

CHAPTER IV

RESULTS AND DISCUSSION OF SURFACTANT BILAYER ADSORPTION

4.1 Abstract

The adsorption isotherms of hexadecylpyridinium chloride monohydrate (CPC, cationic surfactant), dodecylbenzenesulfonic acid sodium salt (DBSA, anionic surfactant), 3-(4-Heptyl)phenyl-3-hydroxypropyl)dimethylammoniopropanesulfonate (C7BzO, zwitterionic surfactant) and polyoxyethylene nonylphenol, (NP30, nonionic surfactant) on natural rubber latex particles (NR) were investigated by varied the substrate concentrations (5, 10 and 20 % w/v of NR) and pH of the solution. The isotherms of surfactant were examined to find a suitable condition for surfactant adsorption in admicellar polymerization. The concentrations of filtrates or equilibrium surfactant concentration (equilibrium concentration) were determined by using the UV visible spectroscopy measurement technique. The plot of equilibrium concentration versus the amount of adsorbed surfactant was made yield the surfactant adsorption isotherm. From the results of adsorption isotherms exhibited that the substrate content, the surfactant chain length, the head group size and the pH of solution affected the amount of surfactant adsorption on the NR particles.

Keywords: Adsorption isotherm, Natural rubber

4.2 Introduction

Admicellar polymerization is an innovative technique used to modify the material surface by using an ultra-thin polymeric film coating. Admicellar is a term derived from “adsorption” and “micelle” and it defines a type of polymerization taking place inside an adsorbed surfactant bilayer on a substrate at a surfactant concentration just below the critical micelle concentration (CMC). According to this technique. Surfactant adsorption at the solid-liquid interface is a phenomenon of significant importance for many industrial processes. The adsorption process is a result of two mechanisms. First, the electrostatic interaction between the surface and the ionic surfactant head groups give rise to an adsorption characterized by the lack of any particular configuration of the surfactant molecules at the solid-liquid interface. Subsequently, following the attainment of a critical concentration, lateral hydrophobic interactions among the hydrocarbon chains bring about the reorganization and the aggregation of the adsorbed surfactant molecules at the substrate surface (Aloulou *et al.*, 2004.). In this research, scope of this work is to study surfactant bilayer adsorption by varying the concentrations of 4 different types of surfactant; CPC (cationic surfactant), DBSA (anionic surfactant), C7BzO (zwitterionic surfactant) and NP30 (nonionic surfactant) adsorbed on the surface of the substrate (natural rubber latex particles, NR) and varying the substrate concentration (5, 10 and 20 % w/v of NR) on adsorption isotherm and pH of the solution.

4.3 Experimental

4.3.1 Materials

Natural rubber (60 wt% dry rubber content) (Rubber Research Institute of Thailand), Hexadecylpyridinium chloride monohydrate (CPC) (99% purity) (Sigma), Dodecylbenzenesulfonic acid sodium salt (DBSA) (Fluka), 3-(4-Heptyl)phenyl-3-hydroxypropyl)dimethylammoniopropanesulfonate (C7BzO) (98% purity) (Sigma), Polyoxyethylene nonylphenol (Synperonic[®] NP30) (Aldrich), Sodium hydroxide (NaOH) (MERCK), Hydrochloric acid (HCl) (37%) (Carlo Erba Reagent Company). All materials were used without further purification.

4.3.2 Equipments

The instruments are shown in Table 4.1

Table 4.1 Parameters to be measured for adsorption isotherms

Parameters	Instrument/Technique
Prepared and purified natural rubber	- Centrifuge, KUBOTA 5922 (at 10,000 rpm/20 min) (ASTM 1076-02) - Hot plate and magnetic stirrer
Particle size measurement	- Particle size analyzer, MALVERN Mastersizer X Ver.2.18
Adsorption isotherms	- Shaking bath (MEMMERT) - pH meter, Eutech instruments pH 510 - Microcentrifuge, Sartorius GIBTHAI Co., Ltd - UV visible spectrophotometer (UV-1800), SHIMADZU UV 1800

4.3.3 Natural Rubber Latex Preparation

Natural rubber latex particles were purified by centrifugation (at 20°C, 10000 rpm, 20 min) and were redispersed in distilled water 2 times to remove dissolved impurities and to reduce the particle size distribution. The resulting particles were considered to be clean. After washing, the particles were resuspended in water at suitable pH that depending on type of surfactant.

4.3.4 Particle Size Measurement

The size of NR latex purification was measured using a particle size analyzer according to instructions provided with the instrument and using a 45 mm lens. The results were measured by the principle of beam obscuration (beam length 2.4 mm). The instrument yielded the average particle size, the standard size distribution and the specific surface area. The specific surface area was calculated from the particle diameter with the assumption of spherical particles of constant volume.

4.3.5 Surfactant Adsorption Isotherm Measurements

4.3.5.1 Surfactant Adsorption Isotherm for cationic surfactant (hexadecylpyridinium chloride monohydrate, CPC)

Solutions of various initial surfactant concentrations were prepared in water at pH 8. The concentration of surfactant prepared from 1 to 30 mM. Then, 19 ml of each of the surfactant solutions was added into a vial screw cap test tube containing NR solution 5, 10 and 20 %w/v (1, 2 and 4 g dry rubber content) and was adjusted to pH 8 then make volume to 20 ml. The tubes were agitated in a shaking bath at 30°C for a period of equilibrium surfactant adsorption (4 hrs). The NR particles were separated from the mixture by filtering the mixture through a cellulose acetate membrane. The concentrations of filtrates or equilibrium surfactant concentration (equilibrium concentration) were determined by using the UV visible spectroscopy measurement technique. The measurements were carried out at the wavelength of 214 nm. The plot of equilibrium concentration versus the amount of adsorbed surfactant was made yield the surfactant adsorption isotherm.

4.3.5.2 Surfactant Adsorption Isotherm for anionic surfactant (dodecylbenzenesulfonic acid sodium salt, DBSA)

Solutions of various initial surfactant concentrations were prepared in water at pH 3. The concentration of surfactant prepared from 1 to 30 mM. Then, 19 ml of each of the surfactant solutions was added into a vial screw cap test tube containing NR solution 5, 10 and 20 %w/v (1, 2 and 4 g dry rubber content)

and was adjusted to pH 3 then make volume to 20 ml. The tubes were agitated in a shaking bath at 30°C for a period of equilibrium surfactant adsorption (4 hrs). The NR particles were separated from the mixture by filtering the mixture through a cellulose acetate membrane. The concentrations of filtrates or equilibrium surfactant concentration (equilibrium concentration) were determined by using the UV visible spectroscopy measurement technique. The measurements were carried out at the wavelength of 223 nm. The plot of equilibrium concentration versus the amount of adsorbed surfactant was made yield the surfactant adsorption isotherm.

4.3.5.3 Surfactant Adsorption Isotherm for zwitterionic surfactant (3-(4-heptyl)phenyl-3-hydroxypropyl) dimethylammoniopropanesulfonate, C7BzO)

Solutions of various initial surfactant concentrations were prepared in water at pH 3 and 8. The concentration of surfactant prepared from 1 to 30 mM. Then, 9 ml of each of the surfactant solutions was added into a vial screw cap test tube containing NR solution 5, 10 and 20 %w/v (0.5, 1 and 2 g dry rubber content) and was adjusted to pH 3 and 8 then make volume to 10 ml. The tubes were agitated in a shaking bath at 30°C for a period of equilibrium surfactant adsorption (4 hrs). The NR particles were separated from the mixture by filtering the mixture through a cellulose acetate membrane. The concentrations of filtrates or equilibrium surfactant concentration (equilibrium concentration) were determined by using the UV visible spectroscopy measurement technique. The measurements were carried out at the wavelength of 195 nm. The plot of equilibrium concentration versus the amount of adsorbed surfactant was made yield the surfactant adsorption isotherm.

4.3.5.4 Surfactant Adsorption Isotherm for nonionic surfactant (polyoxyethylene nonylphenol, NP30)

Solutions of various initial surfactant concentrations were prepared in water at pH 3, 3.9 and 8. The concentration of surfactant prepared from 1 to 30 mM. Then, 19 ml of each of the surfactant solutions was added into a vial screw cap test tube containing NR solution 5, 10 and 20 %w/v (1, 2 and 4 g dry rubber content) and was adjusted to pH 3, 3.9 and 8 then make volume to 20 ml. The tubes were agitated in a shaking bath at 30°C for a period of equilibrium surfactant

adsorption (4 hrs). The NR particles were separated from the mixture by filtering the mixture through a cellulose acetate membrane. The concentrations of filtrates or equilibrium surfactant concentration (equilibrium concentration) were determined by using the UV visible spectroscopy measurement technique. The measurements were carried out at the wavelength of 195 nm. The plot of equilibrium concentration versus the amount of adsorbed surfactant was made yield the surfactant adsorption isotherm.

4.4 Results and discussion

4.4.1 Particle size measurement

From the histogram in Figure 4.1, it shows that particle diameter of NR covered a wide range. The diameter of NR was in the range of 0.28 - 2.83 μm , confirming that the particle size of NR was naturally polydisperse. The mean diameter of NR was 0.81 μm by volume average. This result compares well to values from Bunsomsit *et al.*, 2002. This specific surface area of NR was 9.5201 m^2/g . The particle size of NR was measured after purification.

4.4.2 Surfactant adsorption isotherms

4.4.2.1 Surfactant Adsorption Isotherms of cationic surfactant (hexadecylpyridinium chloride monohydrate, CPC)

The adsorption isotherms of CPC surfactant onto the NR particle surfaces showed the characteristic of surfactant adsorbed on non-highly charged surface. CPC adsorption was measured with various NR concentrations as shown in Figure 4.1. The adsorption isotherms of CPC on NR particles illustrated the region of surfactant bilayer formation (fast adsorption) starting from the equilibrium concentration of CPC about 86 μM until 891 μM which was below the critical micelle concentration of CPC = 900 μM (Rosen *et al.*, 2012). Beyond this region, there was a slow adsorption region followed by a plateau region (no more adsorption), which was the region where micelles could be formed. At NR 5 % w/v, the amount of CPC adsorption at plateau region was 70.29 $\mu\text{mol/g}$ rubber. If we assume a bilayer adsorption, the surface area occupied by one surfactant molecule

would be 46 \AA^2 versus 23 \AA^2 while NR 10 % w/v, the amount of CPC adsorption at plateau region was 73.71 \mu mol/g rubber, the surface area occupied by one surfactant molecule would be 44 \AA^2 versus 22 \AA^2 and for NR 20% w/v, the amount of CPC adsorption at plateau region was 64.90 \mu mol/g rubber, the surface area occupied by one surfactant molecule would be 50 \AA^2 versus 25 \AA^2 for a monolayer adsorption. For the NR surface area of $9.5201 \text{ m}^2/\text{g}$. At 5, 10 and 20 % w/v of NR, the head group area values were smaller than the calculated head group area of CPC, 80 \AA^2 or 40 \AA^2 for the admicelles (bilayer coverage) which is typically achieved for the adsorption on solid particles e.g., glass fiber (Sakhalkar *et al.*, 1995). According to the rubber is a soft matter, it can be expanded in the presence of good solvent or when having good interaction with the neighboring molecules (Magaraphan *et al.*, 2009), thus the amount of adsorbed CPC on the surface of NR could be higher than that of stiff material. The adsorption of CPC molecules was slightly decreased when the substrate was increased according to the steric effect from the chain length of surfactant.

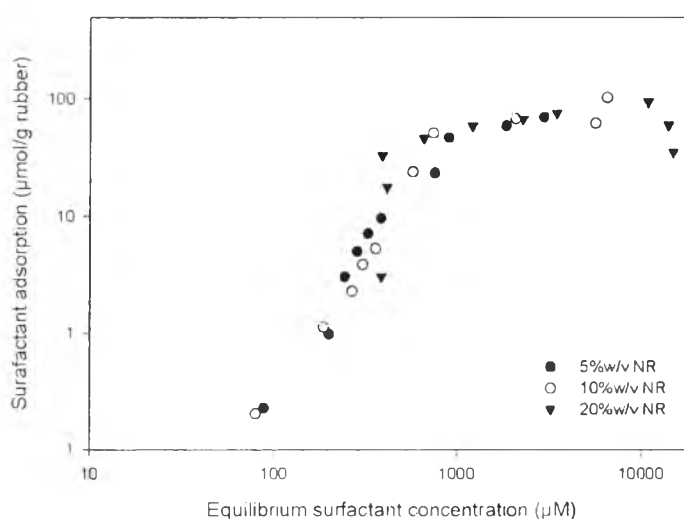


Figure 4.1 Adsorption isotherms of CPC at various NR concentrations.

4.4.2.2 Surfactant Adsorption Isotherms of anionic surfactant (dodecylbenzenesulfonic acid sodium salt, DBSA)

The adsorption isotherms of DBSA surfactant onto the NR particle surfaces showed the characteristic of surfactant adsorbed on non-highly charged surface. DBSA adsorption was measured with various NR concentrations as shown in Figure 4.2. The adsorption isotherms of DBSA on NR particles illustrated the region of surfactant bilayer formation (fast adsorption) starting from the equilibrium concentration of DBSA about 261 μM until 1,189 μM which was below the critical micelle concentration of DBSA = 1,200 μM (Rosen *et al.*, 2012). Beyond this region, there was a slow adsorption region followed by a plateau region (no more adsorption), which is the region where micelles could be formed. At NR 5 % w/v, the amount of DBSA adsorption at plateau region was 259.12 $\mu\text{mol/g}$ rubber. If we assume a bilayer adsorption, the surface area occupied by one surfactant molecule would be 12 \AA^2 versus 6 \AA^2 while NR 10 % w/v, the amount of DBSA adsorption at plateau region was 256.56 $\mu\text{mol/g}$ rubber, the surface area occupied by one surfactant molecule would be 12 \AA^2 versus 6 \AA^2 and for NR 20% w/v, the amount of DBSA adsorption at plateau region was 141.26 $\mu\text{mol/g}$ rubber, the surface area occupied by one surfactant molecule would be 22 \AA^2 versus 11 \AA^2 for a monolayer adsorption. For the NR surface area of 9.5201 m^2/g . For 5, 10 and 20 % w/v of NR, the head group area values were smaller than the calculated head group area of DBSA, 64 \AA^2 or 32 \AA^2 for the admicelles (bilayer coverage) which is typically achieved for the adsorption on solid particles e.g., cotton (Tragoonwichian *et al.*, 2009). According to the rubber is a soft matter, it can be expanded in the presence of good solvent or when having good interaction with the neighboring molecules (Magaraphan *et al.*, 2009), thus the amount of adsorbed DBSA on the surface of NR could be higher than that of stiff material. The adsorption of DBSA molecules was slightly decreased when the substrate was increased according to the steric effect from the chain length of surfactant.

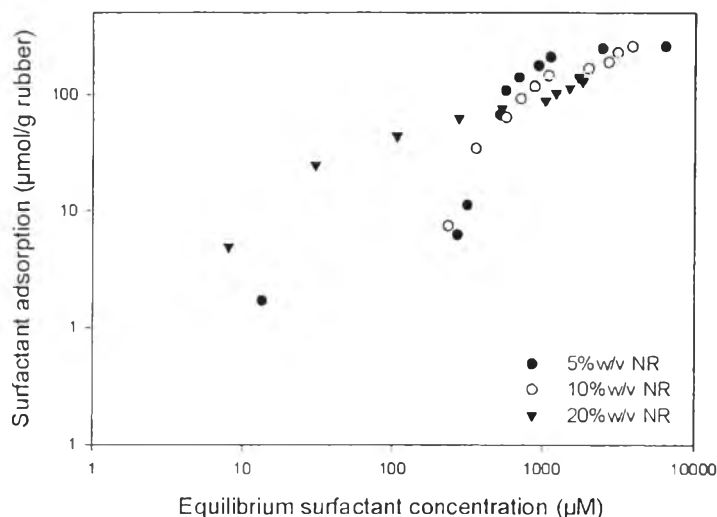


Figure 4.2 Adsorption isotherms of DBSA at various NR concentrations.

4.4.2.3 Surfactant Adsorption Isotherms of zwitterionic surfactant (3-(4-heptyl)phenyl-3-hydroxypropyl) dimethylammoniopropanesulfonate, C7BzO) at pH 3

The adsorption isotherms of C7BzO surfactant onto the NR particle surfaces showed the characteristic of surfactant adsorbed on non-highly charged surface. C7BzO adsorption was measured with various NR concentrations as shown in Figure 4.3. The adsorption isotherms of C7BzO on NR particles illustrated the region of surfactant bilayer formation (fast adsorption) starting from the equilibrium concentration of C7BzO about 1,000 μM until 4,281 μM which was below the critical micelle concentration of C7BzO = 4,600 μM (Rosen *et al.*, 2012). Beyond this region, there was a slow adsorption region followed by a plateau region (no more adsorption), which is the region where micelles could be formed. At NR 5 % w/v, the amount of C7BzO adsorption at plateau region was 452.61 $\mu\text{mol/g}$ rubber. If we assume a bilayer adsorption, the surface area occupied by one surfactant molecule would be 8 \AA^2 versus 4 \AA^2 while NR 10 % w/v, the amount of C7BzO adsorption at plateau region was 240.15 $\mu\text{mol/g}$ rubber, the surface area occupied by one surfactant molecule would be 14 \AA^2 versus 7 \AA^2 and for NR 20% w/v, the amount of C7BzO adsorption at plateau region was 148.27 $\mu\text{mol/g}$ rubber, the surface area occupied by one surfactant molecule would be 22 \AA^2 versus 11 \AA^2

for a monolayer adsorption. For the NR surface area of $9.5201 \text{ m}^2/\text{g}$. For 5, 10 and 20 % w/v of NR, the head group area values were bigger than the calculated head group area of C7BzO, 6 \AA^2 or 3 \AA^2 for the admicelles (bilayer coverage). The adsorbed amount at saturation mainly depends on the chain length and on the nature of the solid substrate on which adsorption is taking place (Luna-Xavier *et al.*, 2002), the chain of the surfactant is long when the substrate increased in the system, surfactant needed space to form a bilayer so it could be harder to form a bilayer adsorption then the amount of surfactant adsorbed decreased resulting the head group area increased compared to the bilayer coverage. Moreover the steric effect from the head group leading to the decreasing on adsorption of surfactant.

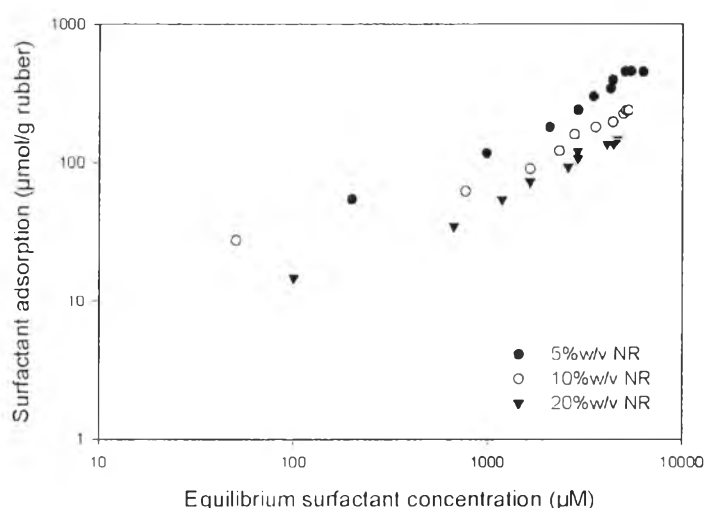


Figure 4.3 Adsorption isotherms of C7BzO, pH 3 at various NR concentrations.

4.4.2.4 Surfactant Adsorption Isotherms of zwitterionic surfactant (3-(4-heptyl)phenyl-3-hydroxypropyl) dimethylammoniopropanesulfonate, C7BzO) at pH 8

The adsorption isotherms of C7BzO surfactant onto the NR particle surfaces showed the characteristic of surfactant adsorbed on non-highly charged surface. C7BzO adsorption was measured with various NR concentrations as shown in Figure 4.4. The adsorption isotherms of C7BzO on NR particles illustrated

the region of surfactant bilayer formation (fast adsorption) starting from the equilibrium concentration of C7BzO about 1,059 μM until 3,703 μM which was below the critical micelle concentration of C7BzO = 4,600 μM (Rosen *et al.*, 2012). Beyond this region, there was a slow adsorption region followed by a plateau region (no more adsorption), which is the region where micelles could be formed. At NR 5 % w/v, the amount of C7BzO adsorption at plateau region was 435.99 $\mu\text{mol/g}$ rubber. If we assume a bilayer adsorption, the surface area occupied by one surfactant molecule would be 8 \AA^2 versus 4 \AA^2 while NR 10 % w/v, the amount of C7BzO adsorption at plateau region was 235.88 $\mu\text{mol/g}$ rubber, the surface area occupied by one surfactant molecule would be 14 \AA^2 versus 7 \AA^2 and for NR 20% w/v, the amount of C7BzO adsorption at plateau region was 135.19 $\mu\text{mol/g}$ rubber, the surface area occupied by one surfactant molecule would be 24 \AA^2 versus 12 \AA^2 for a monolayer adsorption. For the NR surface area of 9.5201 m^2/g . For 5, 10 and 20 % w/v of NR, the head group area values were bigger than the calculated head group area of C7BzO, 4 \AA^2 or 2 \AA^2 for the admicelles (bilayer coverage). The adsorbed amount at saturation mainly depends on the chain length and on the nature of the solid substrate on which adsorption is taking place (Luna-Xavier *et al.*, 2002), the chain of the surfactant is long when the substrate increased in the system, surfactant needed space to form a bilayer so it could be harder to form a bilayer adsorption then the amount of surfactant adsorbed decreased resulting the head group area increased compared to the bilayer coverage. Moreover the steric effect from the head group leading to the decreasing on adsorption of surfactant.

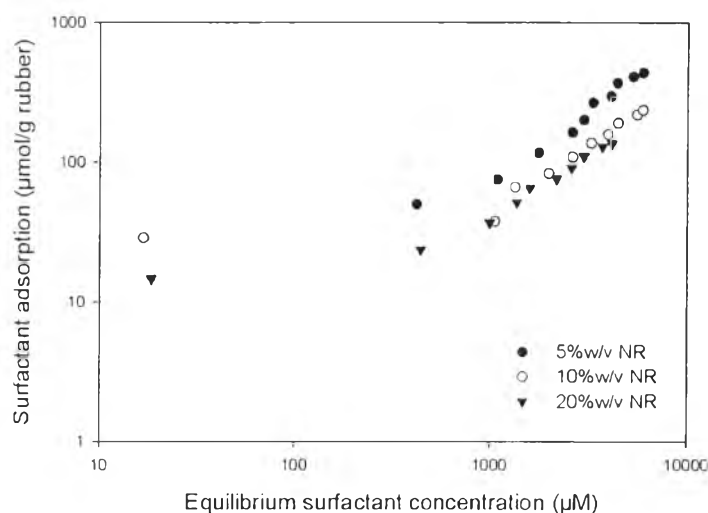


Figure 4.4 Adsorption isotherms of C7BzO, pH 8 at various NR concentrations.

4.4.2.5 Surfactant Adsorption Isotherms of nonionic surfactant (polyoxyethylene nonylphenol, NP30) at pH 3

The adsorption isotherms of NP30 surfactant onto the NR particle surfaces showed the characteristic of surfactant adsorbed on non-highly charged surface. NP30 adsorption was measured with various NR concentrations as shown in Figure 4.5. The adsorption isotherms of NP30 on NR particles illustrated the region of surfactant bilayer formation (fast adsorption) starting from the equilibrium concentration of NP30 about 40 μM until 138 μM which was below the critical micelle concentration of NP30 = 140 μM (Luna-Xavier *et al.*, 2002). Beyond this region, there was a slow adsorption region followed by a plateau region (no more adsorption), which is the region where micelles could be formed. At NR 5 % w/v, the amount of NP30 adsorption at plateau region was 161.97 $\mu\text{mol/g}$ rubber. The surface area occupied by one surfactant molecule would be 9 \AA^2 while NR 10 % w/v, the amount of NP30 adsorption at plateau region was 48.30 $\mu\text{mol/g}$ rubber, the surface area occupied by one surfactant molecule would be 33 \AA^2 and for NR 20% w/v, the amount of NP30 adsorption at plateau region was 32.40 $\mu\text{mol/g}$ rubber, the surface area occupied by one surfactant molecule would be 49 \AA^2 for a monolayer adsorption. For the NR surface area of 9.5201 m^2/g . At 5 % w/v of NR, the head group area value was equal with the calculated head group area of NP30, 9 \AA^2 for the monolayer coverage which is typically achieved for the adsorption on solid particles

e.g., silica and at 10 and 20 % w/v of NR, the head group area value was bigger than the calculated head group area of NP30. The surfactant molecule occupied the area more than silica, the adsorbed amount at saturation mainly depends on the oxyethylene chain length and on the nature of the solid substrate on which adsorption is taking place (Luna-Xavier *et al.*, 2002), the chain of the surfactant is long when the substrate increased in the system, surfactant needed space to form a bilayer so it could be harder to form a bilayer adsorption then the bilayer adsorption could not be formed and the amount of surfactant adsorbed decreased resulting from the steric effect.

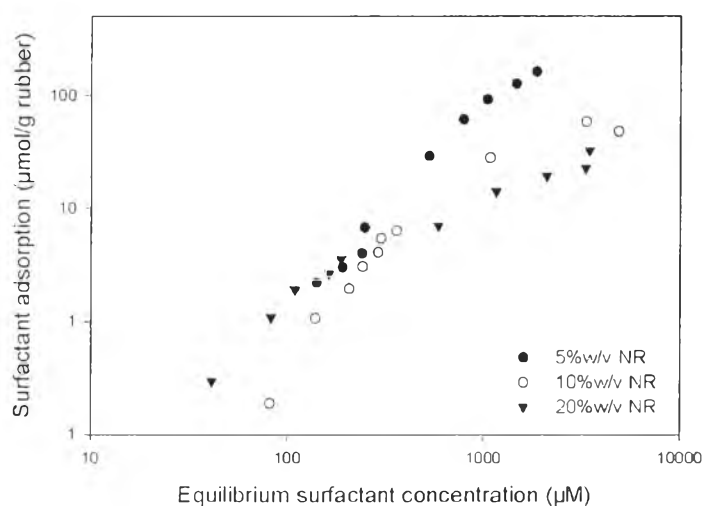


Figure 4.5 Adsorption isotherms of NP30, pH 3 at various NR concentrations.

4.4.2.6 Surfactant Adsorption Isotherms of nonionic surfactant (polyoxyethylene nonylphenol, NP30) at pH 3.9

The adsorption isotherms of NP30 surfactant onto the NR particle surfaces showed the characteristic of surfactant adsorbed on non-highly charged surface. NP30 adsorption was measured with various NR concentrations as shown in Figure 4.6. The adsorption isotherms of NP30 on NR particles illustrated the region of surfactant bilayer formation (fast adsorption) starting from the equilibrium concentration of NP30 about 47 μM until 138 μM which was below the critical micelle concentration of NP30 = 140 μM (Luna-Xavier *et al.*, 2002). Beyond this region, there was a slow adsorption region followed by a plateau region (no more

adsorption), which is the region where micelles could be formed. At NR 5 % w/v, the amount of NP30 adsorption at plateau region was 176.12 $\mu\text{mol/g}$ rubber. The surface area occupied by one surfactant molecule would be 9 \AA^2 while NR 10 % w/v, the amount of NP30 adsorption at plateau region was 90.05 $\mu\text{mol/g}$ rubber, the surface area occupied by one surfactant molecule would be 18 \AA^2 and for NR 20% w/v, the amount of NP30 adsorption at plateau region was 46.53 $\mu\text{mol/g}$ rubber, the surface area occupied by one surfactant molecule would be 34 \AA^2 for a monolayer adsorption. For the NR surface area of 9.5201 m^2/g . At 5 % w/v of NR, the head group area value was equal with the calculated head group area of NP30, 9 \AA^2 for the monolayer coverage which is typically achieved for the adsorption on solid particles e.g., silica and at 10 and 20 % w/v of NR, the head group area value was bigger than the calculated head group area of NP30. The surfactant molecule occupied the area more than silica, the adsorbed amount at saturation mainly depends on the oxyethylene chain length and on the nature of the solid substrate on which adsorption is taking place (Luna-Xavier *et al.*, 2002), the chain of the surfactant is long when the substrate increased in the system, surfactant needed space to form a bilayer so it could be harder to form a bilayer adsorption then the bilayer adsorption could not be formed and the amount of surfactant adsorbed decreased resulting from the steric effect.

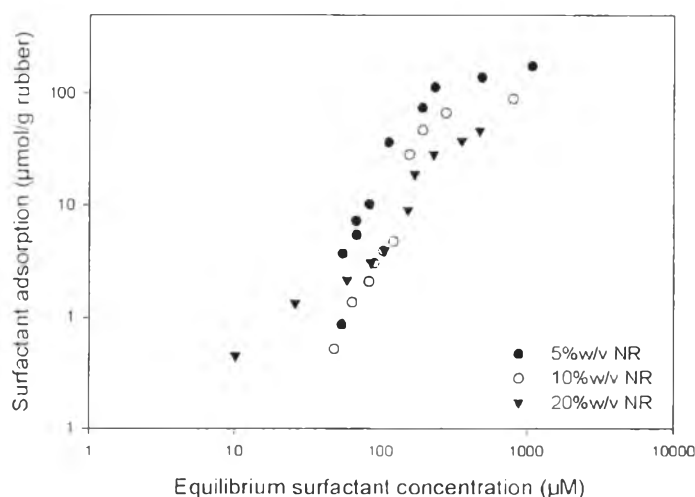


Figure 4.6 Adsorption isotherms of NP30, pH 3.9 at various NR concentrations.

4.4.2.7 Surfactant Adsorption Isotherm of nonionic surfactant (polyoxyethylene nonylphenol, NP30) at pH 8

The adsorption isotherms of NP30 surfactant onto the NR particle surfaces showed the characteristic of surfactant adsorbed on non-highly charged surface. NP30 adsorption was measured with various NR concentrations as shown in Figure 4.7. The adsorption isotherms of NP30 on NR particles illustrated the region of surfactant bilayer formation (fast adsorption) starting from the equilibrium concentration of NP30 about 85 μM until 136 μM which was below the critical micelle concentration of NP30 = 140 μM (Luna-Xavier *et al.*, 2002). Beyond this region, there was a slow adsorption region followed by a plateau region (no more adsorption), which is the region where micelles could be formed. At NR 5 % w/v, the amount of NP30 adsorption at plateau region was 130.14 $\mu\text{mol/g}$ rubber. The surface area occupied by one surfactant molecule would be 12 \AA^2 while NR 10 % w/v, the amount of NP30 adsorption at plateau region was 50.60 $\mu\text{mol/g}$ rubber, the surface area occupied by one surfactant molecule would be 31 \AA^2 and for NR 20% w/v, the amount of NP30 adsorption at plateau region was 43.82 $\mu\text{mol/g}$ rubber, the surface area occupied by one surfactant molecule would be 36 \AA^2 for a monolayer adsorption. For the NR surface area of 9.5201 m^2/g . At 5, 10 and 20 % w/v of NR, the head group area value was bigger than the calculated head group area of NP30, 9 \AA^2 for the monolayer coverage which is typically achieved for the adsorption on solid particles e.g., silica. The surfactant molecule occupied the area more than silica, the adsorbed amount at saturation mainly depends on the oxyethylenic chain length and on the nature of the solid substrate on which adsorption is taking place (Luna-Xavier *et al.*, 2002). the chain of the surfactant is long when the substrate increased in the system, surfactant needed space to form a bilayer so it could be harder to form a bilayer adsorption then the bilayer adsorption could not be formed and the amount of surfactant adsorbed decreased resulting from the steric effect.

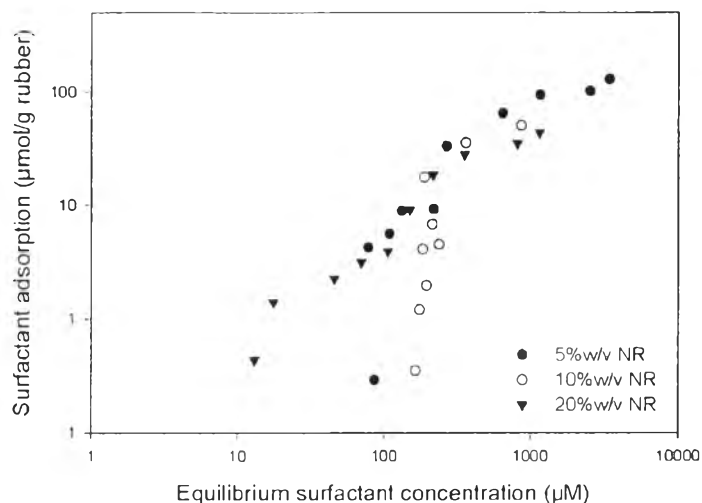


Figure 4.7 Adsorption isotherms of NP30, pH 8 at various NR concentrations.

4.5 Conclusions

In this research, the adsorption isotherms of CPC, DBSA and C7BzO exposed bilayer adsorption which could be formed to allow admicellar polymerization while NP30 revealed the forming of monolayer adsorption for all NR content and the amount of surfactant adsorption was decreased with NR content according to the occupied volume of surfactant resulting from the steric effect of the chain length.. The adsorption isotherm of C7BzO at pH 3 was higher than pH 8 at all NR content resulting from the steric effect from the head group of surfactant. Altering on the pH value revealed a significant changing on the adsorption of the surfactant on the surface of NR particles for NP30, at pH 3.9 exhibited the highest amount of surfactant adsorption and at 5 %w/v of NR provided better adsorption compare to 10 and 20 %w/v of NR.

4.6 Acknowledgements

The authors would like to acknowledge the Rachadapisek Sompoch Endevelopment (RU), Chulalongkorn University for funding and to the Petroleum and Petrochemical College, Chulalongkorn University for partial scholarship.

4.7 References

- Aloulou, F., Boufi, S., Belgacem, N., and Gandini, A. (2004) Adsorption of cationic surfactants and subsequent adsolubilization of organic compounds onto cellulose fibers. *Colloid Polymer Science*, 283, 344-350.
- Bunsomsit, K., (2002) Polypyrrole coated latex by admicellar polymerization. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.
- Hourston, D.J., and Romaine, J. (1991) Modification of natural rubber latex III. Natural rubber-polystyrene composite latexes synthesized using azobisisobutyronitrile as initiator. *Journal of Applied Polymer Science*, 43, 2207-2211.
- Esumi, K., Watanabe, N., and Meguro, K. (1991) Polymerization of styrene adsolubilized in polymerizable surfactant bilayer on alumina. *Langmuir*, 7(8), 1175-1178.
- Funkhouser, G.P., Arevalo, M.P., Glatzhofer, D.T., and O'Rear, E.A. (1995) Solubilization and adsolubilization of pyrrole by sodium dodecyl sulfate: polypyrrole formation on alumina surfaces. *Langmuir*, 11(5), 1443-1447.
- Kasawahara, S., Kawazura, T., Sawada, T., and Isono, Y. (2003) Preparation and characterization of natural rubber dispersed in nano-matrix. *Journal of Applied Polymer Science*, 44, 4527-4531.
- Kitiyanan, B., O'Haver, J.H., Harwell, J.H., and Osuwan, S. (1996) Adsolubilization of styrene and isoprene cetyltrimethylammonium bromide admicelle on precipitated silica. *Langmuir*, 12(9), 2162-2168.

- Luna-Xavier, J.L., Guyot, A., and Bourgeat-Lami, E. (2002) Synthesis and characterization of silica/poly(methyl methacrylate) nanocomposite latex particles through emulsion polymerization using a cationic azo initiator. Journal of Colloid and Interface Science, 250, 82-92.
- Magaraphan, R., Srinarang, V. (2009) Admicellar polymerization of styrene on natural rubber particles. Journal of Elastomers and Plastics, 41, 457-477.
- Maserti, B.E., Della Croce, C.M., Luro, F., Morillon, R., Cini, M., and Caltavuturo, L. (2007) A general method for the extraction of citrus leaf proteins and separation by 2D electrophoresis: A follow up. Journal of Chromatography B, 849, 351-356.
- Nontasorn, P., Chavadej, S., Rangsunvigit, P., O'Haver, J.H., Chasirimahamorakot, S., and Na-Ranong, N. (2005) Admicellar polymerization modified silica via a continuous stirred-tank reactor system: Comparative properties of rubber compounding. Chemical Engineering Journal, 108, 213-218.
- O'Haver, J.H., Harwell, J.H., Evans, L.R., and Waddel, W.H. (1996) Formation of Poly(tetrafluoroethylene) thin films on alumina by admicellar polymerization. Journal of Applied Polymer Science, 59, 1427-1435.
- Pongprayoon, T., Yanumet, N., and O'Rear, E.A. (2002) Admicellar polymerization of styrene on cotton. Journal of Colloid and Interface Science, 249, 227-234.
- Pongprayoon, T., Yanumet, N., Edgar, A., O'Rear, E.A., Walter, E.A., and Daniel, E.A. (2004) Admicellar polymerization of styrene on cotton. Journal of colloid and Interface Science, 281(2), 307-315.
- Preechasup, N. (2006) A novel processible-white natural rubber modified by admicellar polymerization of styrene as nano-core shell structure. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.
- Rosen, M.J., Kunjappu, J.T. *Surfactants and Interfacial Phenomena*, Wiley, New York, 2012.
- Rungruang, P., Grady, B.P., and Supaphol, P. (2006) Surface-modified calcium carbonate particles by admicellar polymerization to be used as filler for

- isotactic polypropylene. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 275, 114-125.
- Sakhalkar, S.S., and Hirt, D.E. (1995) Admicellar polymerization of polystyrene on glass fibers. Langmuir, 11(9), 3369-3373.
- See, H.C., and O'Haver, J.H. (2003) Atomic force microscopy characterization of ultrathin polystyrene films formed by admicellar polymerization on silica disks. Journal of Applied Polymer Science, 89, 36-46.
- Srinarang, V. (2004) Admicellar polymerization of polystyrene on natural rubber particles. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.
- Srirachya, N. (2009) Extrusion of admicelled natural rubber filled with nanomagnetic particles. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.
- Thammathadanukul, V., O'Haver, J.H., Harwell, J.H., Osuwan, S., Na-Ranong, N., and Weddell, W.H. (1996) Admicellar polymerization modified silica via a continuous stirred-tank reactor system: comparative properties of rubber compounding. Journal of Applied Polymer Science, 59, 1741-1751.
- Tragoonwichian, S., O'Rear, E.A., and Yanumet, N. (2009) Double coating via repeat admicellar polymerization for preparation of bifunctional cotton fabric: Ultraviolet protection and water repellence. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 349, 170-175.
- Weddell, W.H., O'Haver, J.H., Evans, L.R., and Harwell, J.H. (1995) Organic polymer-surfactant modified precipitated silica. Journal of Applied Polymer Science, 59, 1741- 1750.
- Wu, J., Harwell, J.H., and O'Rear, E.A. (1987) Two-dimensional reaction solvents: surfactant bilayers in the formation of ultrathin films. Langmuir, 3(4), 531-537.
- Xin, W., Andrew, D.W., Walter, A., and Grady, B.P. (2003) X-ray photoelectron spectroscopic studies of hydrophilic surfaces modified via admicellar polymerization. Journal of Colloid and Interface Science, 264, 292-300.
- Zhao, Y., Qiu, J., Feng, H., Zhang, M., Lei, L., and Wu, X. (2011) Improvement of tensile and thermal properties of poly(lactic acid) composites with

admicellar-treated rice straw fiber. Chemical Engineering Journal, 173, 659-666.