

CHAPTER IV

RESULTS AND DISCUSSION



4.1 Adsorption of Surfactants on High Density Polyethylene (HDPE)

In all experiments, high density polyethylene (HDPE) was used as the plastic substrate. It was in a powder form, having particle size ranging from 65 to 125 μm . The specific area was calculated by the 5 points adsorption isotherm of N_2 gas. The result was found that BET surface area of HDPE is $5 \text{ m}^2/\text{g}$.

4.1.1 Adsorption Isotherm of Sodium Dodecyl Sulfate

The adsorption isotherm of Sodium Dodecyl Sulfate (SDS) on HDPE at pH 6 and 30°C is shown in Figure 4.1. The adsorption isotherm is the relationship between the amount adsorbed of surfactant ($\mu\text{mole/g}$) and the equilibrium concentration of SDS (μM). It is observed that the amount adsorbed of surfactant is greatly increased at the low equilibrium concentration. The isotherm shows an inflection at the concentration of SDS around $1000 \mu\text{M}$ probably due to changing in orientation of surfactant on the solid surface. The surfactant adsorption reaches the maximum of approximately $22 \mu\text{mol}$ of SDS per gram of HDPE corresponding to $8,000 \mu\text{M}$, where the CMC of SDS is $8,200 \mu\text{M}$.

From the maximum SDS adsorption ($22 \mu\text{mol/g}$), the calculated area per adsorbed molecule of SDS is 39 \AA^2 . However the area occupied per molecule for SDS in the closed compact monolayers is reported to be 53 \AA^2 (Dahanayake, 1986). Therefore it is possible that SDS perform a partial bilayer formation on HDPE at the maximum adsorption.

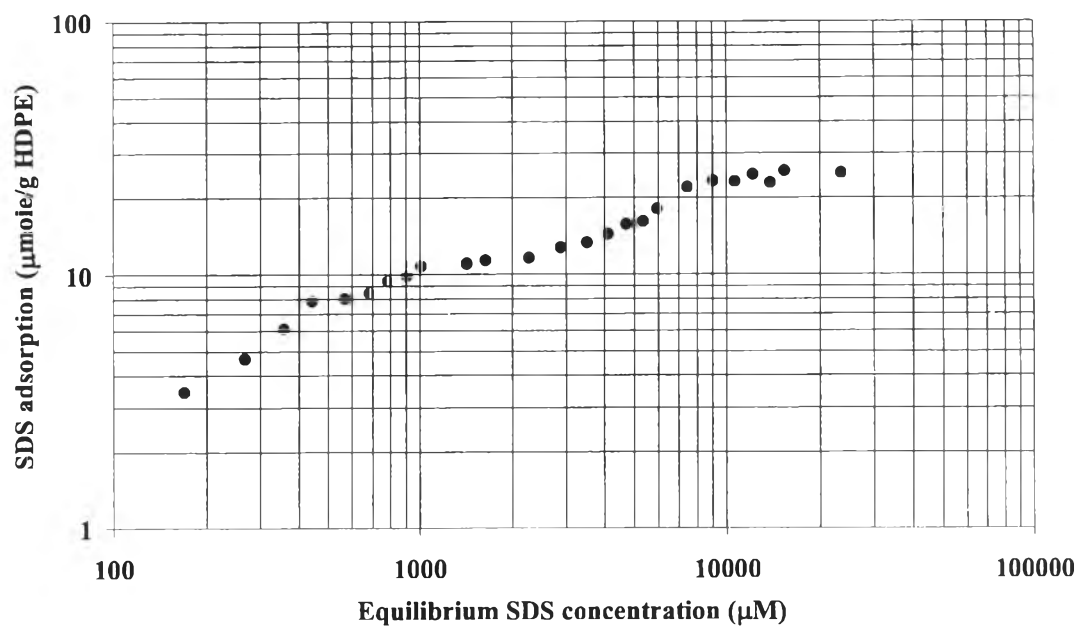


Figure 4.1 Adsorption isotherm of SDS on high density polyethylene at pH 6 and 30 °C.

Figure 4.2 illustrates the relationship between zeta potential and SDS adsorption. The results reveal that, the magnitude of zeta potential shows the negative charge at all equilibrium concentration of SDS. As the adsorption increases, the zeta potential of HDPE is more negative and reaches plateau (57.4 mV) near the CMC similar to the adsorption.

The zeta potential results can give a hint for the orientation of SDS on the substrate. The orientation of SDS on HDPE plastic should be in a head group out configuration (e.g., a bilayer or a tail down /head-out) because the absolute magnitude of a zeta potential shows the negative charge at all equilibrium concentration of SDS.

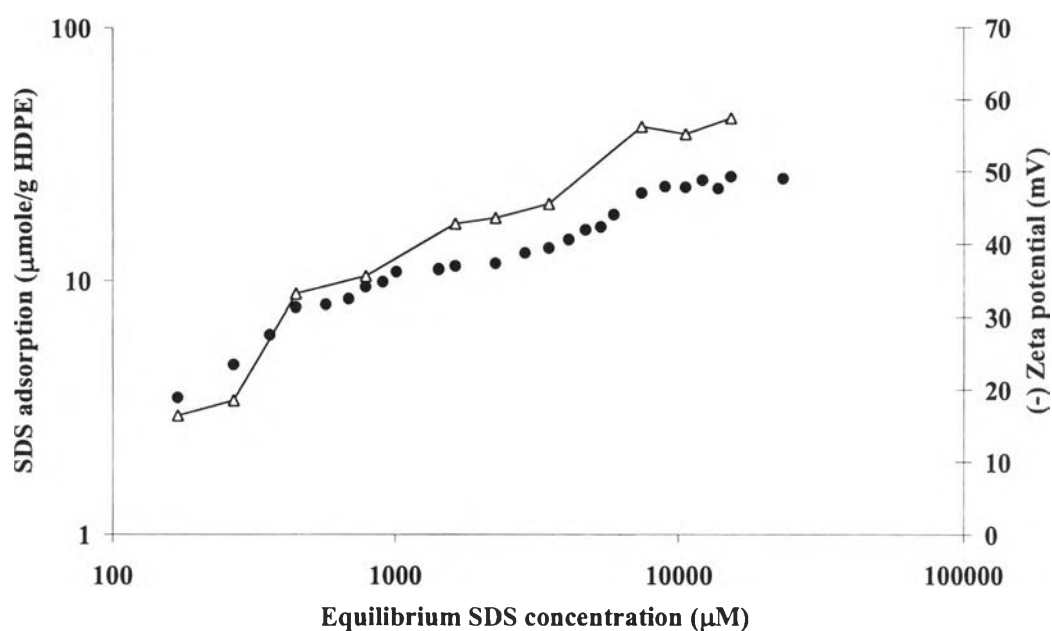


Figure 4.2 Adsorption isotherm of SDS and zeta potential of high density polyethylene at pH 6 and 30 °C; (●) adsorption, (−△) zeta potential.

From the adsorption and zeta potential results it can be proposed that the adsorption of SDS on HDPE plastic would seem to follow the process illustrated in Fig 4.3. At low equilibrium concentration the surfactant adsorption can occur either by electrostatic attraction (anionic head group interacts with cationic charge sites) or hydrophobic bonding (alkyl chain interact with the hydrophobic sites) as depicted in Fig. 4.3(a). At the vicinity of critical micelle concentration the orientation of surfactant occur partial bilayer formations on the plastic surface as depicted in Fig. 4.3(b).

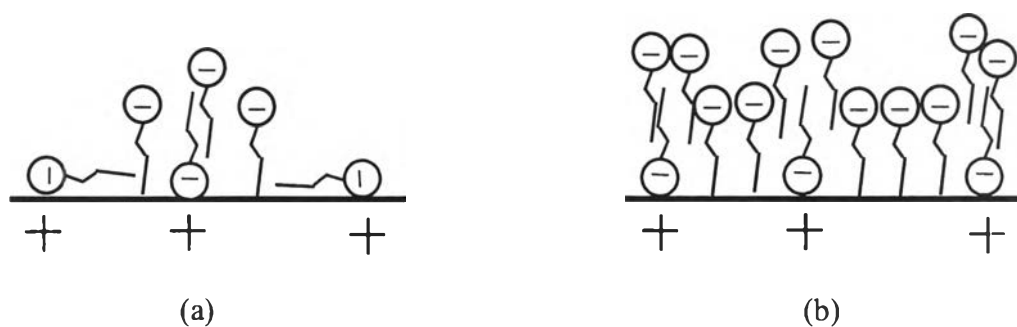


Figure 4.3 The schematic illustration of the adsorption SDS on high density polyethylene. (a) low equilibrium concentration; (b) near CMC.

4.1.2 Effect of Ionic Strength on SDS Adsorption

The effect of ionic strength on the adsorption SDS on HDPE is shown in Figures 4.4. It is observed that the higher ionic strength produces a steeper adsorption isotherm at below CMC, possibly by decreasing the electrical repulsion between the similarly charged adsorbed ions, permitting closer packing and also increasing in ionic strength of the solution. Neutral electrolyte addition also moved the plateau to lower equilibrium concentrations of the surfactant from 8,000 μM to 1,200 μM as a result from CMC lowering. However changing in ionic strength does not have much effect on the amount adsorbed at plateau region.

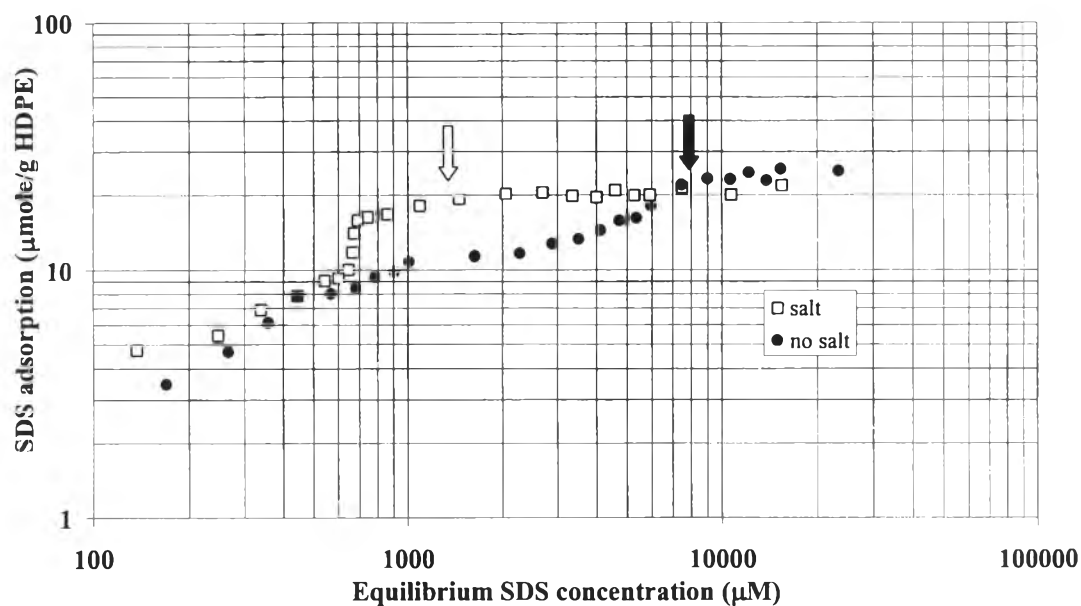


Figure 4.4 Adsorption isotherm of SDS on high density polyethylene at pH 6 and 30 °C; (\square) 0.15 M NaCl, (\bullet) no salt added. \Downarrow CMC with salt, \Downarrow CMC no salt.

4.1.3 Effect of pH on the SDS Adsorption

Conformation that adsorption process involved charge-charge interactions was obtained from studies of the dependence of adsorption on pH. When pH of system was changed, H^+ and OH^- are the potential determining ions for the HDPE surface. As the pH of the aqueous phase is lowered, a plastic surface will become more positive because of adsorption onto surface of protons from the solution. The reversed is true when the pH of the aqueous phase is raised.

Table 4.1 summarizes the zeta potential of the HDPE in water as a function of pH.

Table 4.1 Zeta potential of high density polyethylene at pH 4, 6 and 10

pH	Zeta potential (mV)
4	(+) 4.532
6	(+) 1.712
10	(-) 8.237

Figure 4.5 illustrates the comparison of SDS adsorption on HDPE at pH 4, 6 and 10. These results show that pH has a significant effect on the SDS adsorption. The similar trend in SDS adsorption is observed but the amount of SDS adsorbed on HDPE increases when the pH of system is lowered. This is probably due to H^+ ions covering more on surface at low pH, as a consequence, the electrostatic attraction between SDS and surface is increased. At the higher pH, OH^- dominated more on the surface, causing the increasing in the electrostatic repulsion.

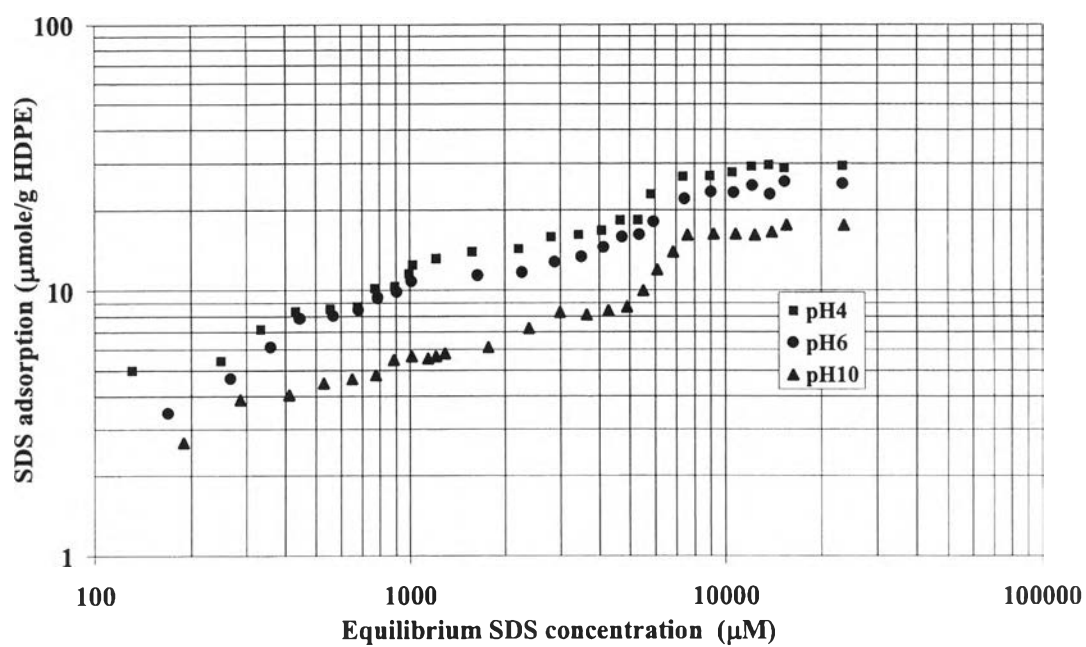


Figure 4.5 Adsorption isotherm of SDS on high density polyethylene at 30 °C; (■) pH 4, (●) pH 6, (▲) pH 10.

Figure 4.6 illustrates the relationship between zeta potential and SDS adsorption with varying pH. It is observed that as the adsorption increases, the zeta potential is more negative, and reaches the plateau near the CMC similar to the adsorption. Increasing pH decreases the absolute magnitude of negative zeta potential. The maximum adsorption and zeta potential value at different pH are represented in Table 4.2.

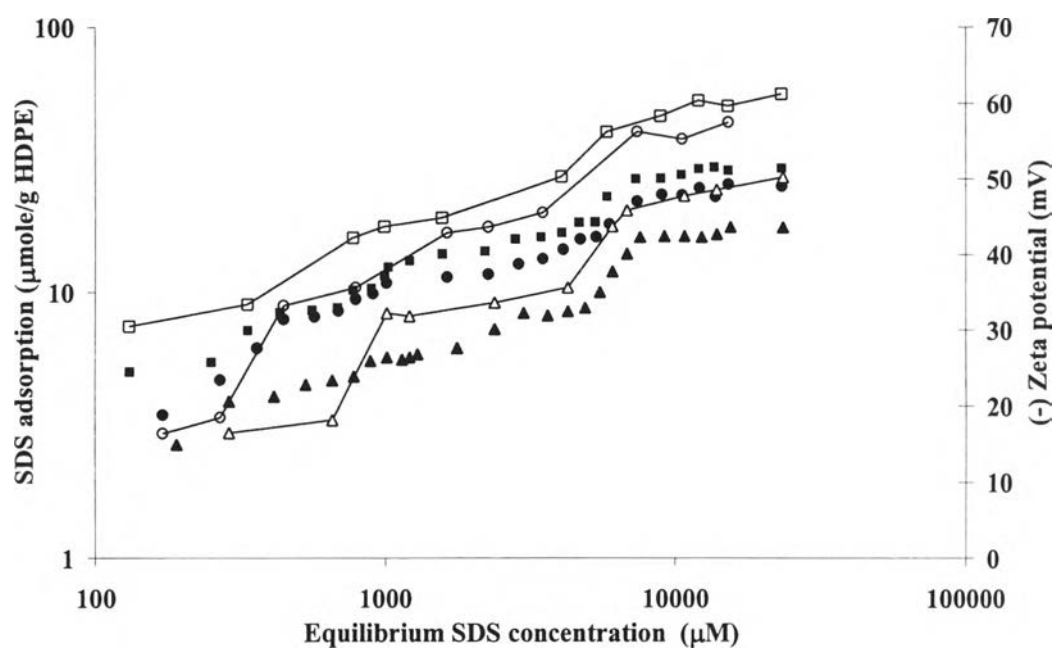


Figure 4.6 Adsorption isotherms of SDS and zeta potential of high density polyethylene at different pH and 30 °C; (■,◆,▲) adsorption at pH 4, 6 and 10 respectively and (□,◇,△) zeta potential at pH 4, 6 and 10, respectively.

Table 4.2 Adsorption and Zeta potential of SDS adsorption on HDPE at saturation from different pH

pH	Adsorption (μ mole/g)	Area/molecule (\AA^2)	Zeta potential (mV)
4	26.95	32	(-) 61.2
6	23.3	39	(-) 57.4
10	16.14	54	(-) 50.2

The amount of adsorption of SDS in the vicinity of CMC is used to calculate the area per adsorbed molecule and the results are shown in Table 4.2.

The results can be compared with area per molecule of closed compact monolayer formation (53\AA^2). It can be implied that, at the maximum adsorption for pH 4 and 6, the formation of surfactant on HDPE plastic is in the form of partial bilayer as depicted in Fig 4.7(a), while for pH 10 the orientation is monolayer on the surface as depicted in Fig 4.7(b).

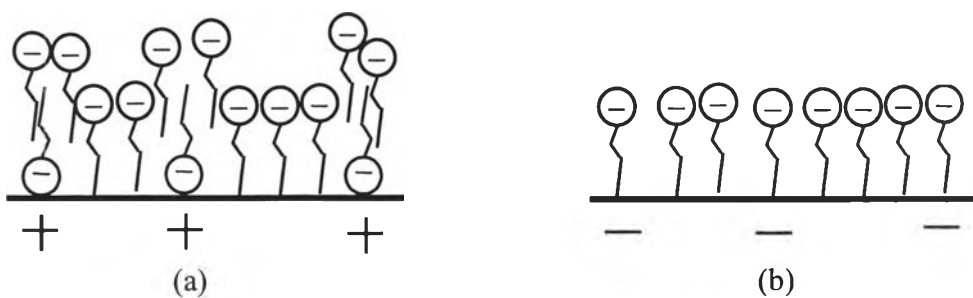


Figure 4.7 The schematic illustration of the adsorption SDS on high density polyethylene at different pH. (a) pH 4 and 6; (b) pH 10.

4.1.4 Adsorption Isotherm of Cetyltrimethylammoniumbromide

The adsorption isotherm of CTAB on HDPE at pH 6 and 30°C is shown in Figure 4.8. It is also observed an inflection at the equilibrium concentration around 200 μM and beyond at this point a slow increase in adsorption is occurred. Following this a more rapid increase in adsorption occurred which reached the plateau region near the CMC (900 μM). A saturation appeared at the maximum adsorption of CTAB on HDPE plastic of approximately 9.3 μmol of CTAB per gram of HDPE.

From the maximum CTAB adsorption (9.3 $\mu\text{mol/g}$), the calculated area per adsorbed molecule of CTAB is 92 \AA^2 . However the area per molecule for SDS in the closed compact monolayers is reported to be 62 \AA^2 (Thakulsukanant, 1989). Hence it is possible that CTAB does not completely cover the HDPE surface.

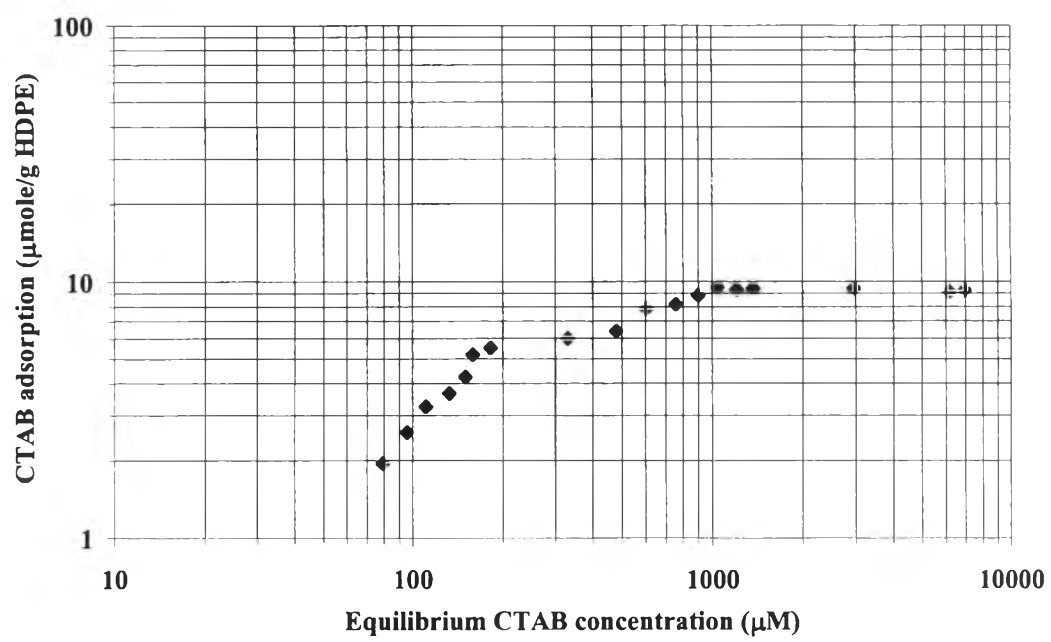


Figure 4.8 Adsorption isotherm of CTAB on high density polyethylene at pH 6 and 30 °C.

The relationship between zeta potential and adsorption of CTAB are shown in Figure 4.9. The results represented that as the amount of adsorbed CTAB increases, the zeta potential of HDPE is increased. The magnitude of zeta potential shows the positive charge at all equilibrium concentration of CTAB and reaches the maximum value (42.2 mV) near the CMC similar to the adsorption.

From the zeta potential results it implied that the adsorbed CTAB on HDPE plastic possibly have the head group oriented toward the solution for all equilibrium concentration of CTAB.

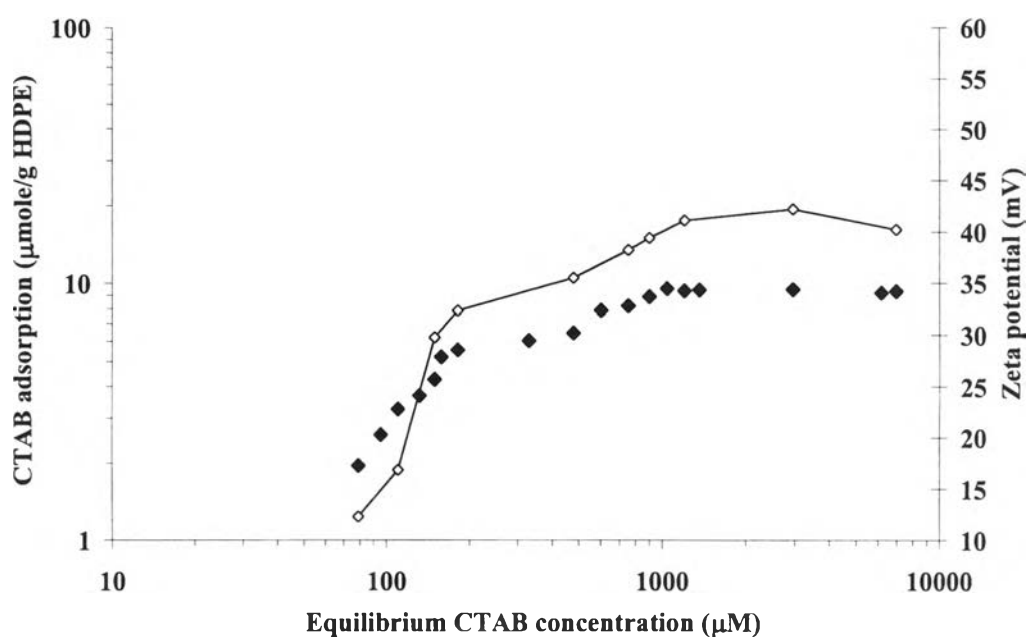


Figure 4.9 Adsorption isotherm of CTAB and zeta potential of high density polyethylene at pH 6 and 30 °C; (◆) adsorption, (◊) zeta potential.

From the adsorption and zeta potential results it can be proposed that the adsorption of CTAB on HDPE plastic follow the process illustrated in Fig 4.10. At low equilibrium concentration the surfactant adsorption occur via hydrophobic bonding between alkyl chain and the hydrophobic sites on the surface. The orientation of surfactant is in a tail-down head out configuration because of the electrostatic repulsion between positive head group of CTAB and the positive charged sites of HDPE surface as shown in Fig. 4.3 (a). As the equilibrium concentration is increased, the surfactants will orient themselves perpendicular to the plastic surface as shown in Fig. 4.3(b).

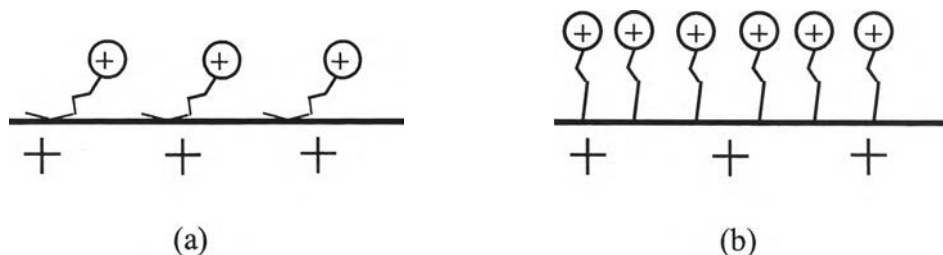


Figure 4.10 The schematic illustration of the adsorption CTAB on high density polyethylene. (a) low equilibrium concentration; (b) near CMC.

4.1.5 Effect of Ionic Strength on CTAB Adsorption

The effect of ionic strength on the adsorption of CTAB on HDPE is illustrated in Figure 4.11. The results show that the higher ionic strength produces a sharper adsorption isotherm at the low equilibrium concentration, probably by decreasing in the electrostatic repulsion between surfactant head group, resulting in more compact adsorption. Adding electrolyte also shifts the CMC to lower equilibrium concentrations of the surfactant from 1000 μM to 250 μM .

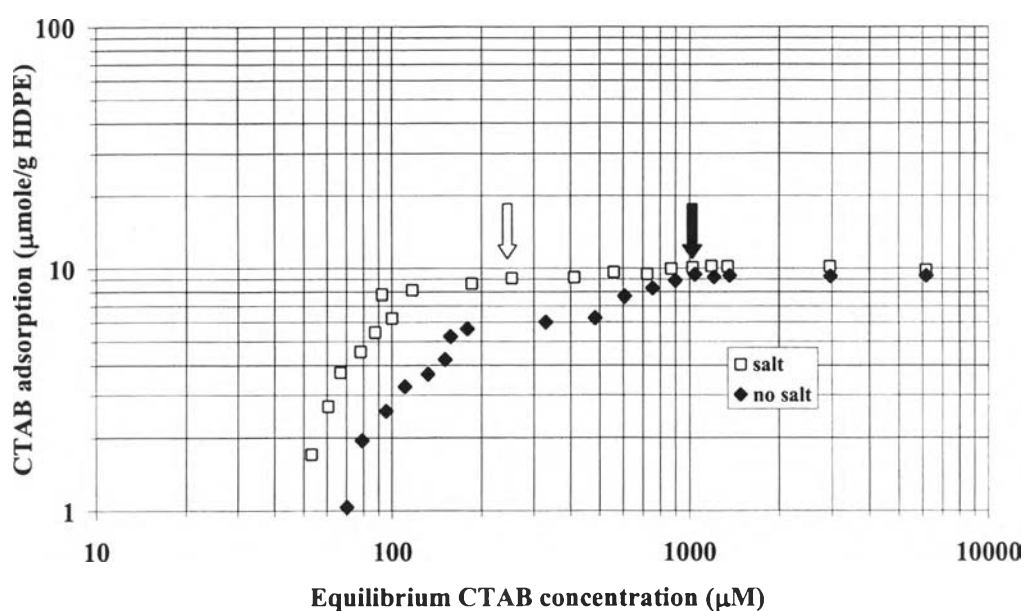


Figure 4.11 Adsorption isotherm of CTAB on high density polyethylene at pH 6 and 30 °C; (■) 0.15 M NaCl, (◆) no salt added. \Downarrow CMC with salt, \Downarrow CMC no salt.

4.1.6 Effect of pH on the CTAB Adsorption

Figure 4.12 illustrates the comparison of CTAB adsorption on HDPE at pH 4, 6 and 10. These data reveal that pH has a significant effect to the CTAB adsorption. The similar trend is observed but the amount of CTAB adsorbed on HDPE increases when pH of system higher. This is possibly due to more H^+ ions covering on surface at low pH and, as a consequence, the electrostatic repulsion between CTAB and surface is increased. At higher pH, OH^- ions dominate on the surface, causing the increase in the electrostatic attraction.

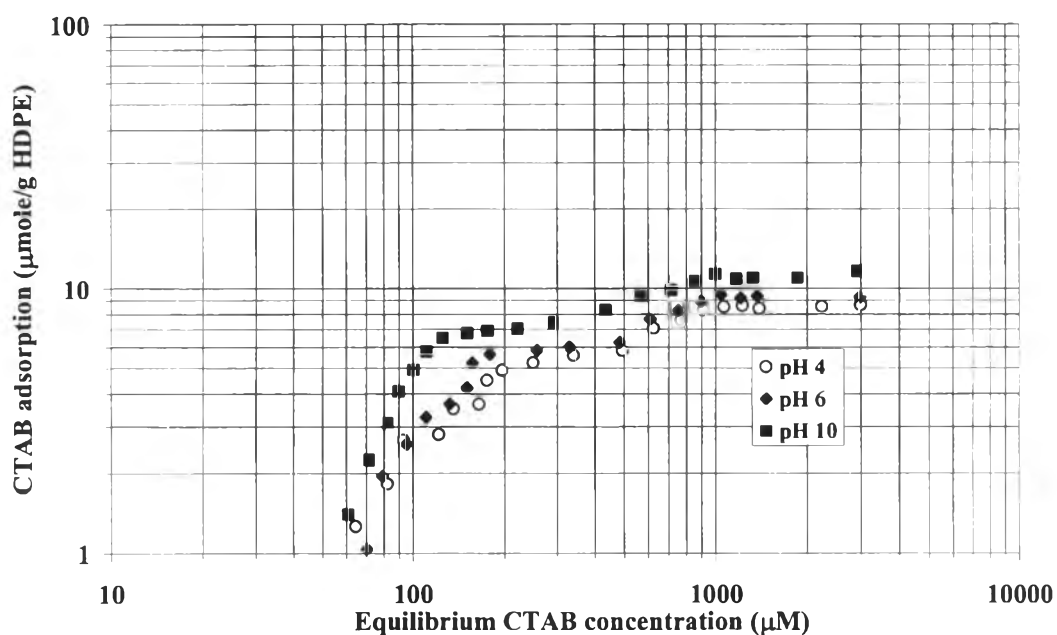


Figure 4.12 Adsorption isotherm of CTAB on high density polyethylene at pH 6 and 30 °C; (○) pH 4, (◆) pH 6, (■) pH 10.

Figure 4.13 illustrates the relationship between zeta potential and adsorption of CTAB with varying pH. The results show the same trend with the adsorption. The magnitude of zeta potential increases with increasing the equilibrium concentration of CTAB. The zeta potential reaches the maximum value near the CMC. These results suggest that increasing pH increases the absolute magnitude of zeta potential. The maximum adsorption and zeta potential value at different pH are represented in Table 4.3.

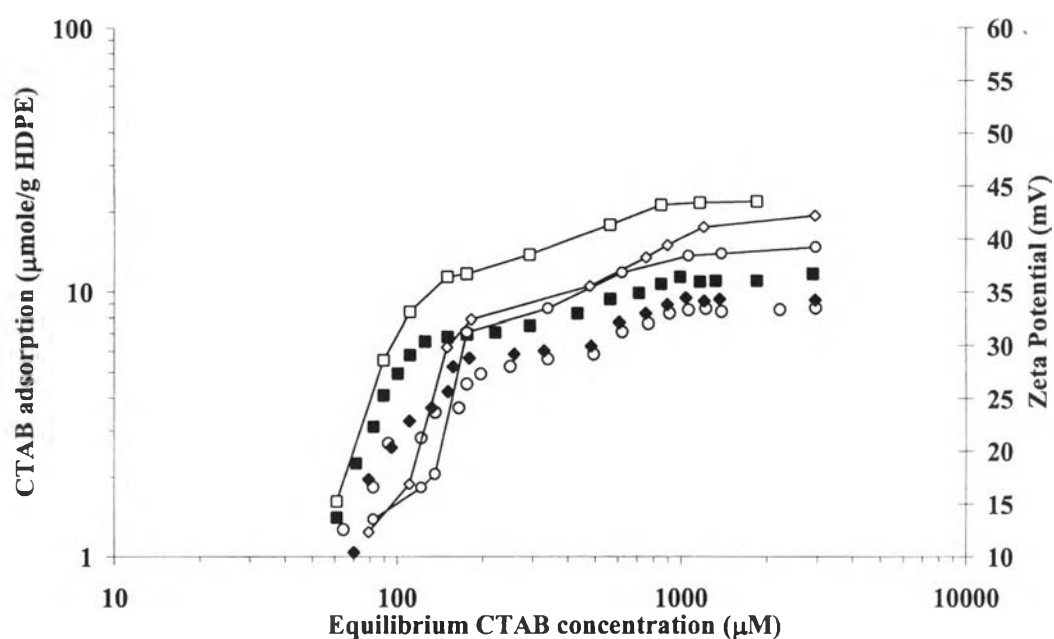


Figure 4.13 Adsorption isotherms of CTAB and zeta potential of high density polyethylene at different pH at 30 °C; (○,◆,■) adsorption at pH 4,6 and 10 respectively and (○,◇,□) zeta potential at pH 4,6 and 10 respectively.

Table 4.3 Adsorption and Zeta potential of CTAB adsorption on HDPE at saturation from different pH

pH	Adsorption (μ mole/g)	Area/molecule (\AA^2)	Zeta potential (mV)
4	8.5	100	38.4
6	9.3	92	42.2
10	10.7	80	43.5

The maximum amount of adsorption of CTAB is used to calculate the area per adsorbed molecule and the results are show in Table 4.3.

The results can be compared with the area per molecule of closed compact monolayer formation (62\AA^2). It can be implied that for all pH the CTAB does not completely cover the HDPE surface.

4.1.7 Adsorption Isotherm of Triton X-114

Figure 4.14 illustrates the adsorption isotherm of Triton X-114 on HDPE at pH 6 at 30 °C. For the adsorption isotherm of Triton X-114, it can not observed a clear inflection on the isotherm as SDS and CTAB. The maximum adsorption occurred at the plateau region of approximately 2.13 μmol corresponding to 200 μM near CMC of Triton X-114.

From the maximum adsorption of Triton X-114 (2.13 $\mu\text{mol/g}$), the calculated area per molecule on the surface is 300 \AA^2 . However the area per molecule at the air-water interface is reported to be approximately 50 \AA^2 (Sigma Co.,ltd, 2000), which is very different from the adsorption from HDPE surface. Therefore it is possible that the orientation of Triton X-114 on the surface is in the horizontal formation.

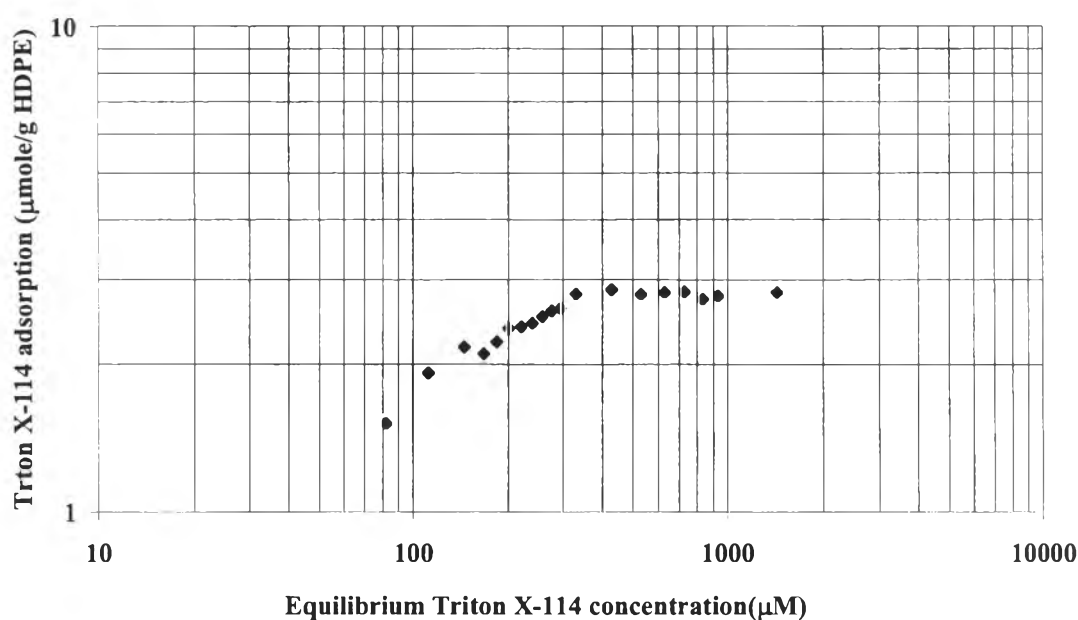


Figure 4.14 Adsorption isotherm of Triton X-114 on high density polyethylene at pH 6 and 30 °C.

4.2 Adsorption of Surfactant on Polypropylene (PP)

In all experiments, polypropylene (PP) was used as the plastic substrate. It was in a powder form, having particle size 65-125 μm . The specific area was calculated from the 5 points adsorption isotherm of N_2 gas. It was found that BET surface area of PP is $3 \text{ m}^2/\text{g}$.

4.2.1 Adsorption Isotherm of Sodium Dodecyl Sulfate

The adsorption isotherm of Sodium Dodecyl Sulfate (SDS) on polypropylene (PP) at pH 6 and 30°C is shown in Figure 4.15. Unlike the adsorption on HDPE, the adsorption isotherm of SDS on PP does not show a clear inflection. The surfactant adsorption reaches the maximum of approximately $7.5 \mu\text{mol}$ of SDS per gram of plastic corresponding to $8,000 \mu\text{M}$ where the CMC of SDS is $8,200 \mu\text{M}$.

From the maximum SDS adsorption ($7.5 \mu\text{mol}/\text{g}$), the calculated area per molecule of SDS is 72 \AA^2 . However the area occupied per molecule for SDS in the closed compact monolayers is 53 \AA^2 . Therefore it is possible that SDS does not completely cover the PP surface at the maximum adsorption.

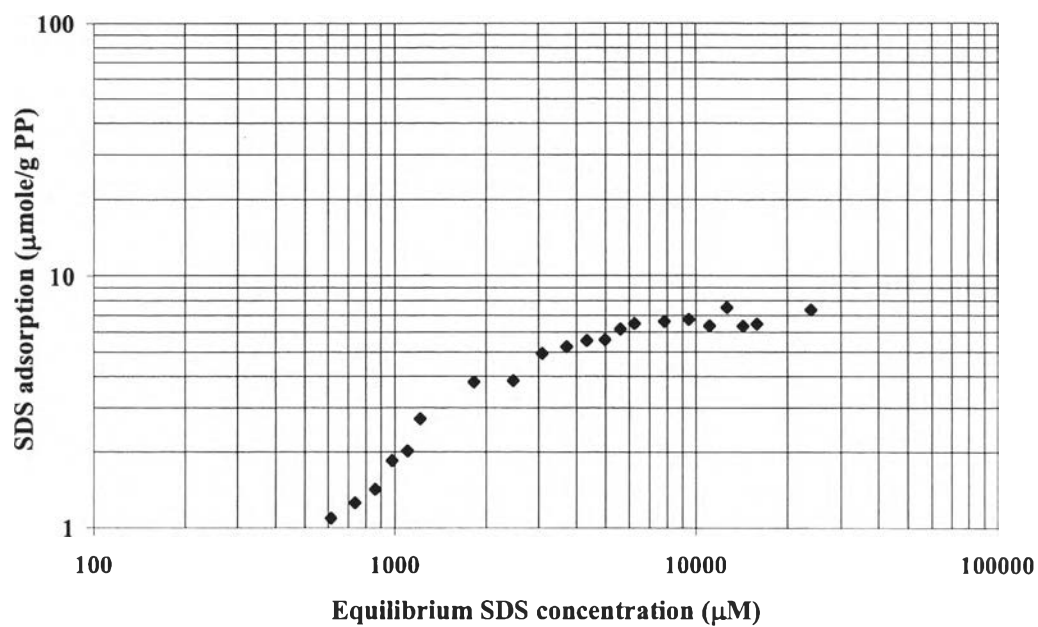


Figure 4.15 Adsorption isotherm of SDS on polypropylene at pH 6 and 30 °C.

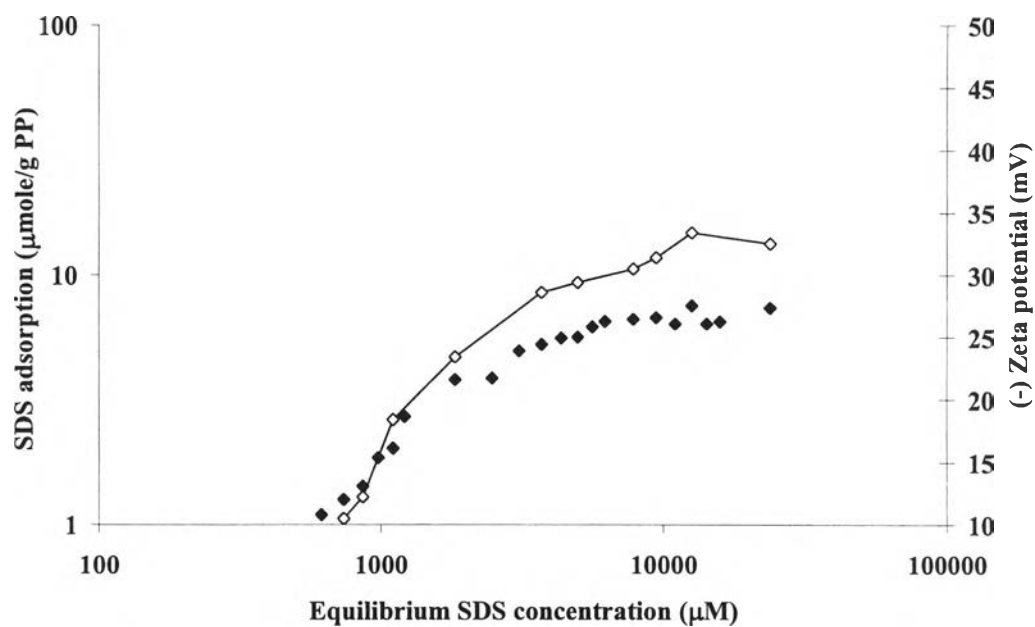


Figure 4.16 Adsorption isotherm of SDS and zeta potential of high density polyethylene at pH 6; (◆) adsorption, (◊) zeta potential.

Figure 4.16 illustrates the relationship between zeta potential and SDS adsorption. The results show that, as the amount of adsorbed SDS increases, the electrical potential of PP is increased. The magnitude of zeta potential shows the negative charge at all equilibrium concentration of SDS and reaches the maximum value (31.5 mV) near the CMC similar to the adsorption.

The orientation of SDS adsorption on PP plastic should be in a head group out configuration because the absolute magnitude of a zeta potential shows the negative charge at all equilibrium concentration of SDS.

4.2.2 Effect of Ionic Strength on SDS Adsorption

The effect of ionic strength on the adsorption of SDS on PP is shown in Figures 4.17. The results show that increase the ionic strength causes the plateau to shift to lower equilibrium concentrations of the surfactant from 8000 μM to 1650 μM as a result from decreasing the electrostatic repulsion between surfactant head group.

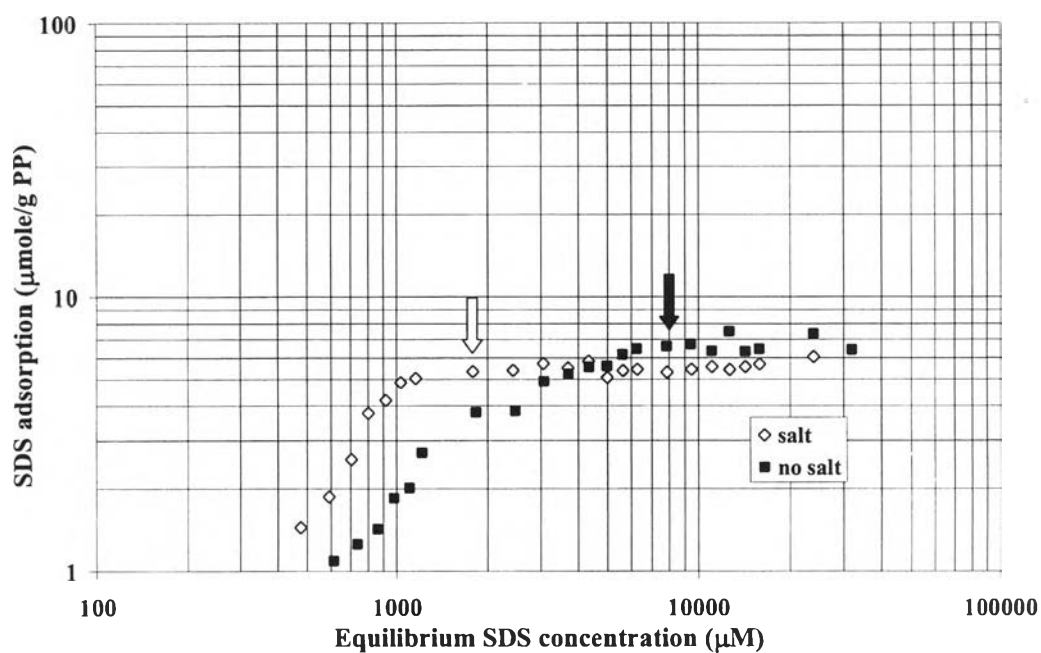


Figure 4.17 Adsorption isotherm of SDS on polypropylene at pH 6 and 30 °C; (\diamond) 0.15 M NaCl, (\blacksquare) no salt added. \Downarrow CMC with salt, \blacktriangledown CMC no salt.

4.2.3 Effect of pH on the SDS Adsorption

Table 4.4 Zeta potential value of polypropylene at pH 4, 6 and 10

pH	Zeta potential (mV)
4	(+) 1.347
6	(+) 1.034
10	(+) 0.956

Table 4.4 summarizes the zeta potential of the PP in water as a function of pH. The results show that, as the pH of the aqueous is higher, a plastic surface will become less positive.

Figure 4.18 illustrates the comparison of SDS adsorption on HDPE at pH 4, 6 and 10. The results show that all curves are similar and almost superimposed, which suggested that pH has no effect to the amount of SDS adsorbed on polypropylene.

This is in agreement with the zeta potential of polypropylene in water as shown in Table 4.4, which suggested that the pH changing did not affect the surface charge of polypropylene.

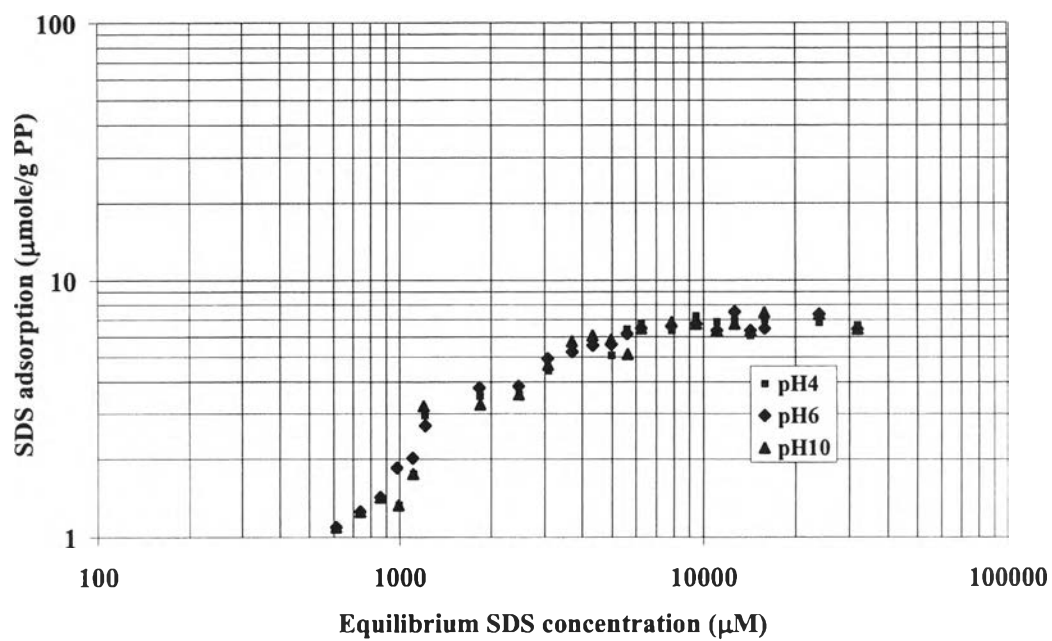


Figure 4.18 Adsorption isotherm of SDS on polypropylene at 30 °C;
(■) pH 4, (◆) pH 6, (▲) pH 10.

Figure 4.19 illustrates the relationship between zeta potential and adsorption value of SDS with varying pH. The results show the same trend with the adsorption. The magnitude of zeta potential is almost the same for all three isotherms, which suggested that pH has no effect to the zeta potential magnitude of the polypropylene.

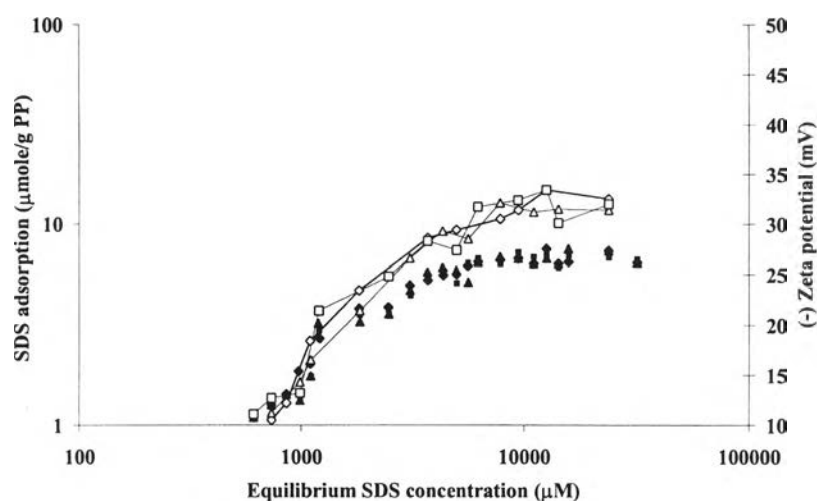


Figure 4.19 Adsorption isotherms of SDS and zeta potential of high density polypropylene at different pH at 30 °C; (■, ◆, ▲) adsorption at pH 4,6 and 10 respectively and (□, ◇, △) zeta potential value at pH 4,6 and 10 respectively.

From the adsorption and zeta potential results, it can be concluded that the adsorption of SDS on PP plastic is not affected by the surface charge of the plastic, which in contrast with the adsorption on HDPE plastic. It is possible that the hydrophobicity of PP plastic is higher than HDPE plastic. As a result, the hydrophobic bonding is the main driving force for the adsorption on PP, whereas for the adsorption on HDPE, the electrostatic is the main driving force.

Because of high hydrophobicity, the orientation of the SDS on PP may be in the tail-down, head-out configuration on the PP surface for all pH.

4.2.4 Adsorption Isotherm of Cetyltrimethylammoniumbromide

The adsorption isotherm of Cetyltrimethylammoniumbromide (CTAB) on polypropylene (PP) at pH 6 and 30 °C is shown in Figure 4.20. Unlike the adsorption on HDPE, the isotherm does not show a clear inflection. The surfactant adsorption reaches the maximum approximately 9 μmol of CTAB per gram of plastic corresponding to 900 μM .

From the maximum CTAB adsorption (9 $\mu\text{mol/g}$), the calculated area per molecule of CTAB is 61 \AA^2 which is very close to the area occupied per molecule for CTAB in the closed compact monolayers (62 \AA^2). Therefore it is possible that the orientation of CTAB at the maximum adsorption is close to the closed compact monolayer formation on the PP surface.

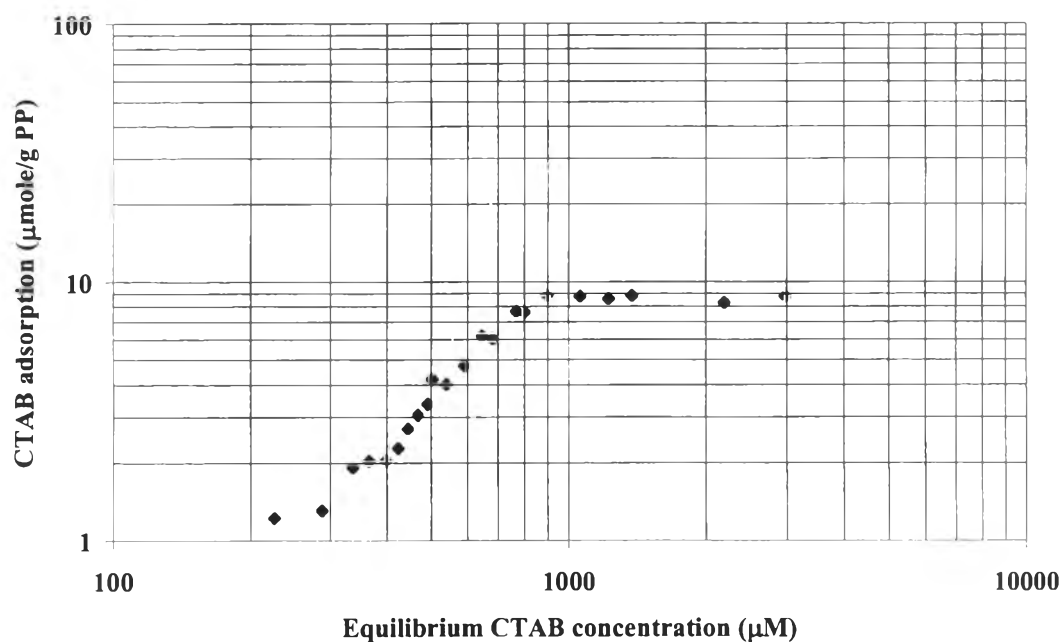


Figure 4.20 Adsorption isotherm of CTAB on polypropylene at pH 6 and 30 °C.

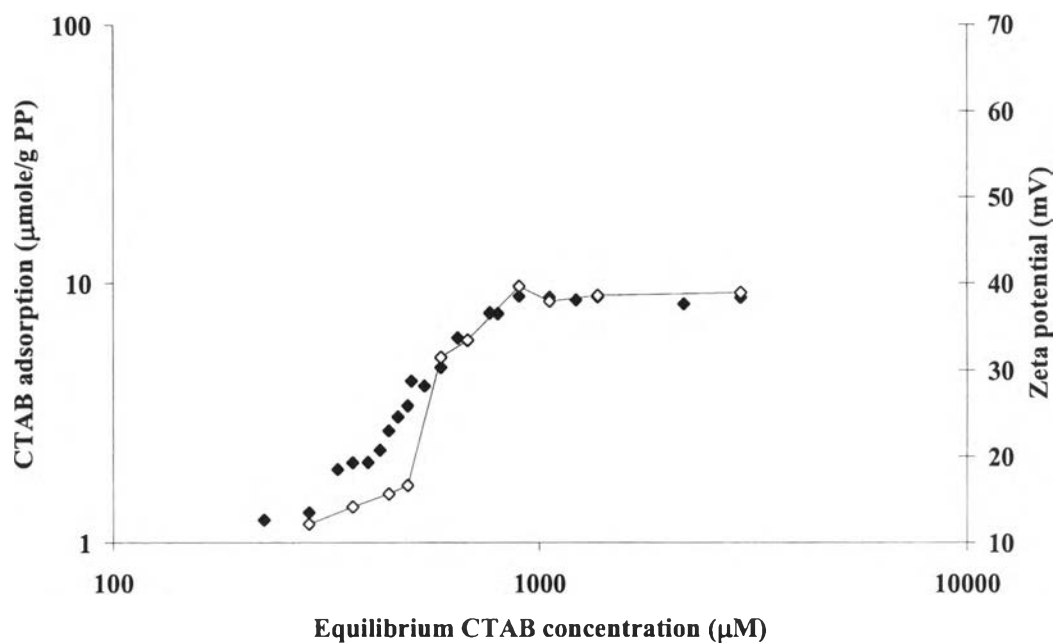


Figure 4.21 Adsorption isotherm of CTAB and zeta potential of polypropylene at pH 6; (◆) adsorption, (◇) zeta potential.

The relationship between zeta potential and adsorption of CTAB are shown in Figure 4.21. The results revealed that, as the amount of adsorbed CTAB increases, the zeta potential of PP is increased. The magnitude of zeta potential shows the positive charge at all equilibrium concentrations of CTAB and reaches the maximum value (38 mV) near the CMC similar to the adsorption.

From the zeta potential results, it can be implied that the orientation of CTAB adsorption on PP plastic is possibly in a head group out configuration for all equilibrium concentrations of CTAB.

4.2.5 Effect of Ionic Strength on CTAB Adsorption

The effect of ionic strength on the adsorption of CTAB on PP is shown in Figures 4.22. The results show that, the ionic strength causes the plateau to move to lower equilibrium concentrations of the surfactant, from 900 μM to 400 μM . This can be explained as the result of decreasing the electrostatic repulsion between surfactant head group. However changing in ionic strength does not have much effect to the amount adsorbed at plateau region.

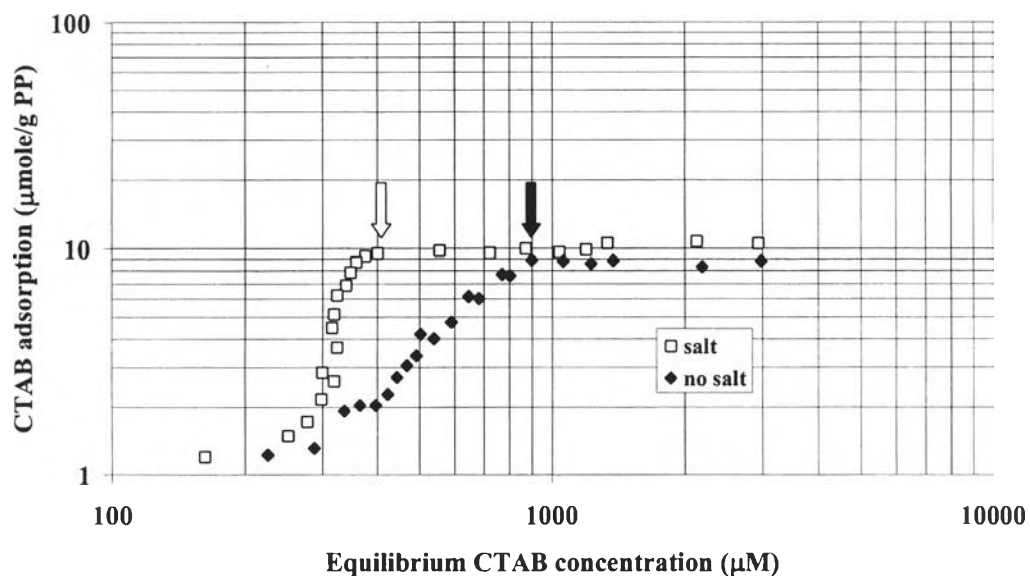


Figure 4.22 Adsorption isotherm of CTAB on polypropylene at pH 6 and 30 °C; (◆) no salt added, (□) 0.15 M NaCl. ↓ CMC no salt, ↯ CMC with salt.

4.2.6 Effect of pH on the CTAB Adsorption

The comparison of CTAB adsorption on polypropylene at pH 4, 6 and 10 are illustrated in Figure 4.23. The results show that all curves are similar and almost superimposed.

The relationship between zeta potential and adsorption of CTAB with varying pH are shown in Figure 4.24. The results show the same trend with the adsorption. The magnitude of zeta potential is almost the same for all three isotherms, which suggested that pH has no effect to the zeta potential magnitude of the polypropylene. From the adsorption and zeta potential results, it can be concluded that that pH has no effect to the adsorption of CTAB on polypropylene.



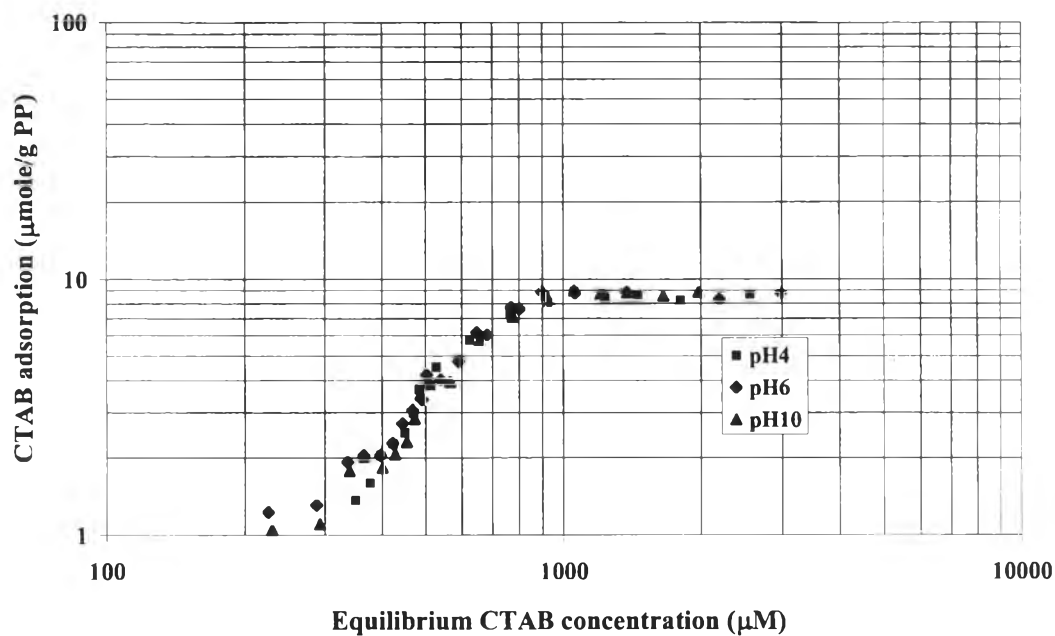


Figure 4.23 Adsorption isotherm of CTAB on polypropylene at pH 6 and 30 °C; (■) pH 4, (◆) pH 6, (▲) pH 10.

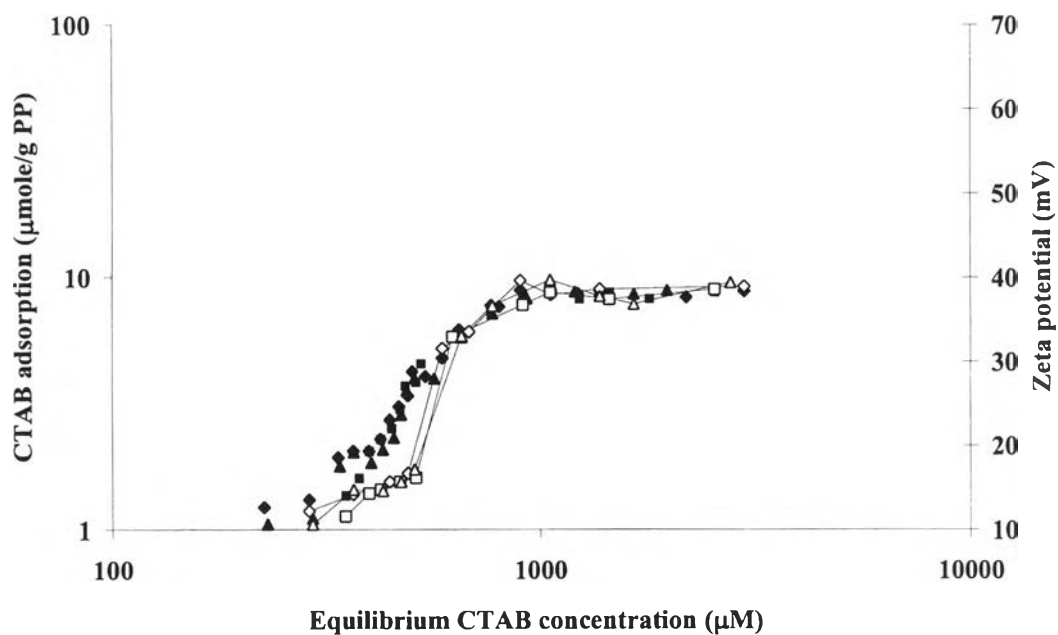


Figure 4.24 Adsorption isotherms of CTAB and zeta potential of polypropylene at different pH at 30 °C; (■,◆,▲) adsorption value at pH 4,6 and 10 respectively and (□,◇,△) zeta potential value at pH 4,6 and 10 respectively.

4.2.7 Triton X-114 Adsorption Isotherm

Figure 4.14 illustrates the adsorption isotherm of Triton X-114 on PP at pH 6 and 30 °C. Similar to HDPE, the adsorption isotherm of Triton X-114 on PP does not show a clear inflection on the isotherm. The maximum adsorption occurred at the plateau region is very close to the adsorption on HDPE plastic (approximately 2 $\mu\text{mol/g}$) corresponding to 200 μM near CMC of Triton X-114.

From the maximum adsorption of Triton X-114 (2 $\mu\text{mol/g}$), the calculated area per molecule of surfactant on the surface is 300 \AA^2 . However the area per molecule at the air-water interface is reported to be approximately 50 \AA^2 (Sigma Co.,Ltd, 2000), which is very different from the adsorption from HDPE surface. Therefore it is possible that the orientation of Triton X-114 on the surface is in the horizontal formation or lying down configuration.

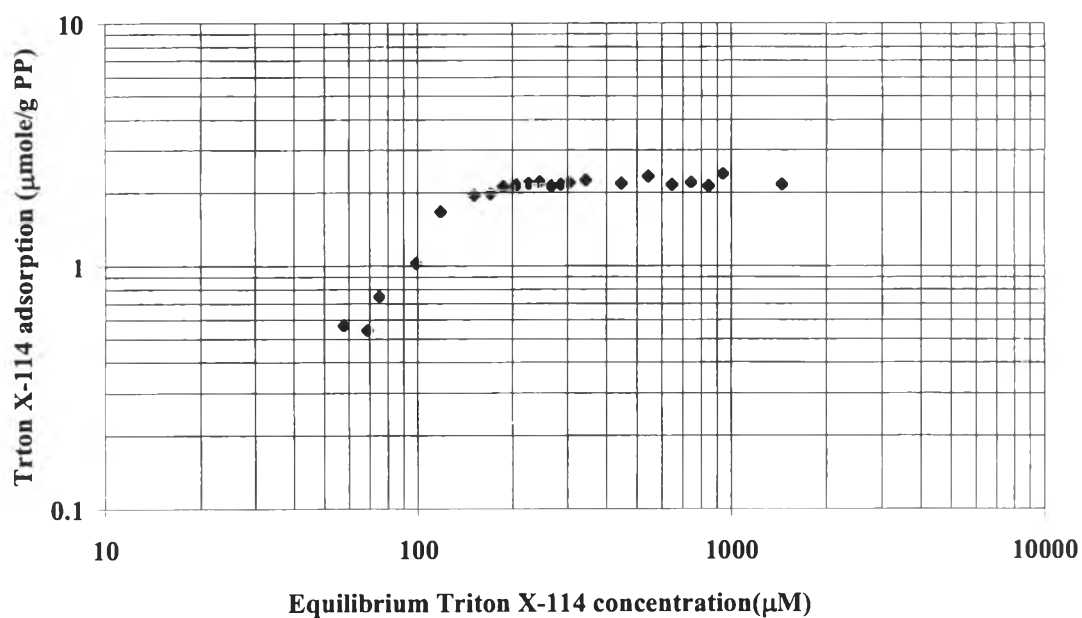


Figure 4.25 Adsorption isotherm of Triton X-114 on polypropylene at pH 6 and 30 °C.