

CHAPTER II

LITERATURE REVIEWS

2.1 Micellar Formation of Cationic Surfactant

In 1998, Lerebours *et al.* investigated the aggregation of surfactant-cetyltrimethylammonium methacrylate (CTAM). They found that CTAM formed spherical micelles in aqueous solution. The CMC determined from surface tension measurement was 9.8×10^{-4} M. From the results of the light scattering, the agreement between the theoretical and experimental aggregation number led to the conclusion that the CTAM micelles were spherical structures. The hydrodynamic radius and the aggregation number were 30 Å and 106, respectively.

Kline (1999) synthesized rodlike structure from polymerizing a wormlike micellar solution of cationic surfactant which contains a polymerizable counterion (cetyltrimethylammonium 4-vinylbenzoate). Cetyltrimethylammonium 4-vinylbenzoate (CTVB) was characterized by electrical conductivity to determine the CMC was 1.6×10^{-4} M. He showed the strong influence of temperature on the equilibrium structure of micelles and intermicellar interaction at low surfactant concentration. The micellar structure has changed from an elongated structure at 30 °C to much shorter micelles at 60 °C. SANS analysis of CTVB solutions showed the cylindrical structure.

McKelvey *et al.* (2000) fixed bilayers by polymerizing divinylbenzene and styrene solubilized in vesicle micelles. The vesicle was produced by mixing cationic and anionic surfactants that called "catanionic" equilibrium vesicles. They used cetyltrimethylammonium tosilate (CTAT) and sodium dodecylbenzenesulfonate (SDBS) or cetyltrimethylammonium bromide (CTAB) and sodium octyl sulfate (SOS) as catanionic surfactants. The bilayer vesicle was characterized by SANS which observed the q^{-2} dependence in SANS data. And these bilayer vesicle formed spherical shape which examined by the Cryogenic Transmission Electron Microscopy.

2.2 Solubilization

The solubilization of aromatic compounds by adsorption at the micellar of cetyltrimethylammonium bromide (CTAB) surfactant was studied by Eriksson and Gillberg (1966). The result obtained from NMR indicated that benzene, nitrobenzene and N,N-dimethylaniline penetrated into that hydrocarbon part of micelle which is close to the polar head of surfactant (micelle-water interface) at low concentration. Because the high polarizability of the aromatic ring and the bonding abilities of substituent groups. At higher concentrations, solubilization in the interior was suggested. In the case of isopropylbenzene and cyclohexane were solubilized in hydrocarbon core. They supposed that the solubilization in the center of the micelle might involve a reorganization of the micellar structure so that a more spherical micelle is obtained instead of the postulated original rod-shaped micelle.

Investigations based on the ultraviolet (UV) spectra of benzene and some derivatives in micelles have been studied extensively. Rehfeld (1970, 1971) studied the spectra of benzene as saturated solution in micelles of sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB). He concluded that the saturated benzene solution was located in the micelle core. Mukerjee and Cardinal (1978) studied dilute solutions of benzene derivatives and naphthalene which were dissolved in micelles of SDS or CTAC. They reported a two-state model for polar and polarizable solubilizates, involving a distribution between a non polar "dissolved state", associated with the hydrocarbon core, and a polar "adsorbed state", associated with the micelle-water interface. Although a distribution favoring the adsorbed state is expected of solubilizates with high polarity, increased concentration of solubilizate appears to produce a redistribution favoring the dissolved state.

Yuan-Chang *et al.* (2003) reported the solubilization of variable amounts of styrene in the DS/n-butanol/water O/W microemulsion system investigated by ^1H NMR method. The results showed that the solubilization site shifts from the palisade layer to the inner core when the molar fraction of styrene reaches 0.312.

The polymerization of styrene solubilized in wormlike micelles was reported by Becerra *et al.* (2003). UV spectroscopy revealed that in the 0.05 wt% CTAT system, styrene is located both at the micelle surfactant and in the

hydrophobic core, whereas in 0.5 wt% CTAT system the monomer was mainly in the micelle core. The result supported by rheology, SAXS, and polarizing light microstructure indicated that the microstructure was preserved. They found that the micelles become shorter upon solubilization of styrene monomer.

2.3 Emulsion Polymerization

In 1980, polymerization in a Lyotropic liquid crystal of sodium undecenoate-water system was carried out at 60 °C by Thundathil *et al.* The liquid crystalline structure prior to polymerization was identified by optical microscopy and low angle x-ray diffraction. It showed hexagonal closely packed cylinders with the hydrophobic part of the soap in the cylinder center. During polymerization, the structure transformed to a lamellar liquid crystal in coexistence with the hexagonal phases.

Lerebours *et al.* (1988) studied the polymerization of cetyltrimethylammonium methacrylate micellar solution. The micellar aggregates were stabilized by inducing polymerization inside the micellar solution. The polymerization of the counterions, followed by the NMR technique, showed that it can be completed. From photophysical and photochemical experiments it was shown that the diluted polymerized micelles' interfaces and hydrophobic character were preserved. These polymerized aggregates were large and their size and shape remain unaffected by dilution. The polymeric aggregate could be a cylinder structure.

The rodlike aggregate structure of the surfactant cetyltrimethylammonium 4-vinylbenzoate (CTVB) was studied by Kline (1999). He found that the highly entangled rodlike aggregates were formed and the polymerized structures were insensitive to temperature changes or dilution. Small-angle neutron scattering revealed the micelle length of 40 °A was unchanged during the polymerization process. The cross-sectional diameter was retained, but the overall length was reduced. The viscoelasticity of the final product decreased due to both the shorter length of the micelle and the confinement of polymerized counterions on the micelle surface.

In 2000, McKelvey and co-worker formed hollow polymer spheres from styrene and divinyl benzene in cationic vesicles. The particles had an average radius of ~60 nm and a membrane shell less than 10 nm thick as observed by Cryo TEM and SANS. The cross-linked hollow polymer vesicles were robust and withstand complete drying and resuspension in water with no apparent change in microstructure. They functionalized the polymer membrane surface by sulfonation or surfactant adsorption to prevent the aggregation of polymer particle in water.

The successful freezing of the wormlike micellar microstructure had been achieved by Becerra *et al.* (2003). They reported the polymerization of styrene solubilized in wormlike micelles of cationic surfactant cetyltrimethylammonium tosylate (CTAT). The polymerization of styrene in these micelles followed a second-order kinetics, which implied that bimolecular reaction termination was the controlling termination mechanism. They conclude that; at low CTAT concentrations, the polymerization of styrene yielded small and rigid rods in coexistence with wormlike micelles that formed from the excess surfactant after the polymerization process. At high CTAT concentrations, polymeric rods of large aspect ratio, spheroid polymer particles, and wormlike micelles coexist.