the pIL with n = 8 to that with shorter alkyl group (n = 4), the R_h also increases with x_{pIL}. However, it was found that the R_h value is appreciably smaller for the n = 4 system than that for the n = 8 system in the high x_{pIL} region. It has been established in the previous studies that the imidazolium-based IL with n = 8 has a high efficiency for lowering surface tension because of its long hydrophobic alkyl-chain in comparison with that with n = 4. It is thus expected that IL cation (in this case, protic C$_n$ImH$^+$) acts as a cosurfactant for RM formation, which plays a key role in the formation of RMs. From structural investigations with DLS and SAXS, the following facts were disclosed: (1) The size of RMs increases linearly with C_W. (2) The size of RMs increases with increasing x_{pIL}. (3) The alkyl-chain length of pIL cation also influences the RM size, particularly, at high pIL mole fraction. On the basis of the above results, I pointed out that
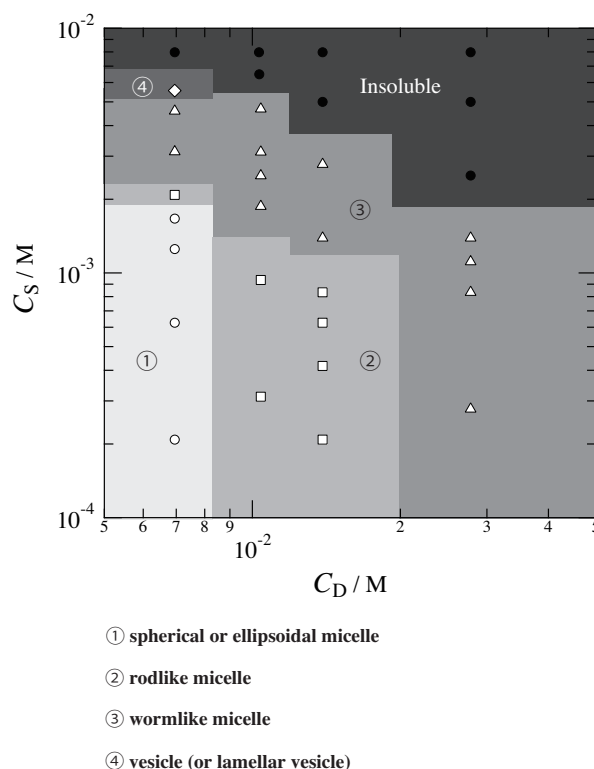

① spherical or ellipsoidal micelle

② rodlike micelle

③ wormlike micelle

④ vesicle (or lamellar vesicle)

Fig.4 Schematic phase diagram of aggregates formed by trimeric surfactants, 3C$_{12}$trisQ, in salt (NaSal) solutions at 25 °C.
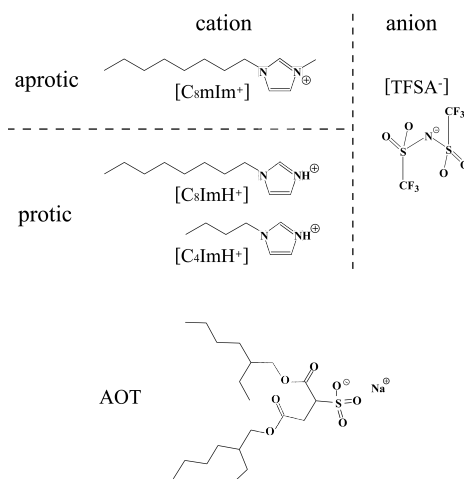

Fig.5 Chemical structures of aIL and pIL, and ionic gemini surfactant (AOT).

the size of RMs formed in this system strongly depends on pIL content in aIL/pIL mixtures. Furthermore, RM systems were successfully prepared using a different surfactant, star-type trimeric surfactant $3C_{12}trisQ$, indicating that this pIL method can be widely applied to other surfactant systems. The results obtained here give valuable insights for controlling the size of RMs in ionic liquid.

In conclusion, oligomeric surfactants are useful in various fields because of their unique aggregation behavior. Furthermore, with increasing number of carbon chains, they exhibit better performance as surfactants. In this thesis, the aggregation behavior of mainly trimeric surfactants was investigated because they exhibit various aggregation structures as a consequence of their higher packing parameter that stems from their multiple hydrocarbon chains. The applications to which specific surfactant aggregates are best suited depend on the aggregates' structures. Therefore, elucidating the relationship between the aggregation structure and the chemical structure of surfactants is an important research topic. The experimental results indicated that trimeric surfactants form large aggregates at surfactant concentrations lower than those of corresponding gemini and monomeric surfactants because of their unique packing shapes and high hydrophobicities. From an environmental viewpoint, the unique

Fig.6 C_W dependence of the radius of RMs, R, with $C_{AOT} = 0.075$ M and $x_{pIL} = 0.2$.

Fig.7 pIL mole fraction dependence of the R_h values in the aIL/pIL mixture systems with $C_{AOT} = 0.075$ M and $C_W = 0.83$ M.

properties of trimeric surfactants are important for reducing the amounts of surfactants used. However, surfactants that possess multiple alkyl carbon chains tend to exhibit greater hydrophobicity. The selection of a surfactant suitable for a given application is important. Trimeric or gemini surfactants are highly promising for use in various applications. The results in this thesis will not only be useful in industrial and consumer applications but will also provide important information for fun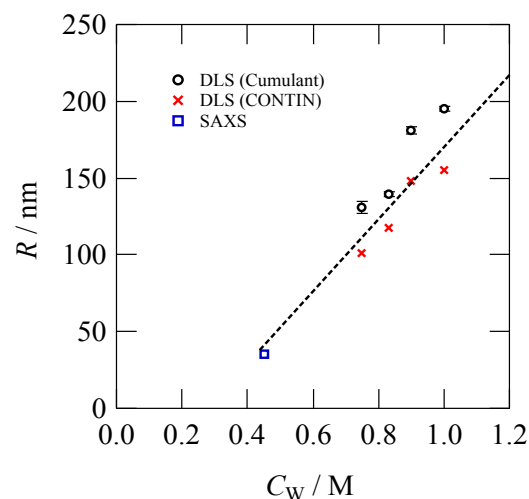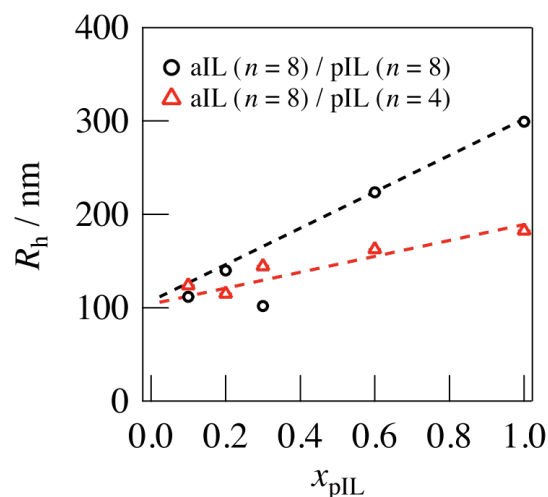damental studies related to oligomeric surfactants.