

CHAPTER II

LITERATURE SURVEY



2.1 Adsorption Isotherm

The adsorption isotherm of cetyltrimethylammonium bromide (CTAB) onto precipitated silica was studied by O'Haver *et al.* (1993) and Thakulsukanant *et al.* (1997). Hi-Sil[®]223 silica which has the reported BET surface area of 150 m²/g was studied. The maximum adsorption of CTAB on silica surface was approximately 300 μmol/(g of silica). And Thakulsukanant *et al.* (1997) studied the adsorption of octadecyltrichlorosilane (ODS) which was chemically bonded with silanol groups on the silica surface compare to the adsorption of CTAB which was physically adsorbed on silica surface. The results showed the maximum ODS adsorption of 340 μmol/(g of silica), slightly higher than the maximum adsorption of CTAB. The extrapolated CMC of CTAB from adsorption isotherm curve was approximately 3000 μM. The ODS adsorption increased with increasing ODS concentration in the bulk phase and reached a constant value when the equilibrium ODS concentration was higher than 17000 μM.

Kitiyanan *et al.* (1996) and Chaisirimahamorakot (2001) investigated the adsorption of CTAB onto Hi-Sil[®]225 silica, precipitated which had the reported specific surface area of 170 m²/g. The isotherm illustrated the characteristics of regions II, III, and IV. The slope of the isotherm was greater than one from a concentration of CTAB in the aqueous solution of 70 μM to 120 μM. From the plateau adsorption region, the maximum adsorption were approximately 600 μmol/(g of silica).

Pradubmook (2001) studied the effect of pH (5 and 8) on adsorption of CTAB on Hi-Sil[®]225 silica. The results showed that for every equilibrium concentration, CTAB adsorption at pH 8 was higher than that at pH 5. This was because higher pH resulted in more negatively charge on the silica surface leading to higher amount of surfactant head adsorbed on the precipitated silica.

2.2 Adsolubilization Isotherm

In 1993, O'Haver studied the adsolubilization of styrene in adsorbed CTAB on Hi-Sil[®] 223 silica. The results gave a maximum adsolubilization of 150 μ moles CTAB per gram of silica with an adsorption of 267 μ moles CTAB/g of silica. The ratio of the adsorbed surfactant molecule to the adsolubilized monomers molecule was in the ratio of roughly 2 to 1.

The adsolubilization of styrene, isoprene, and mixtures of styrene and isoprene into cetyltrimethylammonium bromide (CTAB) bilayers (admicelles) on precipitated silica (Hi-Sil[®] 255) was investigated by Kitiyanan *et al.* (1996). The results showed that the adsolubilization constant of styrene was nearly unchanged and that of isoprene increased with increasing concentration in the aqueous phase. These results meant that styrene adsolubilized into both the palisade layer and the core of the micelle. The isoprene adsolubilized into the palisade layer. In the comonomer system, styrene adsolubilization is slightly increased in the presence of isoprene but isoprene adsolubilization was significantly enhanced in the presence of styrene.

2.3 Admicellar Polymerization

The formation of ultra-thin films in adsorbed surfactant bilayer has been first investigated since by Wu *et al.* (1987). The polymerization of styrene which adsolubilized in sodium dodecyl sulfate (SDS) admicell on alumina was found. Sodium persulfate was used as initiator. The results show 75% conversion of adsolubilized monomer to polymer after 25 minutes. The formation of polymeric film was confirmed by UV detector and FTIR. The thickness of film was determined on alumina plate by ellipsometry. Uniform films of 3.4-3.6 nm were formed for reaction times of 30–45 minutes. Film thickness of 13.0 nm was obtained by increasing initiator concentration and extending reaction time.

In 1993, O'Haver *et al.* formed ultra-thin polystyrene film on silica. Polystyrene was successfully polymerized in cationic surfactant cetyltrimethyl ammonium bromide (CTAB), and using water-insoluble initiator, 2,2'-azobis-2-

methylpropionitrile (AIBN). The polymer formed was extracted and characterized by techniques, including FTIR and GPC. The molecular weight of formed polymer was investigated with respect to polymerization time. Polymeric film on porous silica cause increase in particle size and decrease in surface area of silica. FTIR was used to determine the presence of polystyrene on the silica and GPC was used to study molecular weight distribution of extracted polymer.

Application of modified silica by admicellar polymerization has been studied since 1995. Waddel and co-worker (1995) modified surface of silica with polymerized styrene, isoprene, butadiene and copolymer to improve the physical properties in silica-filled tire compound. Polystyrene-modified silica caused reduction in physical properties but polybutadiene-modified silica showed an increasing in tear strength and cut growth resistance. The results showed that copolymer modifications of styrene and butadiene are the most promising polymer since it showed decreasing cure time, hysteresis and increasing tear modulus, good cut growth resistance values of compound.

In 1995, Sakhalkar, S.S. and Hirt, D.E carried out polymerization of styrene on a new substrate. Polystyrene was formed on glass fiber by admicellar polymerization. Treated films have been observed and evaluation of the film by scanning electron microscopy (SEM) was carried out. The micrographs showed a nonuniform coating on the fiber surface. The result appears that polymer formation was not restricted to the surface aggregates but also occurred in the aqueous supernatant.

The attempt to improve properties of rubber by reinforcing with non-black filler (e.g. silica) was applied. Kudisri (1997) formed polystyrene-isoprene copolymer on clay by *in-situ* polymerization of monomer in surfactant admicelle. The research studied the effect of the amount of surfactant and monomer on physical properties compared with unmodified clay. The results show that this process increases the compound cure rate, decreases cure time, and improves tensile property, tear strength, hardness, flex cracking resistance, and compression set.

In 1998, Grady studied modified glass cloth by admicellar polymerization for using as a composite manufacture. The forming of thin polymeric film of polystyrene-isoprene on glass cloth was successfully carried out using SDS as the

surfactant. The treated glass cloths were combined with epoxy and polyester resins to make a composite. The composite shows improvement in flexural strength and physical properties when compared to the untreated glass cloth composite.

A continuous reactor for the admicellar polymerization was developed by Chaisirimahamorakot (2001). CTAB, styrene, isoprene, and porous silica were used as surfactant, comonomer, and substrate respectively. FTIR technique proved the existence of styrene and isoprene polymer on modified silica. Effects of reaction time and monomer loading on amount of silica were studied. The results show that the 5g co-monomer per kilogram silica and 60 minutes polymerization time provided the largest amount of polymer on silica surface.