CHAPTER IV
RESULTS AND DISCUSSION

The adsorption isotherms as well as contact angle measurements of CPC and NaOBS were done on three plastic surfaces; HDPE, PS and PET. These experiments were done with varying salt concentrations: 0, 0.005, 0.02, and 0.05 M of NaCl in case of CPC, and 0, 0.02, and 0.05 M in case of NaOBS. In addition, the liquid/vapor surface tension and CMC of CPC and NaOBS solutions at different salt concentrations were also measured.

4.1 Properties of Plastics

The contact angle of water on plastics and the specific surface area of the plastics used in this study are shown in Table 4.1.

Table 4.1 Properties of plastics

Plastics	Contact angle of water (degree)	Specific surface area (m^2/g)
HDPE	94	4.1
PS	84	5.2
PET	74	3.2

4.2 The Liquid/Vapor Surface Tension and CMC of CPC

The liquid/vapor surface tension (γ_{LV}) of CPC solutions are plotted as a semi-logarithmic function of equilibrium CPC concentration as shown in Figure 4.1. The CMC of solutions is the concentration at the break point of the plot. The CMC of CPC solution in the absence of salt is 950 μM. As expected, the CMC of CPC is respectively decreased to 300, 130, and 80 μM in the present of NaCl at concentration 0.005 M, 0.02 M and 0.05 M, respectively.
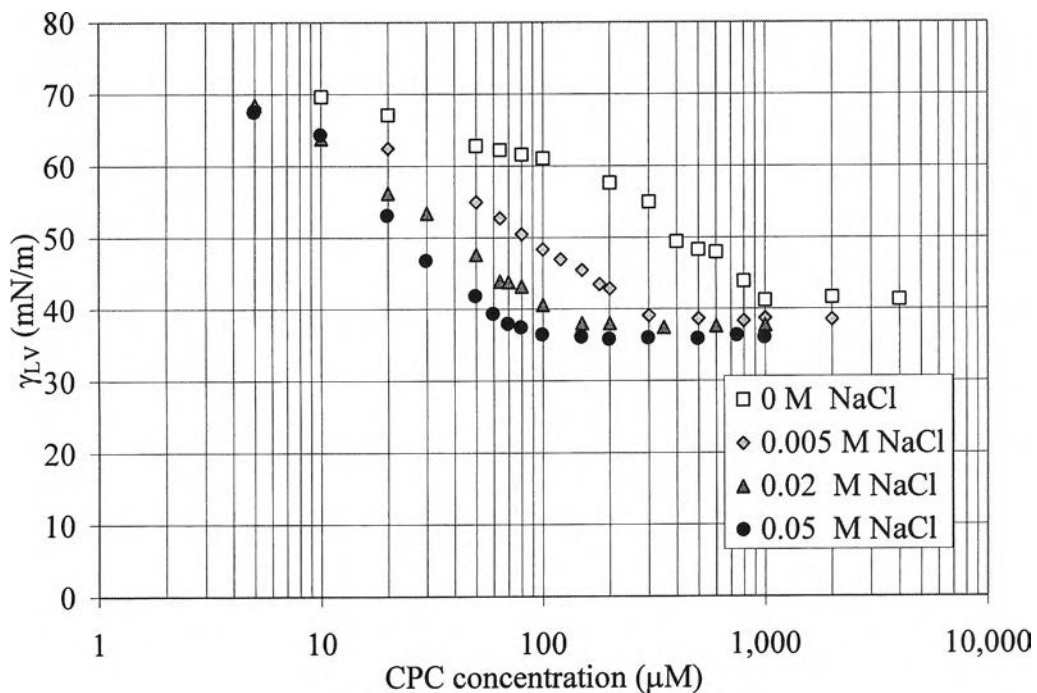

Figure 4.1 Liquid/vapor surface tension as a function of CPC concentration at various salt concentration.

4.3 Adsorption of CPC and Its Wetting on Plastics

4.3.1 Adsorption Isotherm of CPC

The adsorption isotherms of CPC on HDPE, PS and PET with varying salt concentrations are shown in Figures 4.2 - 4.4 respectively. For pure CPC solution, the adsorption gradually increases with surfactant concentration at low concentration of surfactant with less-than-proportional increase; while the adsorption sharply increases with increasing surfactant concentration in the presence of ionic strength. All isotherms level out to the plateau at about the CMC region. It is observed that the addition of electrolyte has little effect on the maximum adsorption of CPC (i.e., adsorption beyond CMC). However, the effect of adding electrolyte is more pronounced at CPC concentration below CMC. For this region, the increased amount of CPC adsorbed on the plastics is probably due to a reduction of electrical repulsion between the head groups of adsorbed CPC, so called "shielding effect".
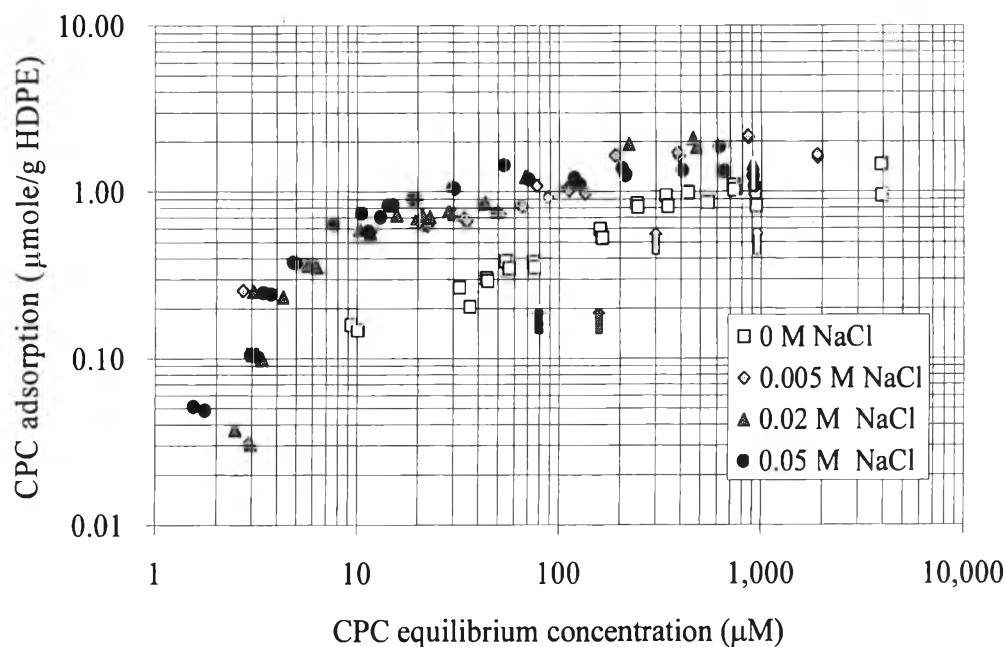

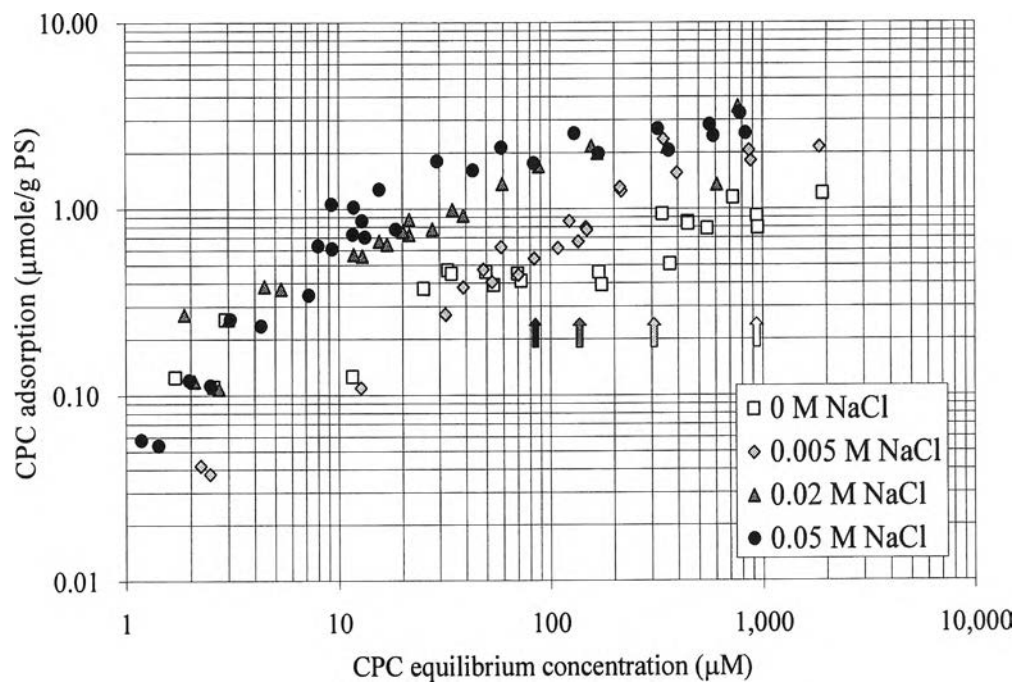**Figure 4.2** Adsorption isotherms of CPC on HDPE.

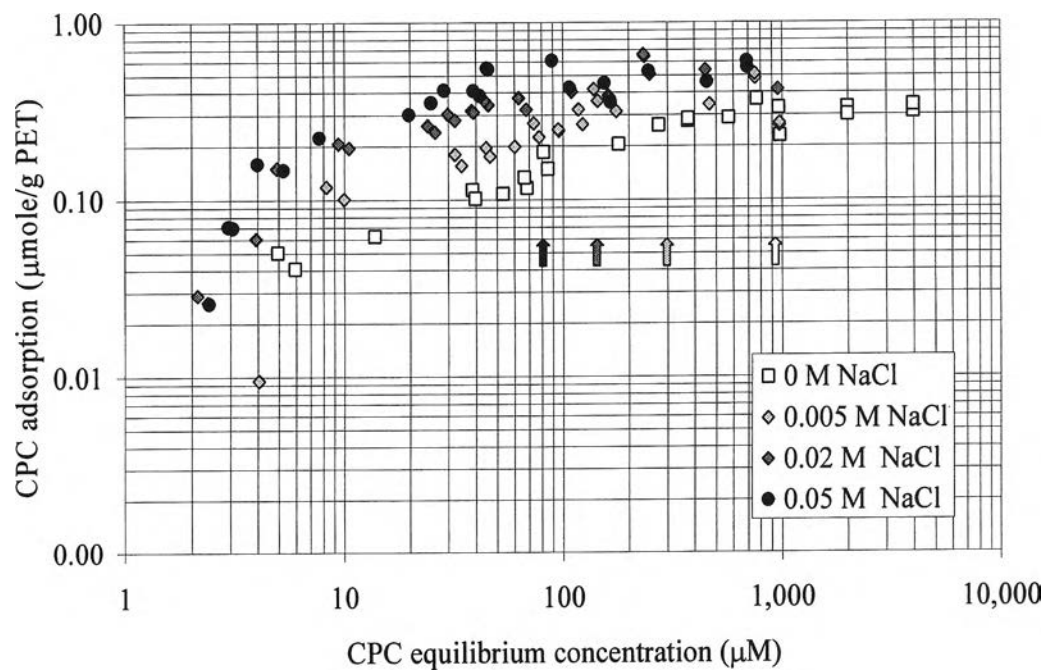**Figure 4.3** Adsorption isotherms of CPC onto PS.

Figure 4.4 Adsorption isotherm of CPC on PET.

4.3.2 Contact Angle of CPC Solution on Plastics

The static contact angles of CPC solutions on HDPE, PS and PET are shown in Figures 4.5 - 4.7 respectively. For all cases, the contact angles decreased significantly with increasing CPC concentration and became nearly constant above the CMC.

When comparing the contact angles on different plastics at the same CPC and NaCl concentration, they were in the following order: $\theta_{HDPE} > \theta_{PS} > \theta_{PET}$. This order corresponds to the order of polarity of plastics as shown in Table 4.1.

The addition of NaCl produces smaller contact angle at the same equilibrium CPC concentration. This implies that the addition of NaCl provides better wetting when considered at the same equilibrium concentration. This effect is found to be more pronounced with increasing concentration of NaCl.
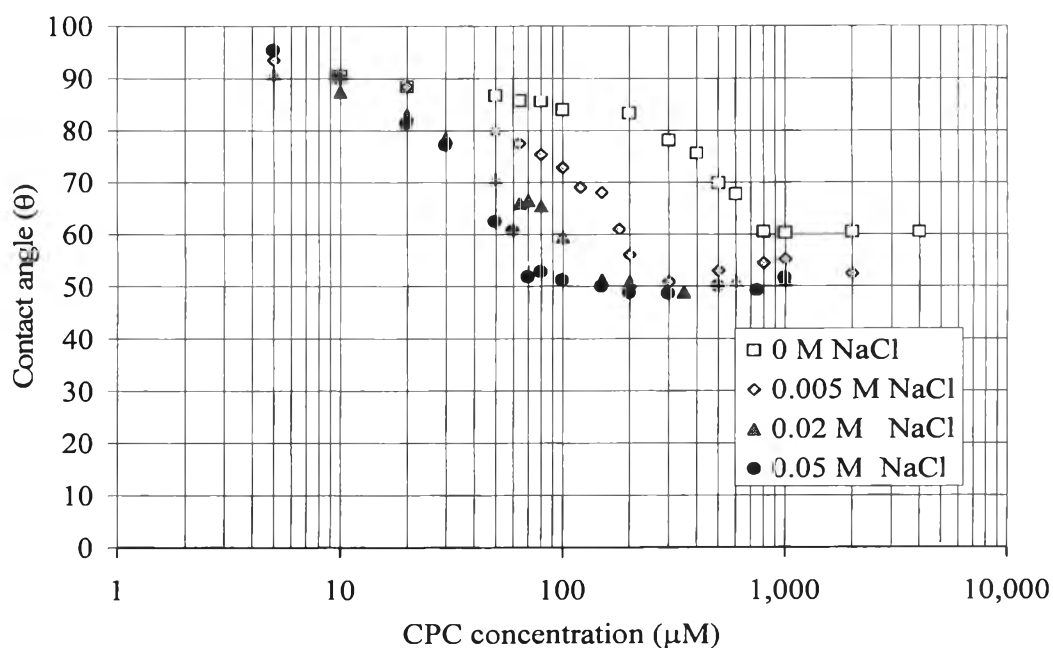

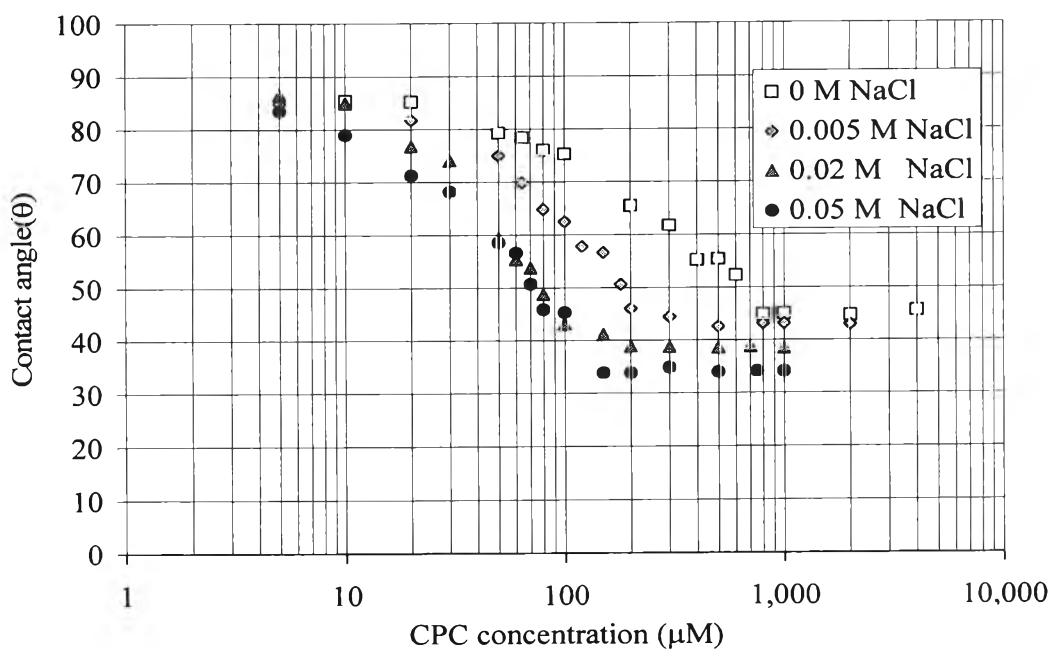**Figure 4.5** Contact angle of CPC solution on HDPE with varying CPC and NaCl concentration.

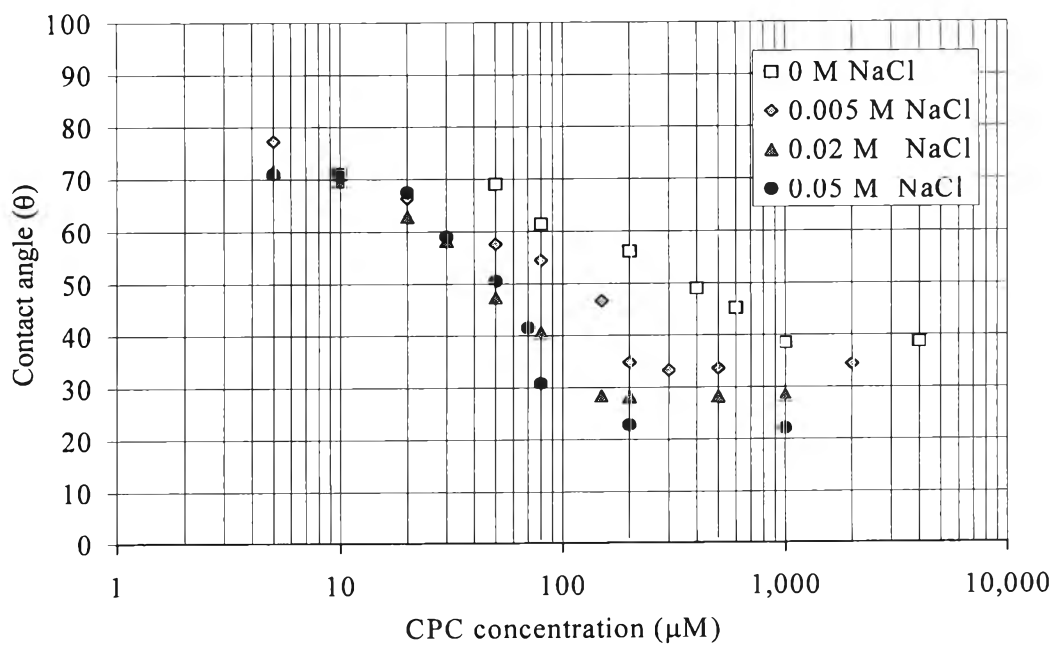**Figure 4.6** Contact angle of CPC solution on PS with varying CPC and NaCl concentration.

Figure 4.7 Contact angle of CPC solution on PET with varying CPC and NaCl concentration.

4.3.3 Wetting Enhancement by CPC

From Equation 2.1, if γ_{SV} and γ_{SL} were constant, the plot between cos θ and $1/\gamma_{LV}$ should be linear with the slope of (γ_{SV} - γ_{SL}) and intercept at zero. However, Figures 4.8 - 10 do not show this relationship since the intercept values do not equal zero.

Another possible way to examine the variation of the (γ_{SV} - γ_{SL}) term is to look at the product of cos θ multiply with γ_{LV} (or γ_{LV} cos θ). From Equation 2.1, if (γ_{LV} cos θ) is constant, the value of (γ_{SV} - γ_{SL}) will be constant. As depicted in Figures 4.11 - 41.3, this is not the case. The value of (γ_{LV} cos θ) varies with CPC equilibrium concentration. Therefore, it can be concluded that the value of (γ_{SV} - γ_{SL}) is not constant for all experimental cases.

Because the dry solid has not been contacted by the solution yet and transfer of the nonvolatile surfactants to the solid-air interface during measurement of contact angles via vapor phase seems unlikely (Gau and Zografi, 1990), the value of γ_{SV} can theoretically be assumed to be independent of the surfactant concentration. This indicates that γ_{SL} is not constant but varies with surfactant concentration.
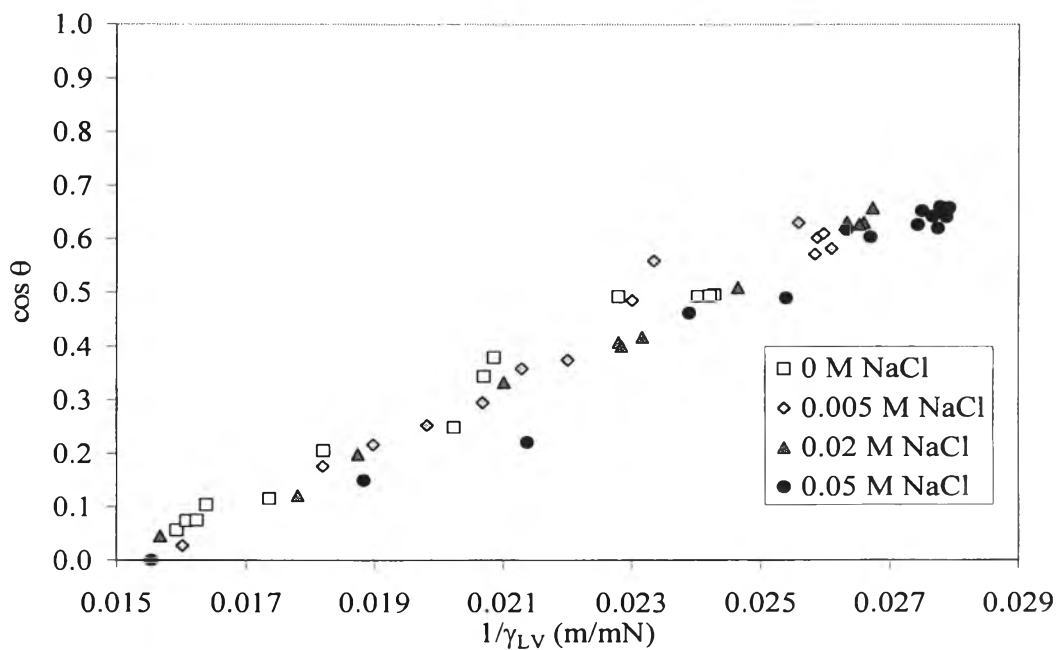
Figure 4.8 Contact angle on HDPE related to inversion of liquid/vapor surface tension of CPC solution.
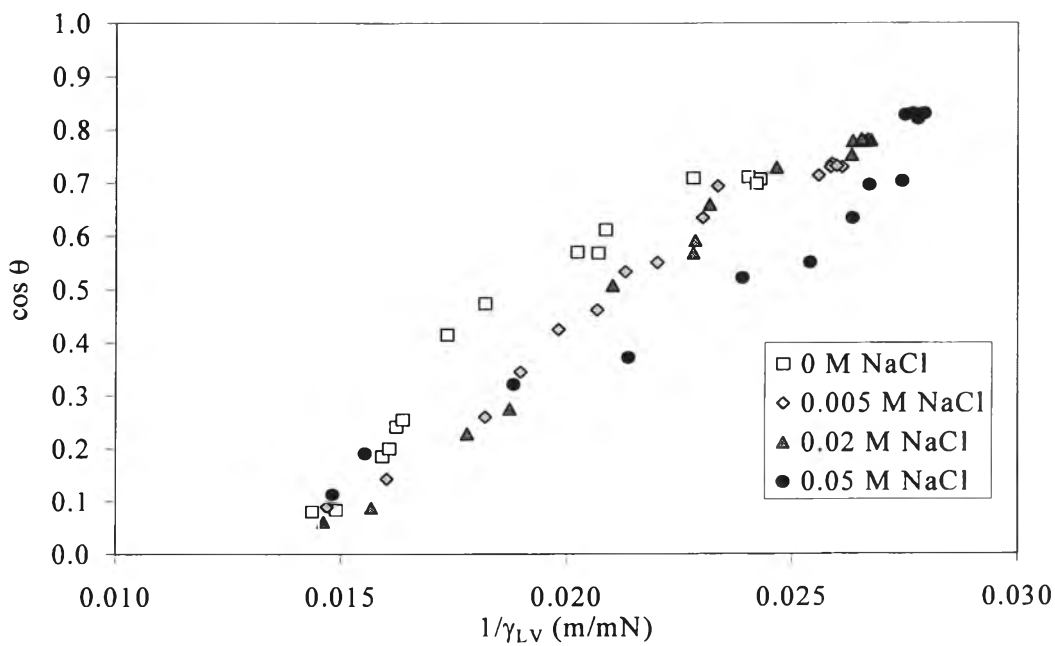

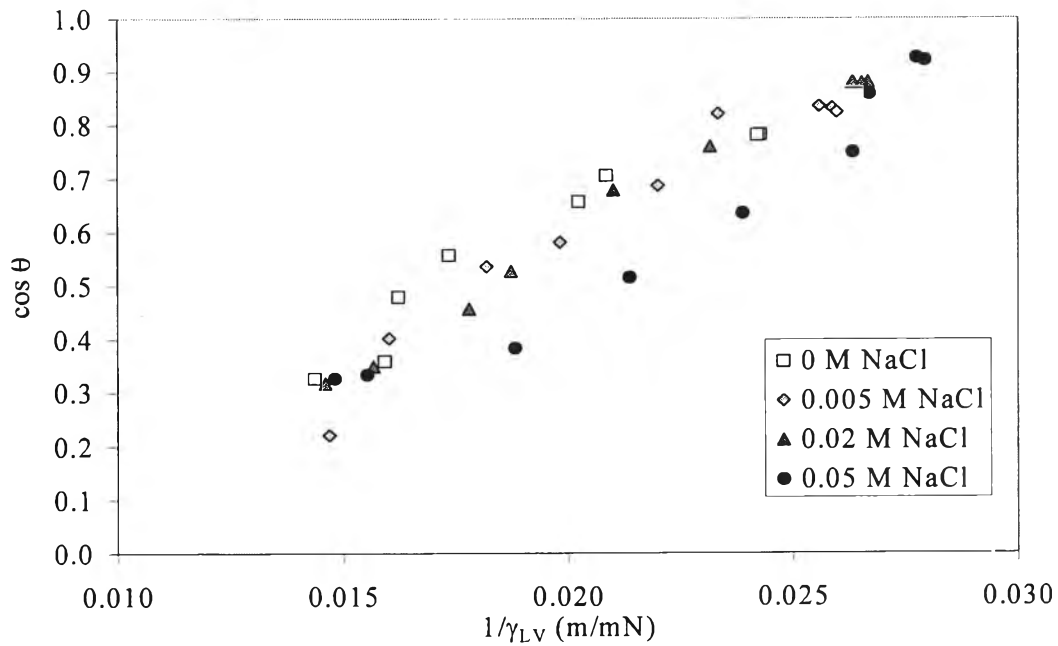**Figure 4.9** Contact angle on PS related to inversion of liquid/vapor surface tension of CPC solution.

Figure 4.10 Contact angle on PET related to inversion liquid/vapor surface tension of CPC solution.
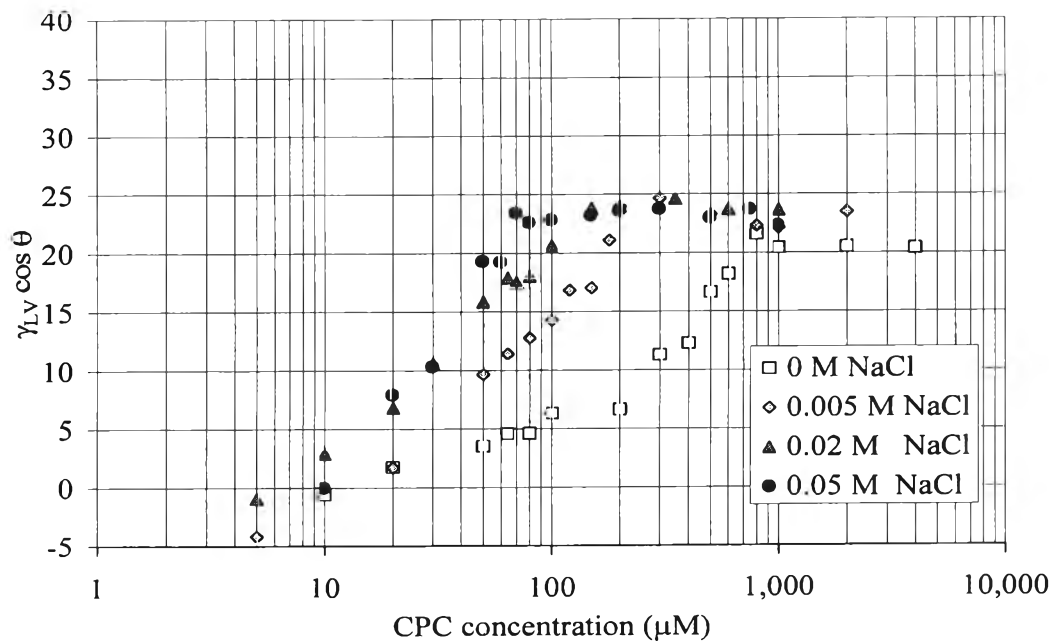

Figure 4.11 $\gamma_{LV} \cos \theta$ on HDPE related to equilibrium concentration of CPC solution.
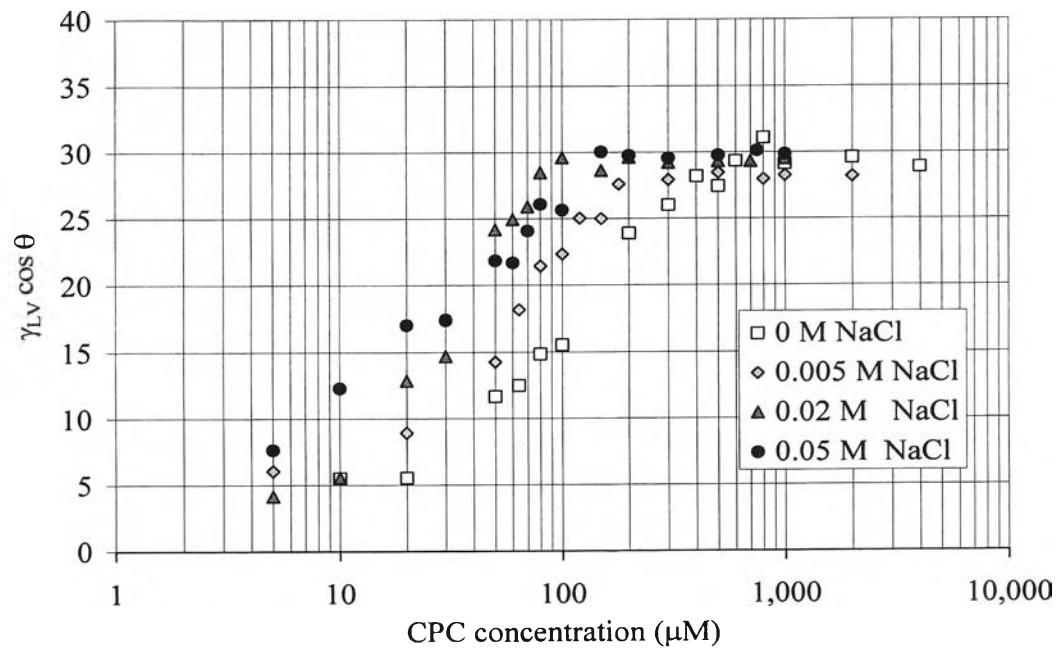
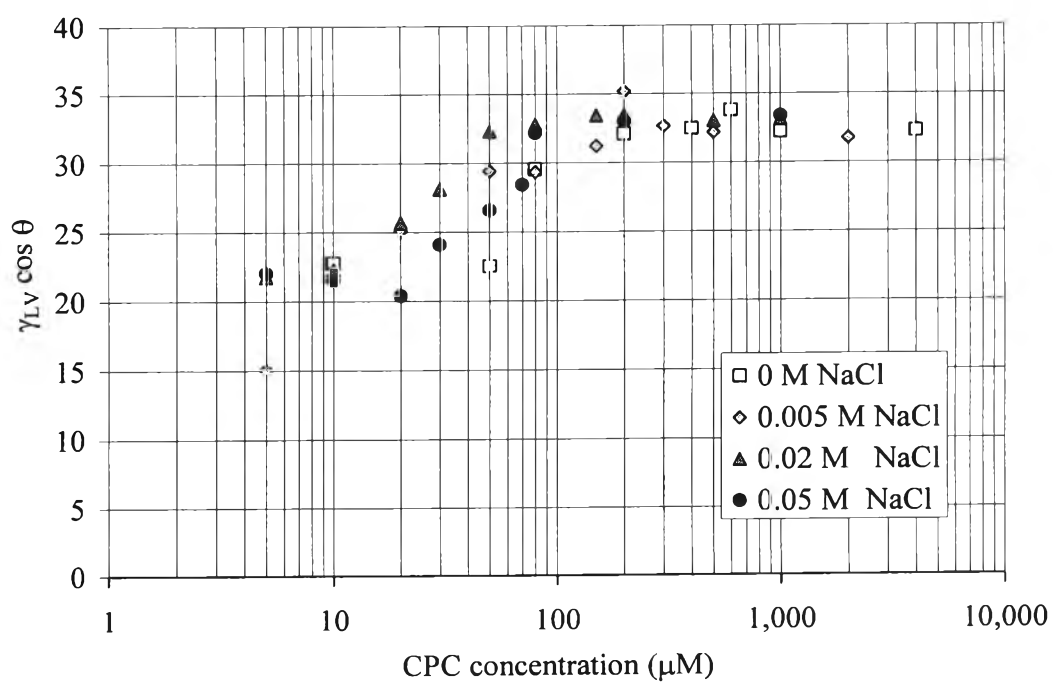**Figure 4.12** $\gamma_{LV} \cos \theta$ on PS related to equilibrium concentration of CPC solution.

Figure 4.13 $\gamma_{LV} \cos \theta$ on PET related to equilibrium concentration of CPC solution.

Some difficulties arise in measuring γ_{SL} because it is not experimentally and directly accessible; however, we can calculate γ_{SL} relative to γ_{SL} at a reference state ($\gamma_{SL}°$), which is chosen to be at the state at which no CPC presents, using the contact angle and the liquid/vapor surface tension data. Equation 2.1 may be written as

$$\gamma_{LV}°(\cos\theta)° - \gamma_{LV}(\cos\theta) = (\gamma_{SV}-\gamma_{SL})° - (\gamma_{SV}-\gamma_{SL})$$

$$= (\gamma_{SL} - \gamma_{SL}°) \qquad (4.1)$$

where the superscript ° refers to the standard state when no CPC presents (pure water). As illustrated in Figures 4.14 - 4.19, the relative solid/liquid interfacial tension ($\gamma_{SL} - \gamma_{SL}°$) can be related to surfactant concentration as well as surfactant adsorption using the adsorption data in Figures 4.2 - 4.4. The initial CPC concentration is assumed to be the same as the equilibrium CPC concentration. Even if CPC adsorbed as a complete bilayer on the plastic surface, the depletion in CPC concentration due to adsorption is a maximum of 22% (Balasuwatthi et al., 2002).

Figures 4.15, 4.17, and 4.19 indicate that the increase in CPC adsorption is the cause of reduction in γ_{SL}, which, according to Equation 2.1, results in reduction of the contact angle. Therefore, the changes in contact angles induced by surfactant attribute not only to the changes in liquid/vapor surface tension but also to the changes in solid/liquid interfacial tension.

The addition of NaCl has slight effect on the solid/liquid interfacial tension. It can be observed that γ_{SL} decreases with increasing NaCl concentration for the same surfactant equilibrium concentration. The presence of NaCl allows surfactant to adsorb more on the surface; thus resulting in more reduction of the value of γ_{SL}.

However, at the same CPC adsorption density, the addition of NaCl has the negative effect on the reduction of γ_{SL}. The system with higher ionic strength could reduce γ_{SL} less than the system with lower ionic strength. This could be due to the shielding of hydrophilic head by ions of electrolyte, which reduces the hydrophilic nature of the head group and deteriorates the ability to lessen the solid/liquid interfacial tension. Nevertheless, this observation cannot be clearly observed for the HDPE surface.
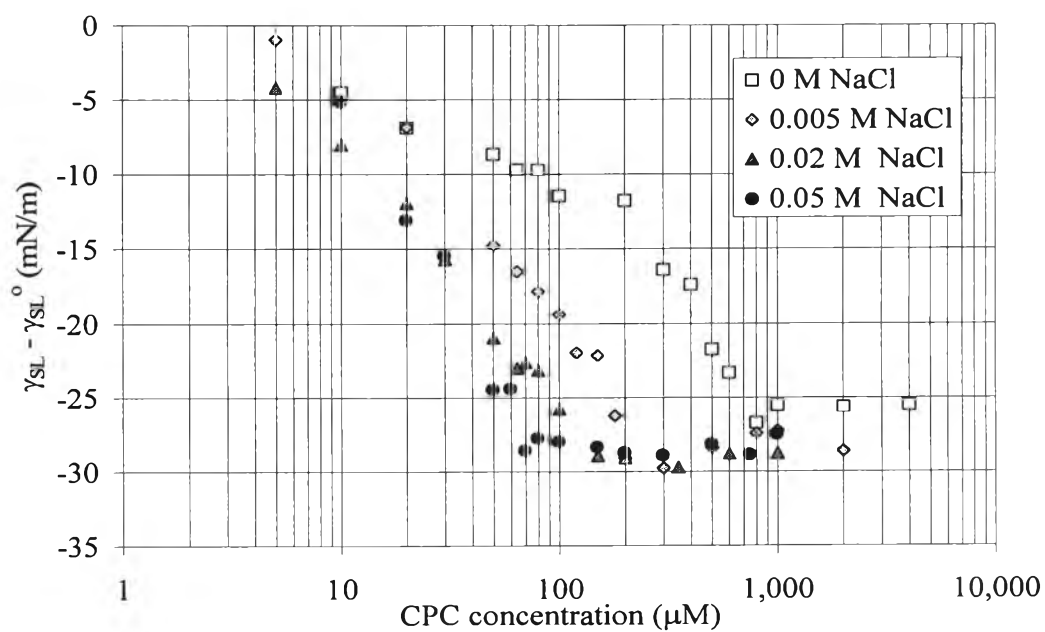
Figure 4.14 Relative solid/liquid interfacial tension of HDPE as a function of CPC concentration.
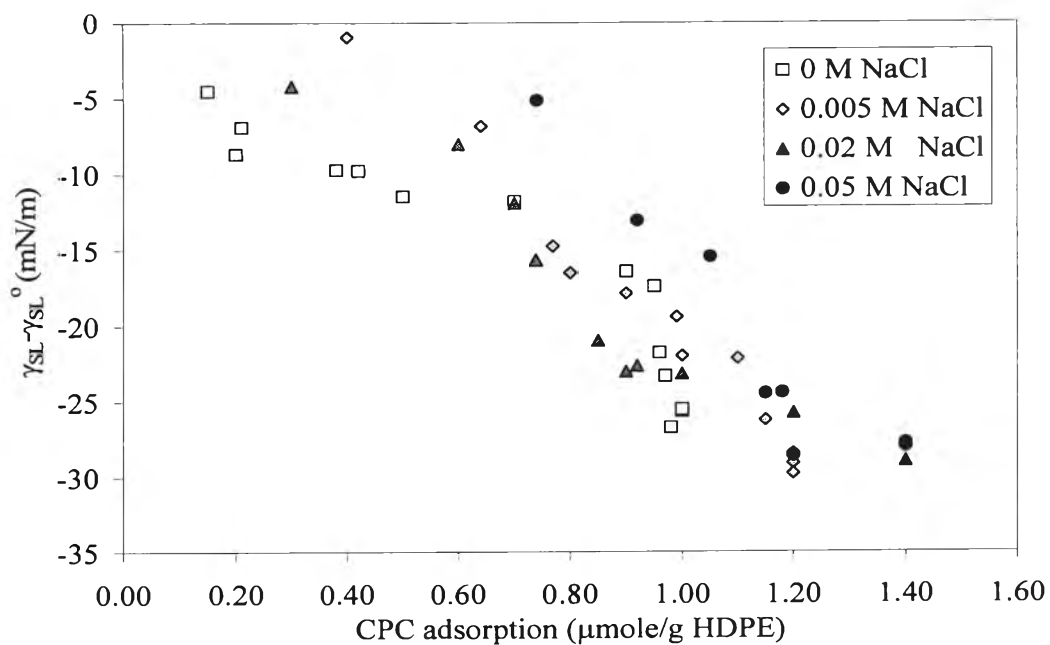

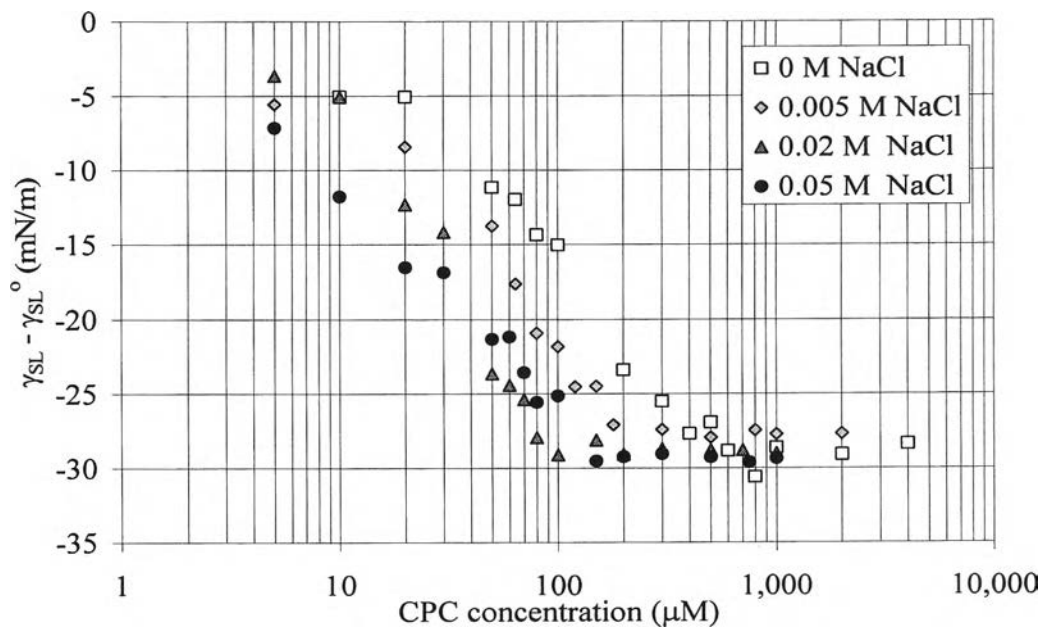**Figure 4.15** Relative solid/liquid interfacial tension of HDPE as a function of CPC adsorption.

Figure 4.16 Relative solid/liquid interfacial tension of PS as a function of CPC concentration.
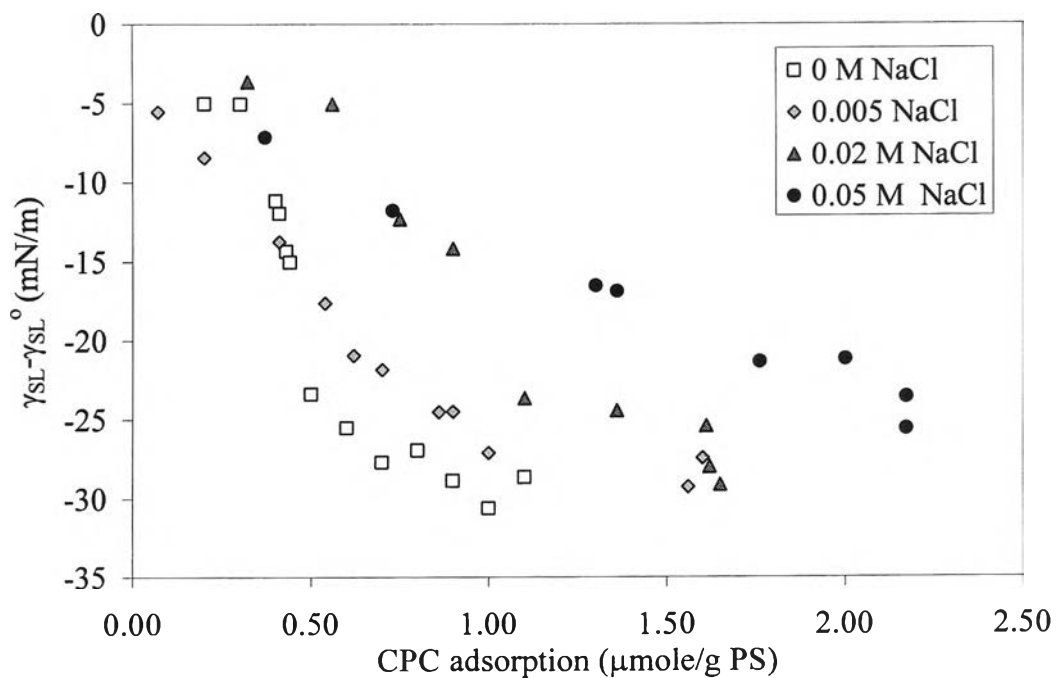

Figure 4.17 Relative solid/liquid interfacial tension of PS as a function of CPC adsorption.
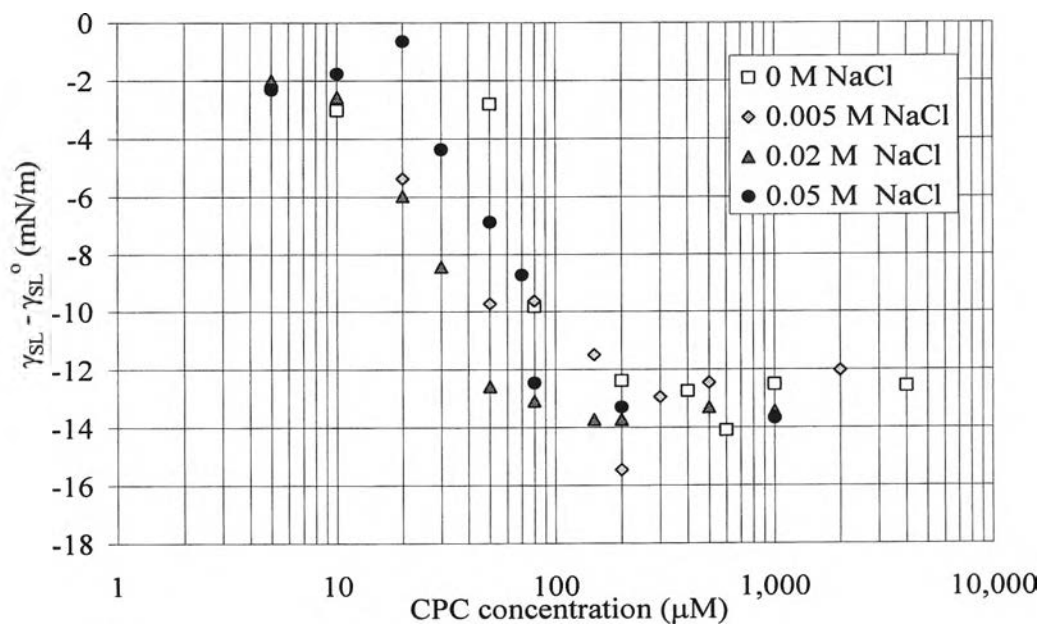
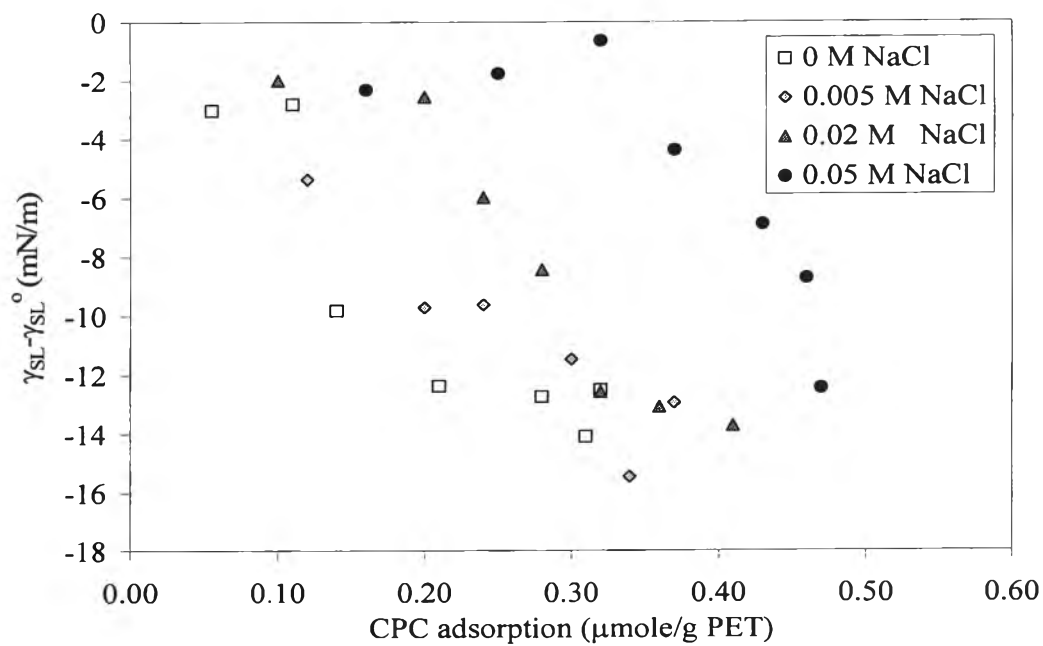**Figure 4.18** Relative solid/liquid interfacial tension of PET as a function of CPC concentration.

Figure 4.19 Relative solid/liquid interfacial tension of PET as a function of CPC adsorption.

In case of PS and PET, it is also found that, the addition of salt hinders the ability to reduce the contact angle at the same γ_{LV} as depicted in Figures 4.21 - 4.22. Having the same γ_{LV}, the CPC solution with less ionic strength produces smaller contact angle (higher value of cos θ; thus, better wetting) than the solution that has higher ionic strength. NaCl in the system helps reduces both the γ_{LV} and γ_{SL}; however, as can be seen from the results, it does not reduce γ_{SL} as effectively as γ_{LV}.

This might be explained by comparing the nature of solid/liquid with the nature of liquid/air. The liquid/air interface can be considered as truly hydrophobic, while the solid/liquid interface is not, because there are some polarities on the solid surface. If we classify the site for surfactant adsorption into two types: polar site, and non-polar site, the liquid/air interface will consist of only the non-polar site, but the solid/liquid interface will consist of both sites. The adsorption of surfactant onto the hydrophobic surface will be the tail-down orientation. For PS and PET, the non-polar adsorption site will be partly separated by the polar site. Thus, surfactant molecules adsorbed onto this non-polar site will not be close to one another but separated from one another by the presence of polar site. Consequently, the addition of NaCl will not effectively help reduce the electrostatic repulsion between head groups much and allow more surfactant molecules to adsorb, since they are already apart. This is not true for the surfactant adsorption on the liquid/air interface since this interface contains only the non-polar site. Adsorbed surfactant molecules are closed to one another. Addition of NaCl will effectively reduce the electrostatic repulsion and this will allow more surfactant molecules to adsorb.

However, the plot of cos θ versus γ_{LV} for HDPE (Figure 4.20) is not clearly deviated as observed from Figures 4.21 - 4.22. This could be attributed to the nature of the HDPE surface that could be considered as strong hydrophobic surface. Hence, fro HDPE, the nature of solid/liquid interface and liquid/air are similar and the presence of salt does not significantly affect the wettability of surfactant solution that have the same γ_{LV}.
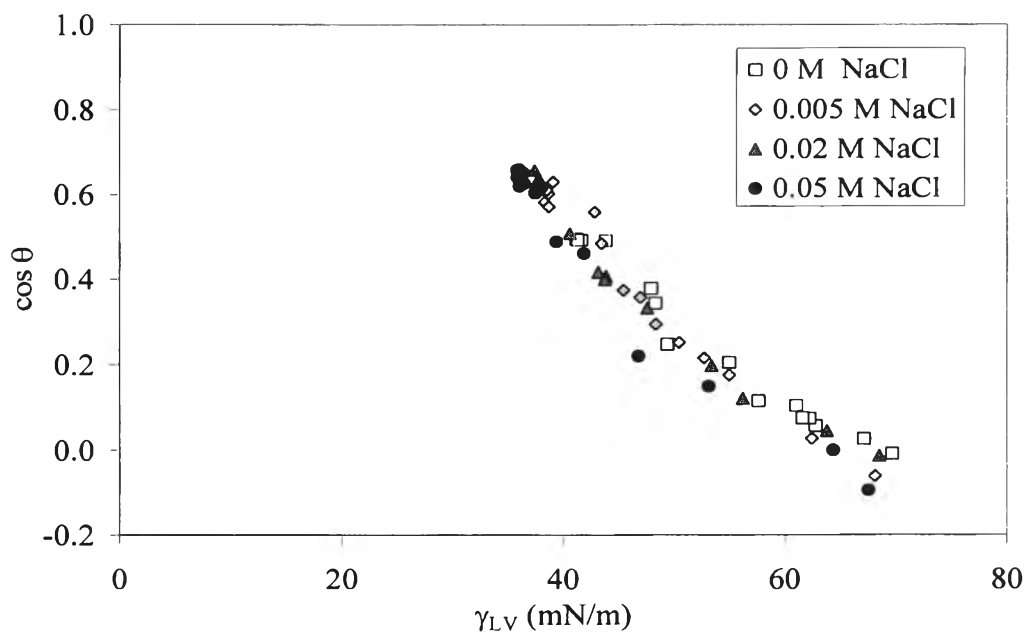
Figure 4.20 Contact angle of CPC on HDPE as a function of its liquid/vapor surface tension.
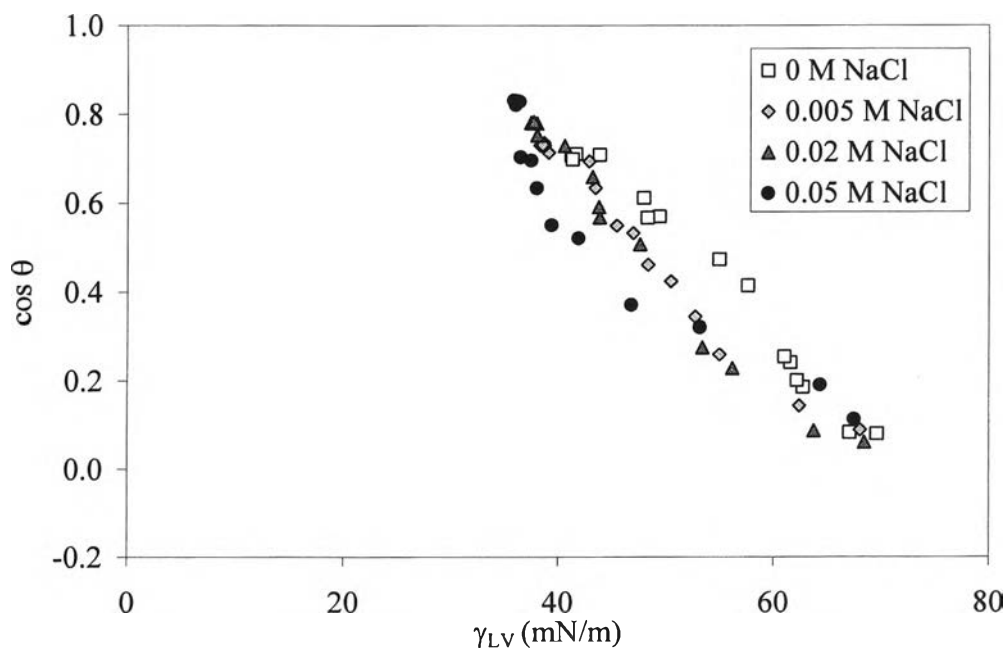

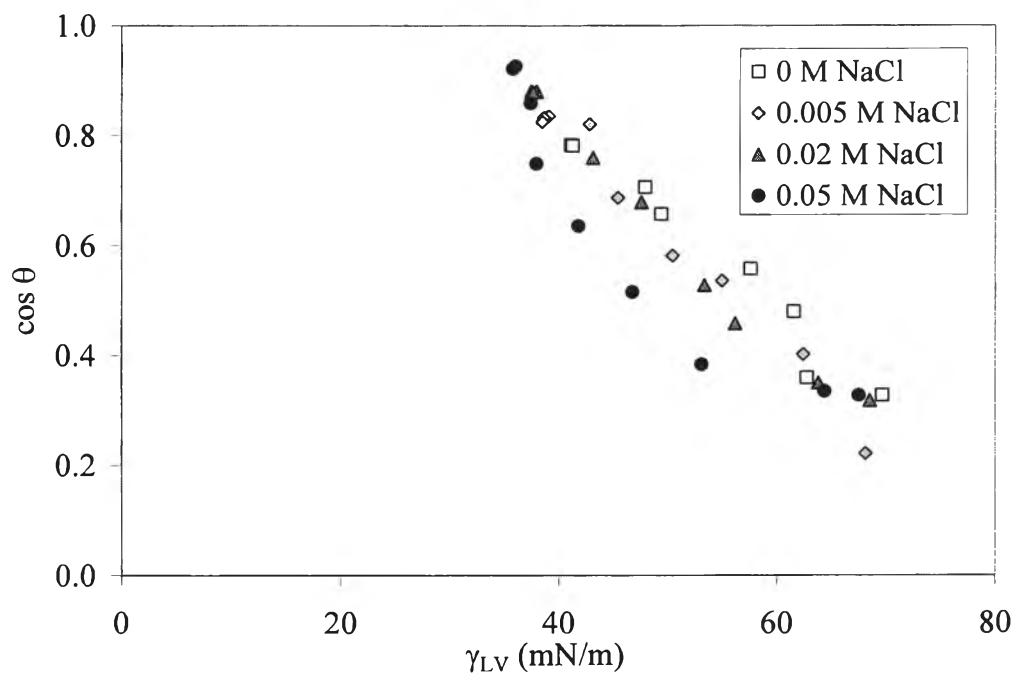**Figure 4.21** Contact angle of CPC on PS as a function of its liquid/vapor surface tension.

Figure 4.22 Contact angle of CPC on PET as a function of its liquid/vapor surface tension.

4.4 The Liquid/Vapor Surface Tension and CMC of NaOBS

Figure 4.23 is a plot of the liquid/vapor surface tension (γ_{LV}) of CPC solutions as a semi-logarithmic function of equilibrium CPC concentration. The CMC of pure NaOBS solution is 10,000 μM which corresponds well to the literature value (Somasundaran *et al.,* 1992 and Dao *et al.,* 1998). The CMC of NaOBS is reduced to 5000, and 7000 μM upon addition of NaCl at concentration 0.02 M and 0.05 M, respectively.
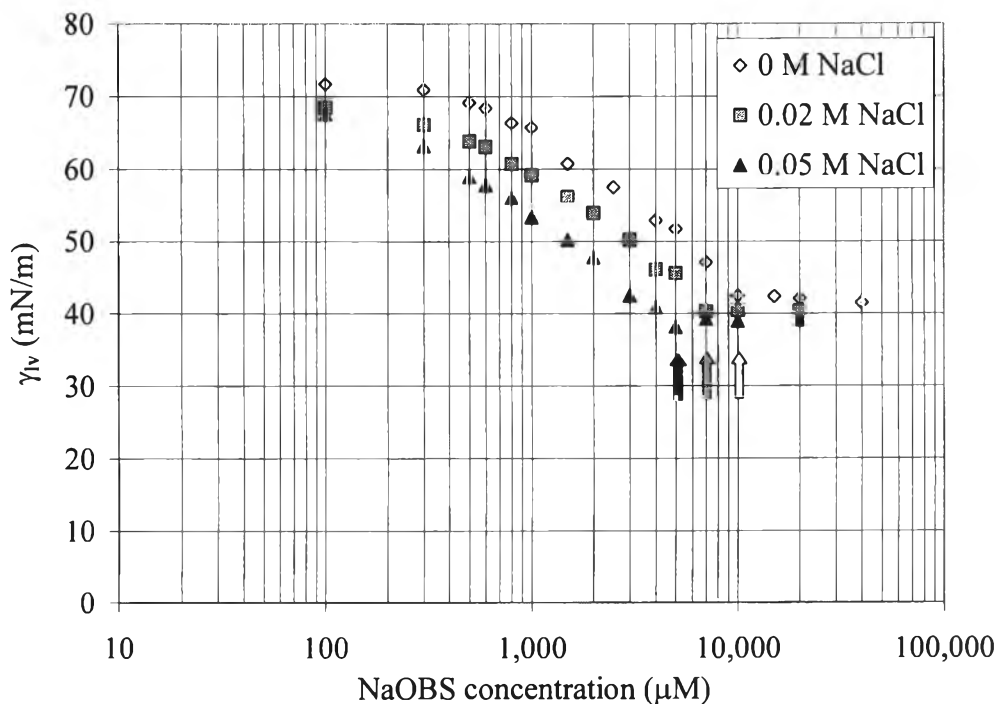
Figure 4.23 Liquid/vapor surface tension as a function of NaOBS concentration.

4.5 Adsorption of NaOBS and Its Wetting on Plastics

4.5.1 Adsorption Isotherm of NaOBS

The adsorption isotherms of NAOBS on HDPE, PS and PET with different salt concentrations are shown in Figu res 4.24 - 4.26 respectivel y. As expected, the adsorption increases with NaOBS equilibrium concentration until reach plateau at about CMC region. The addition of NaCl has little effect on the adsorption at the plateau since it slightly increases the adsorption amount at this region. However, at low equilibrium concentration region, the present of NaCl considerably increases the NaOBS adsorption, thus making the adsorption sharply increases with NaOBS equilibrium concentration.
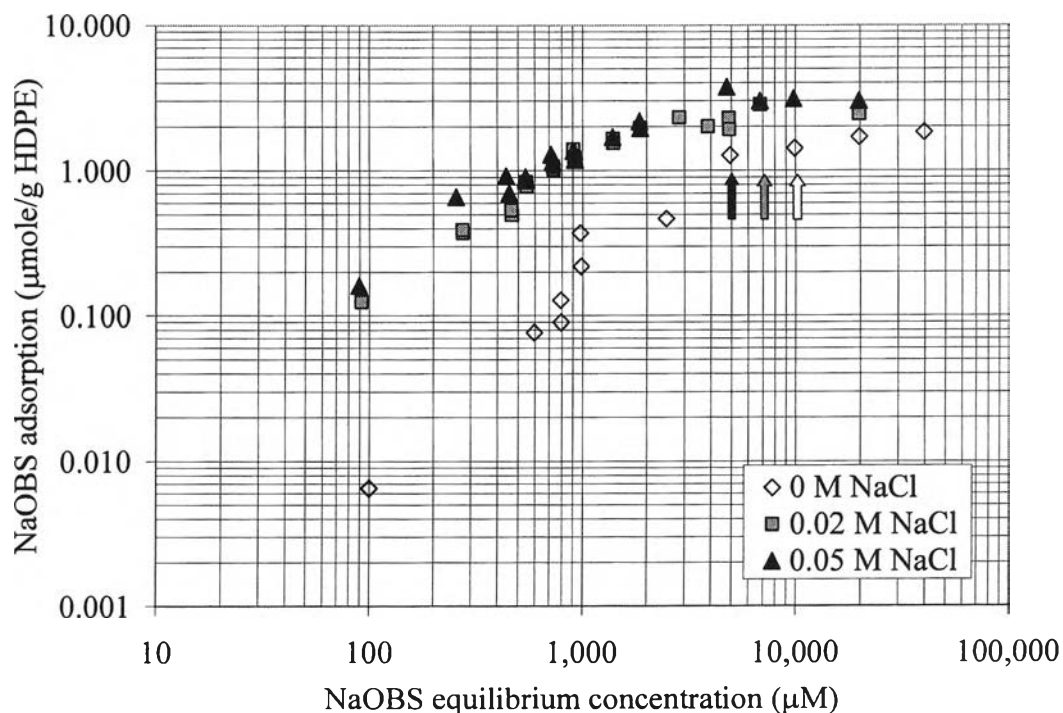
Figure 4.24 Adsorption isotherms of NaOBS on HDPE.
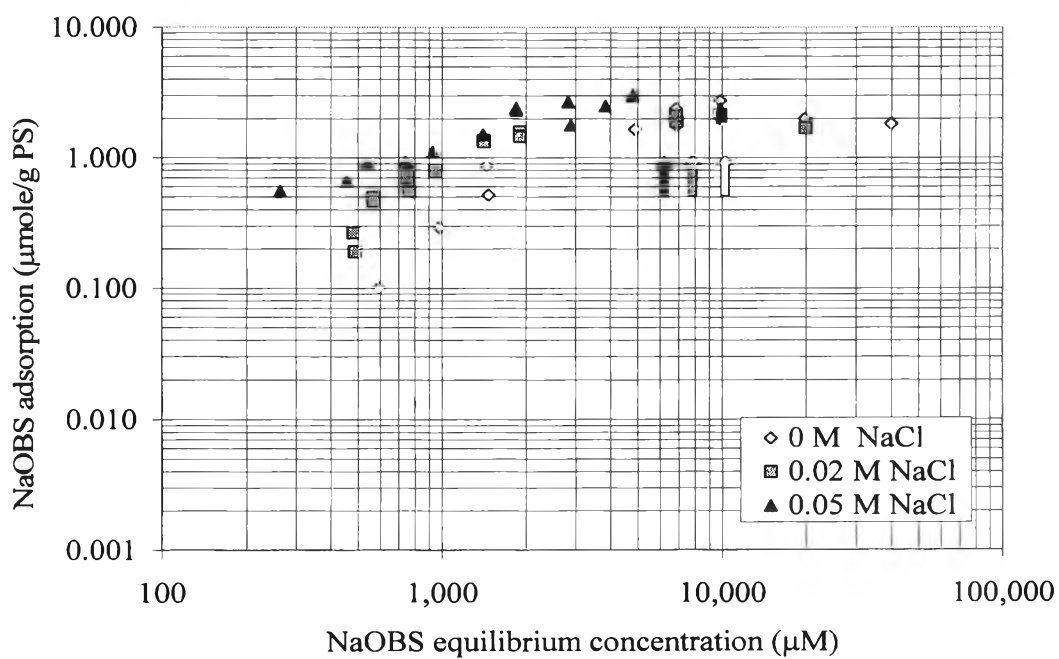
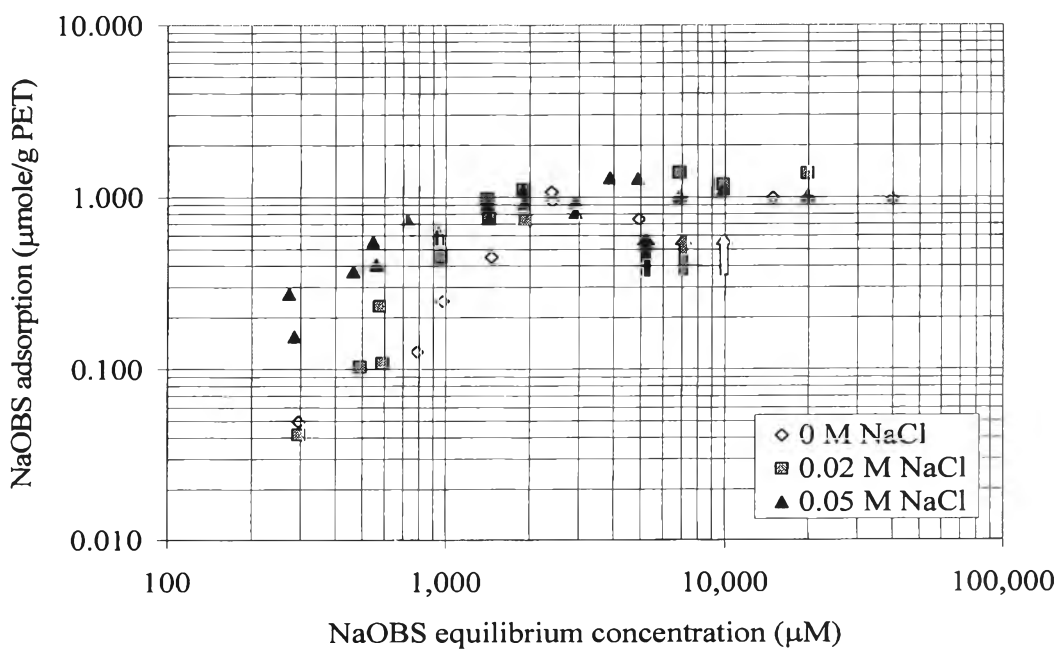**Figure 4.25** Adsorption isotherms of NaOBS on PS.

Figure 4.26 Adsorption isotherms of NaOBS on PET.

4.5.2 Contact Angle of NaOBS Solution on Plastics

The static contact angles of NaOBS solutions on HDPE, PS and PET are illustrated in Figures 4.27 - 4.29, respectively. For all cases, the contact angles decrease significantly with increasing NaOBS concentration until becoming constant at above the CMC. The values of contact angle on three plastics at the same NaOBS and NaCl concentration are in the same order as found in CPC ($\theta_{HDPE} > \theta_{PS} > \theta_{PET}$).

As in the case of CPC solution, the presence of NaCl results in better wetting for solutions that have the same NaOBS concentration.
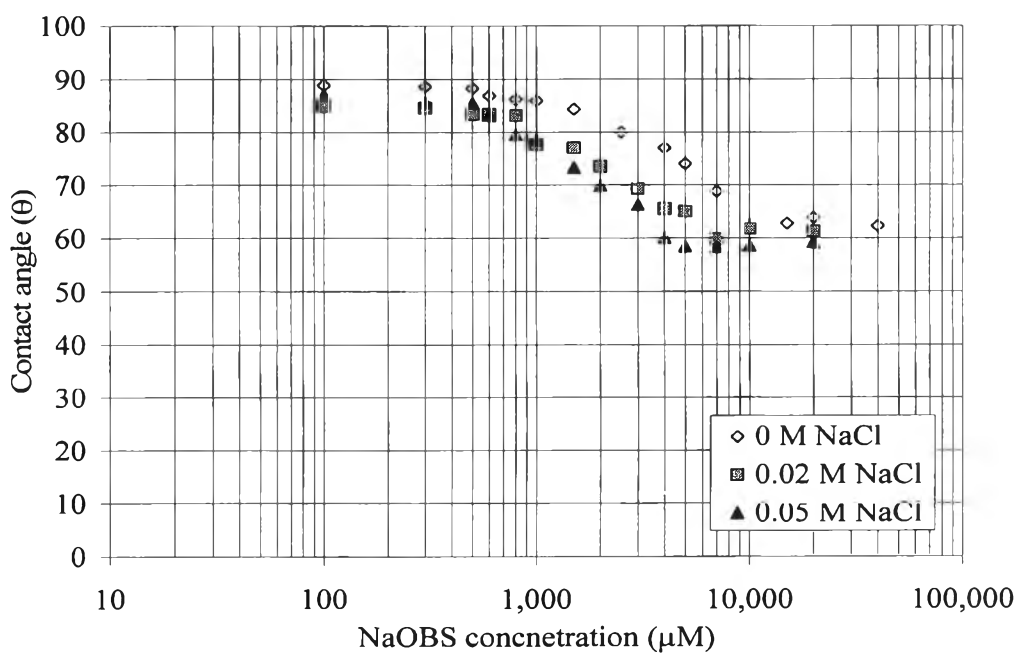
Figure 4.27 Contact angle of NaOBS solution on HDPE with varying NaOBS and NaCl Concentration.
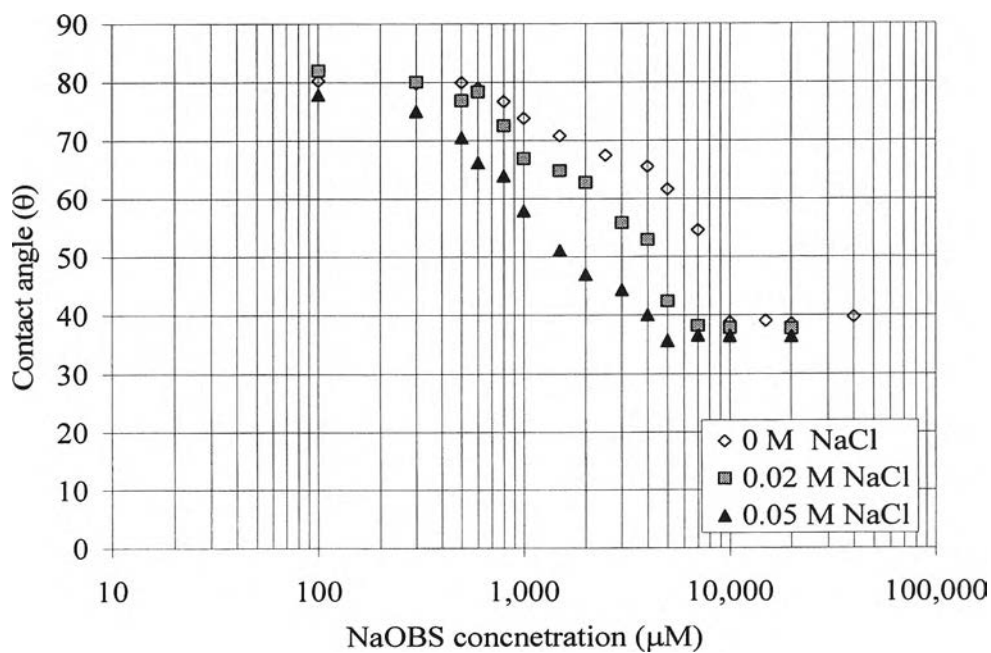
Figure 4.28 Contact angle of NaOBS solution on PS with varying NaOBS and NaCl Concentration.
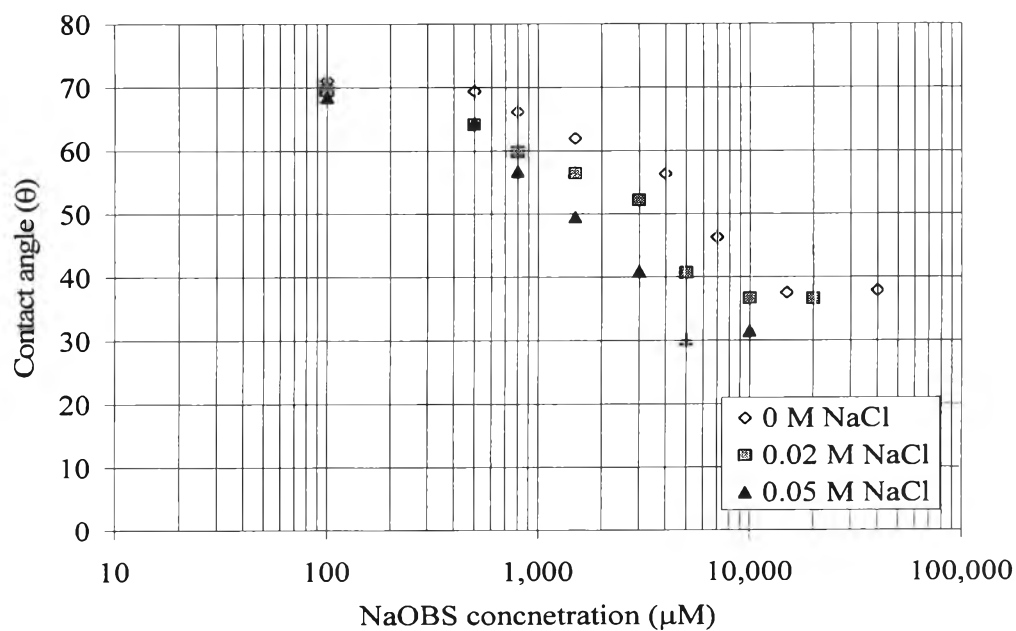

Figure 4.29 Contact angle of NaOBS solution on PET with varying NaOBS and NaCl Concentration.

4.5.3 Wetting Enhancement by NaOBS

As illustrated in Figures 4.30 - 4.32, the plot between cos θ and $1/\gamma_{LV}$ does not show the linear relationship that intercepts at zero. This implies that the value of (γ_{SV} - γ_{SL}) is not constant. As mentioned early, Figures 4.33 - 4.35 also confirm this. With the above assumption that γ_{SV} does not vary with concentration; γ_{SL} should be a function of surfactant concentration
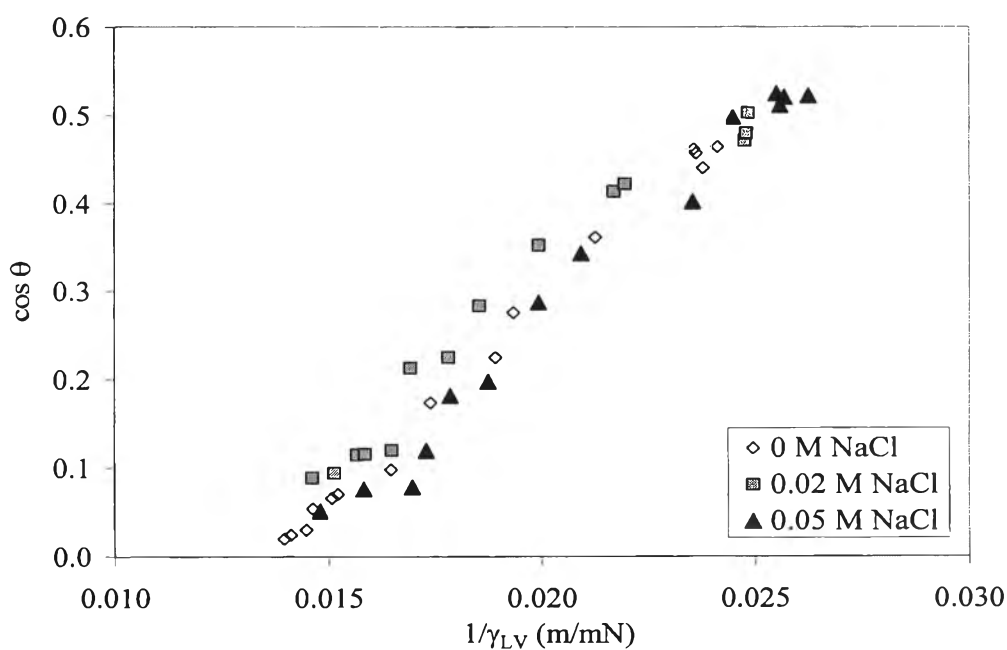
Figure 4.30 Contact angle on HDPE related to inversion of liquid/vapor surface tension of NaOBS solution.

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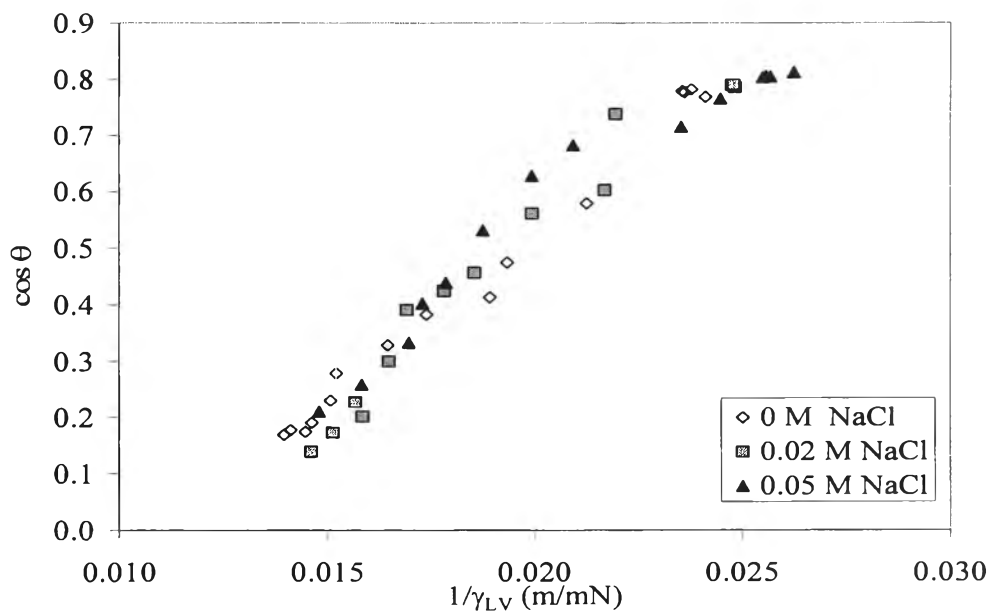
Figure 4.31 Contact angle on PS related to inversion of liquid/vapor surface tension of NaOBS solution.
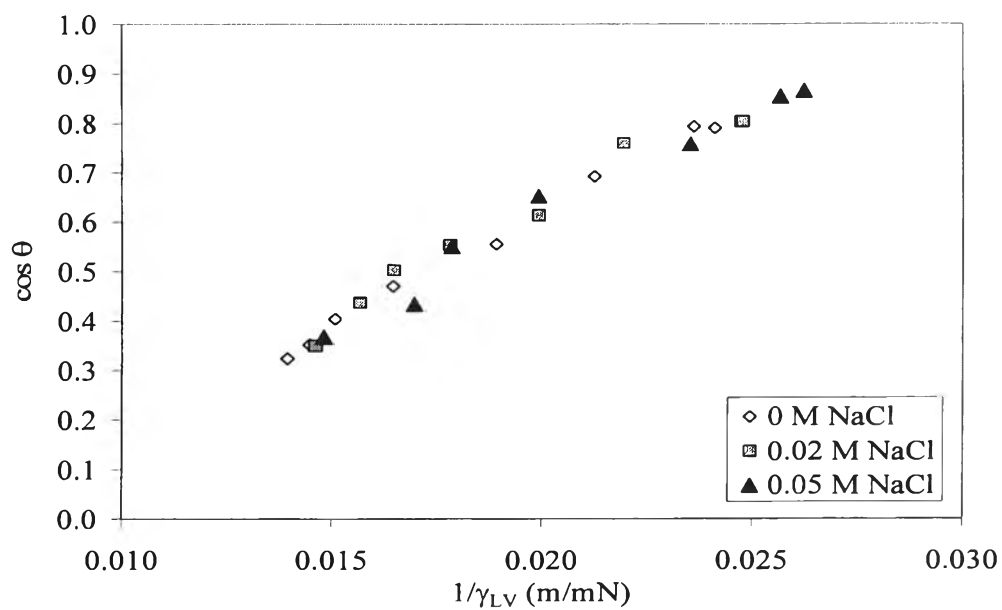

Figure 4.32 Contact angle on PET related to inversion of liquid/vapor surface tension of NaOBS solution
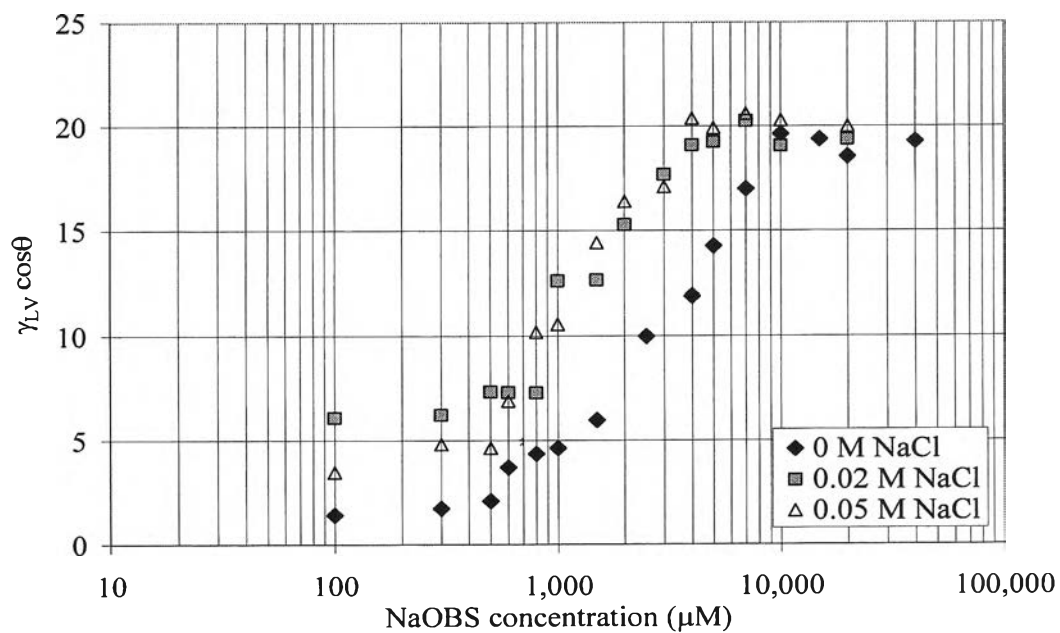
Figure 4.33 $\gamma_{LV} \cos \theta$ on HDPE related to equilibrium concentration of NaOBS solution.
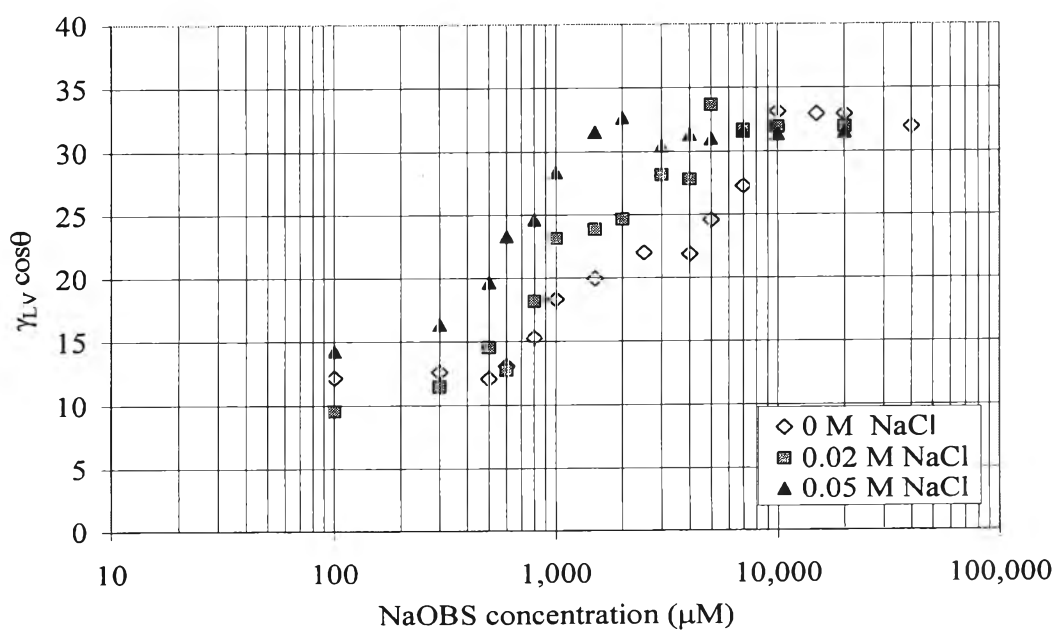

Figure 4.34 $\gamma_{LV} \cos \theta$ on PS related to equilibrium concentration of NaOBS solution.
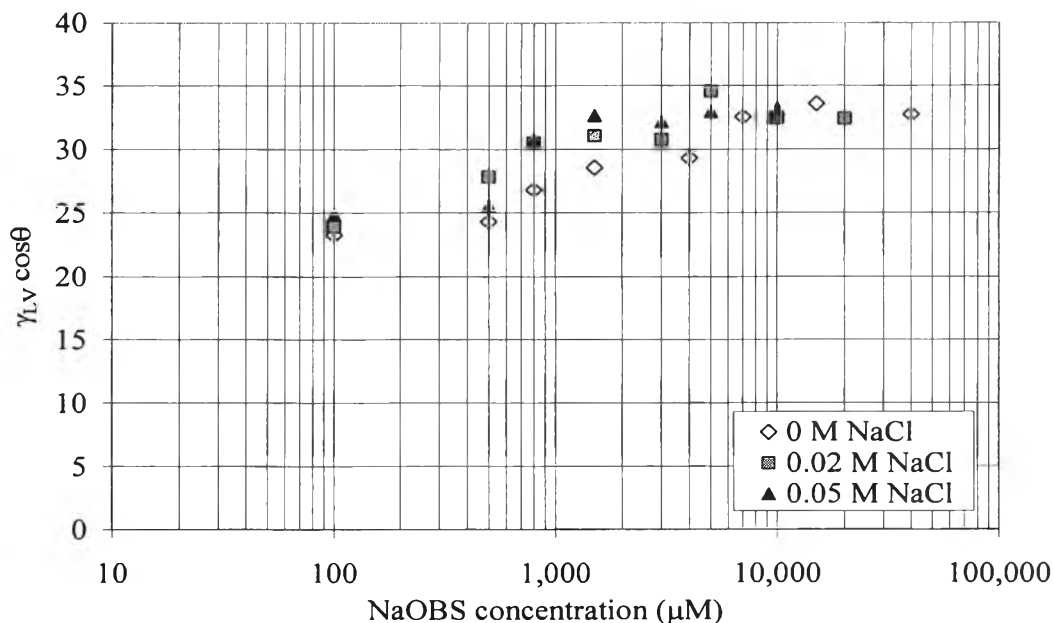
Figure 4.35 $\gamma_{LV} \cos \theta$ on PET related to equilibrium concentration of NaOBS solution.

Figures 4.36 - 4.38 illustrate that the solid/liquid interfacial tension is a function of NaOBS concentration. The solid/liquid interfacial tension decreases with NaOBS concentration. If the adsorption data in Figures 4.24 - 4.26 are incorporated into Figures 4.36 - 4.38, the results will reveal the relationship between solid/liquid interfacial tension and the NaOBS adsorption. Figures 4.39 - 4.41 demonstrate that the solid/liquid interfacial tension decrease with NaOBS adsorption.

The addition of NaCl also has the effect on the solid/liquid interfacial tension, as γ_{SL} decreases with increasing in the concentration of NaCl at constant surfactant concentration. The presence of NaCl allows surfactant to adsorb more on the surface resulting in more reduction of the value of γ_{SL}. This corresponds to the above observation that the solid/liquid interfacial tension decrease with the adsorption amount.

However, NaCl seems to have no clear effect on the reduction of solid/liquid interfacial tension when comparing at the same adsorption density on the same plastic as can be seen from Figures 4.39- 4.41.
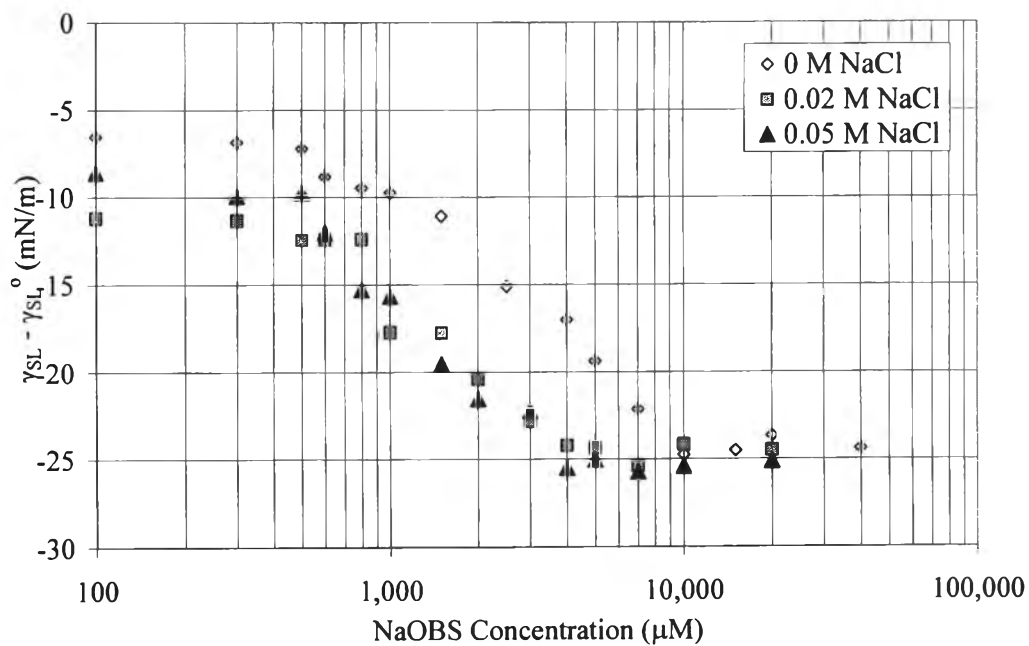
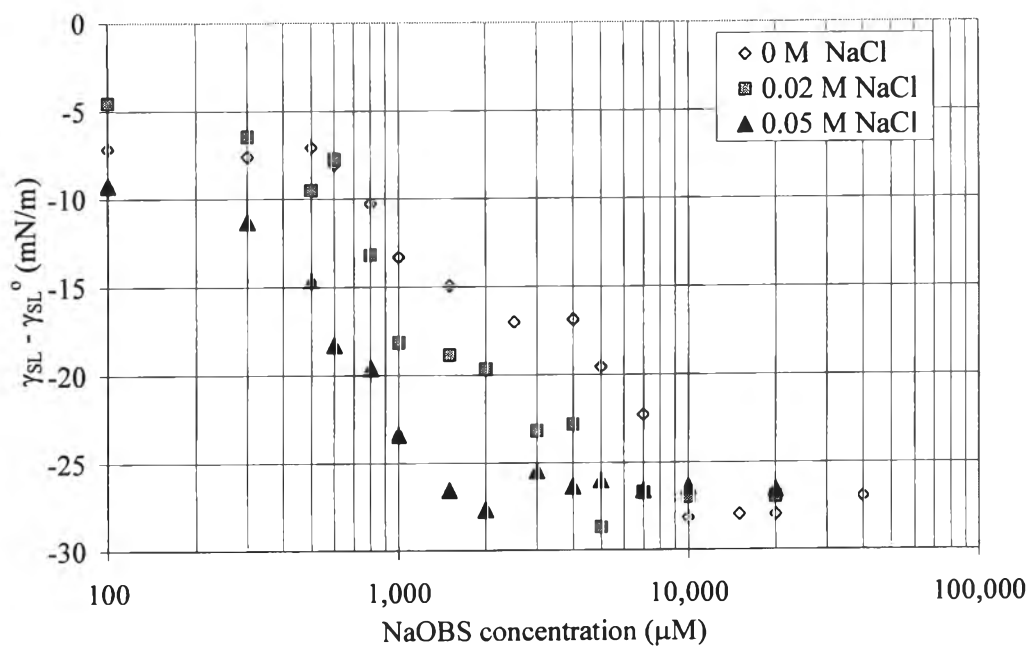**Figure 4.36** Relative solid/liquid interfacial tension of HDPE as a function of NaOBS concentration.

Figure 4.37 Relative solid/liquid interfacial tension of PS as a function of NaOBS concentration.
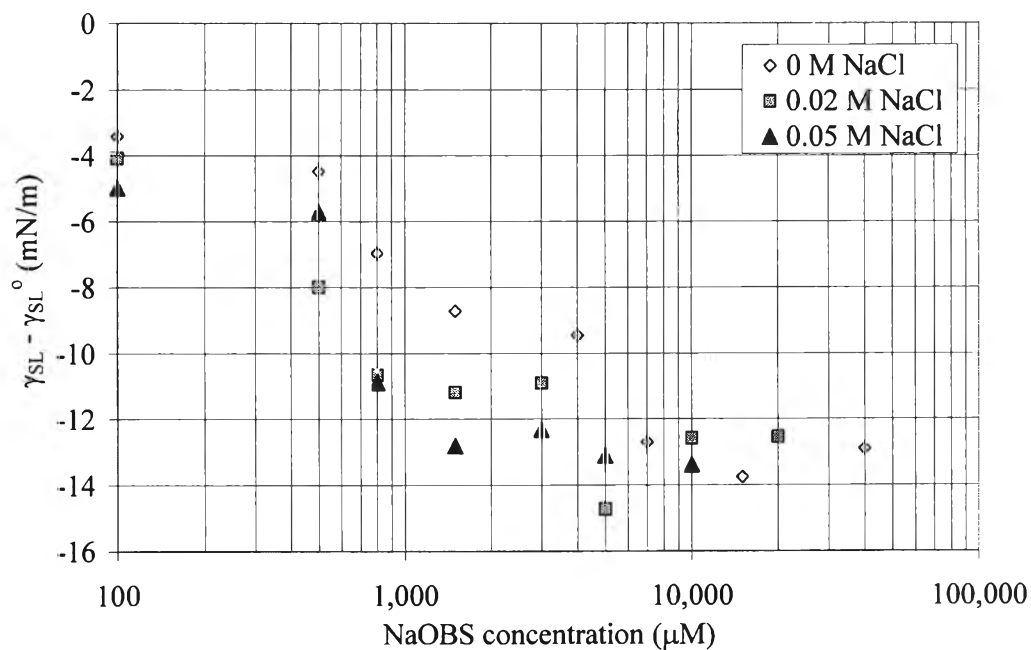
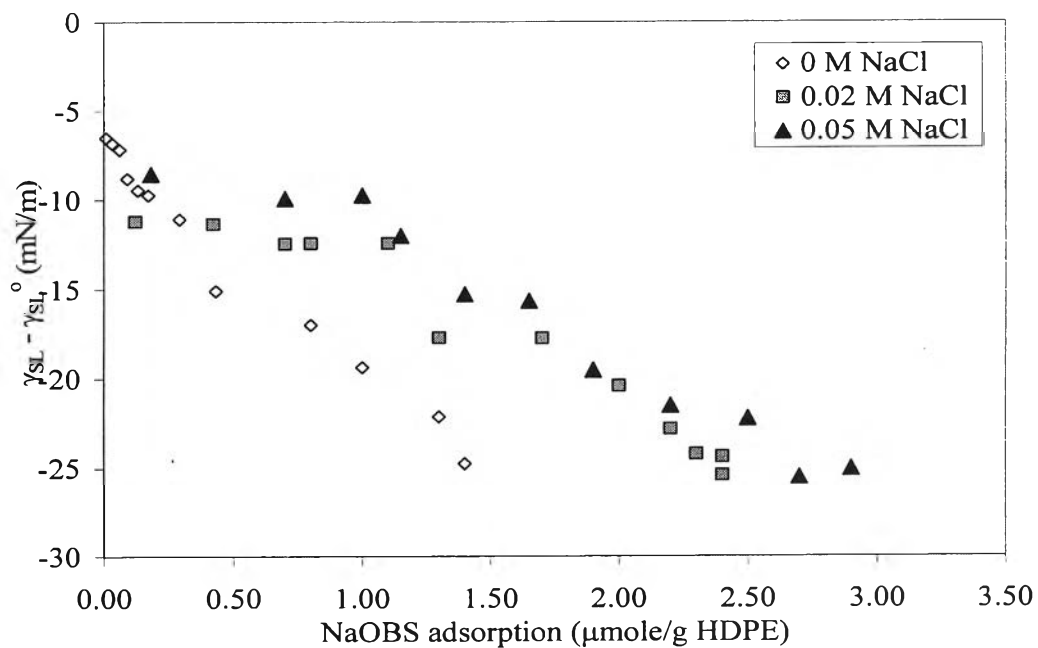**Figure 4.38** Relative solid/liquid interfacial tension of PET as a function of NaOBS concentration.

Figure 4.39 Relative solid/liquid interfacial tension of HDPE as a function of NaOBS adsorption.
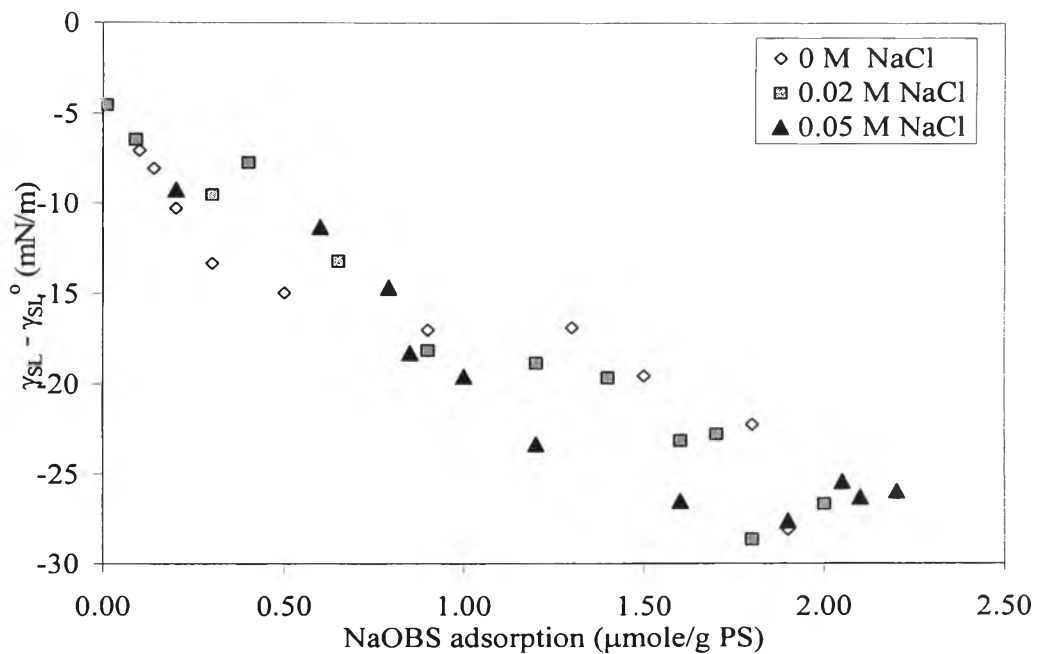
Figure 4.40 Relative solid/liquid interfacial tension of PS as a function of NaOBS adsorption.
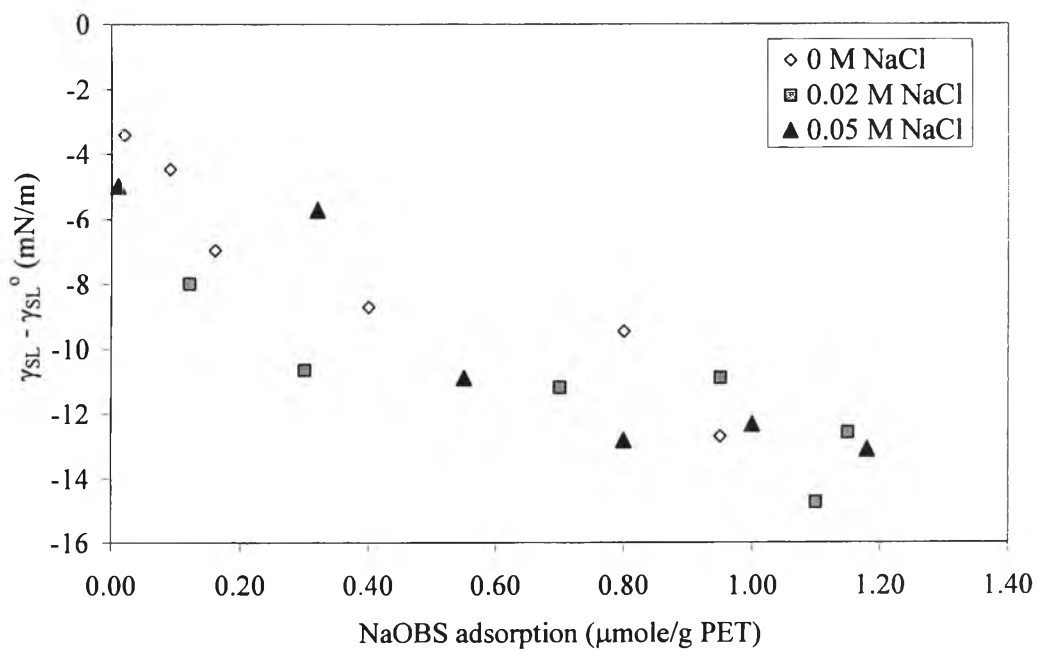

Figure 4.41 Relative solid/liquid interfacial tension of PET as a function of NaOBS adsorption.

From Figures 4.42 - 4.44, the presence of NaCl seems to have no effect on the contact angle of solution with the same γ_{LV}, as observed above for CPC. On the same type of plastic, all NaOBS solutions that have the same γ_{LV} produce almost the same contact angle. Polarity of plastic appears to have no effect for NaOBS.

One possible reason is the difference in the structure of CPC and NaOBS. The hydrophobic tail of CPC has 16 carbon atoms while NaOBS has eight carbon atoms. Since CPC has a long tail, its adsorption on plastic surface is likely to be in the tilt position (part of the tail attached to the surface). Part of CPC tail that attach to surface will act like an anchor that hold CPC molecule to the surface. This anchor-like structure together with the assumption of polar sites of the plastic surface will limit the movement of CPC molecules. Hence, the addition of NaCl may not be able to allow more CPC to adsorb.

On the other hand, NaOBS molecules that have only eight carbon atoms in the tail prone to adsorb more freely on the plastics surface. Even though the polar sites assumption are still stand, the non-polar site that surfactant adsorb on still have some room for more surfactant to adsorb. Consequently, the addition of NaCl will still be able to allow more surfactant to adsorb on the surface. The γ_{SL} would be reduced almost as effectively as γ_{SL}.
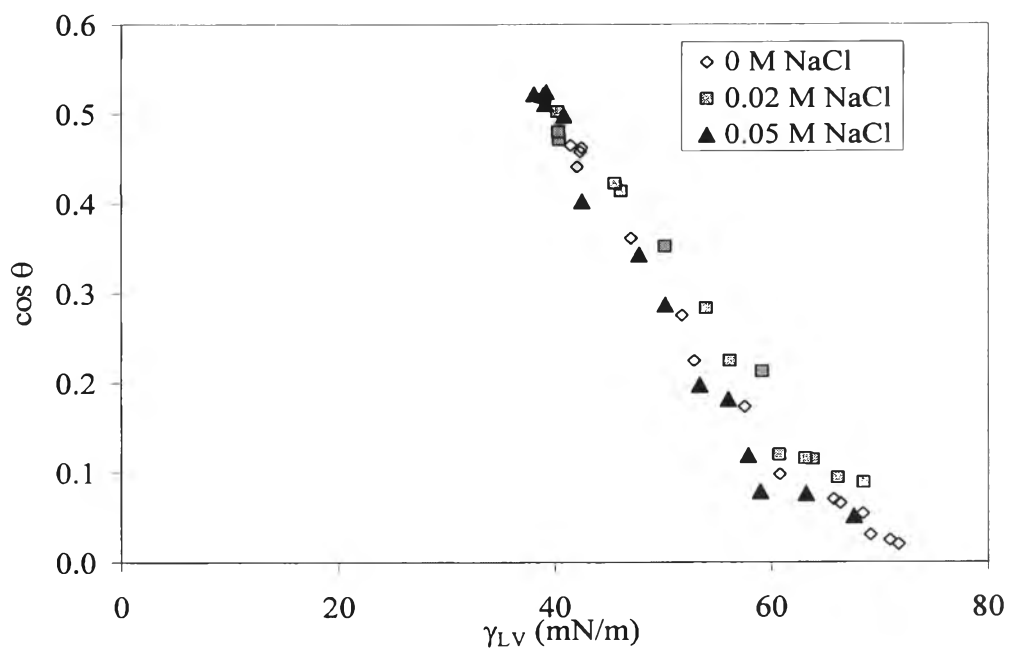
Figure 4.42 Contact angle of NaOBS on HDPE as a function of its liquid/vapor surface tension.
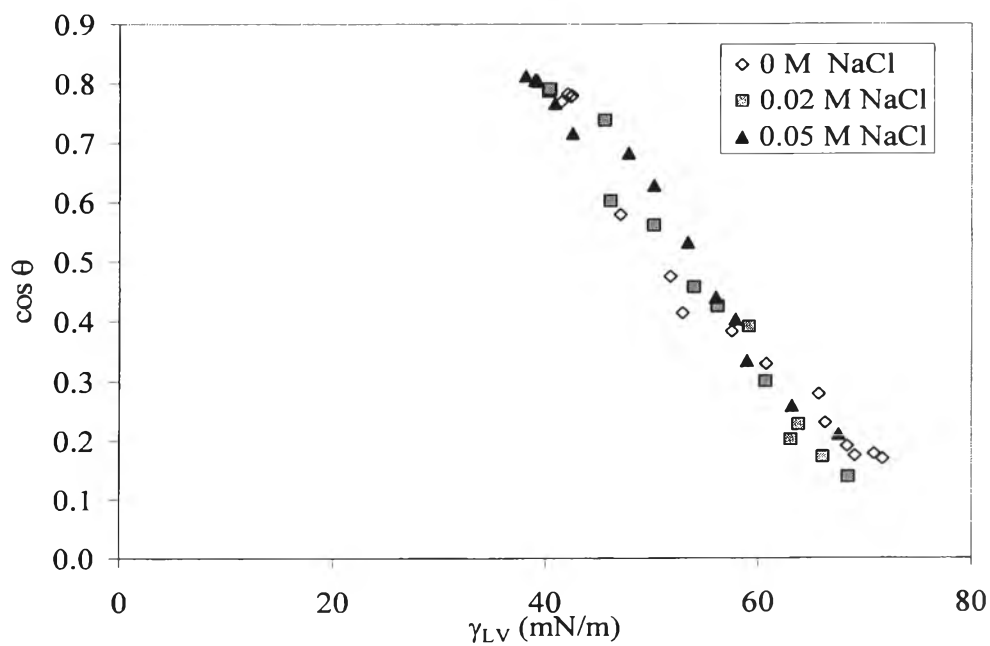

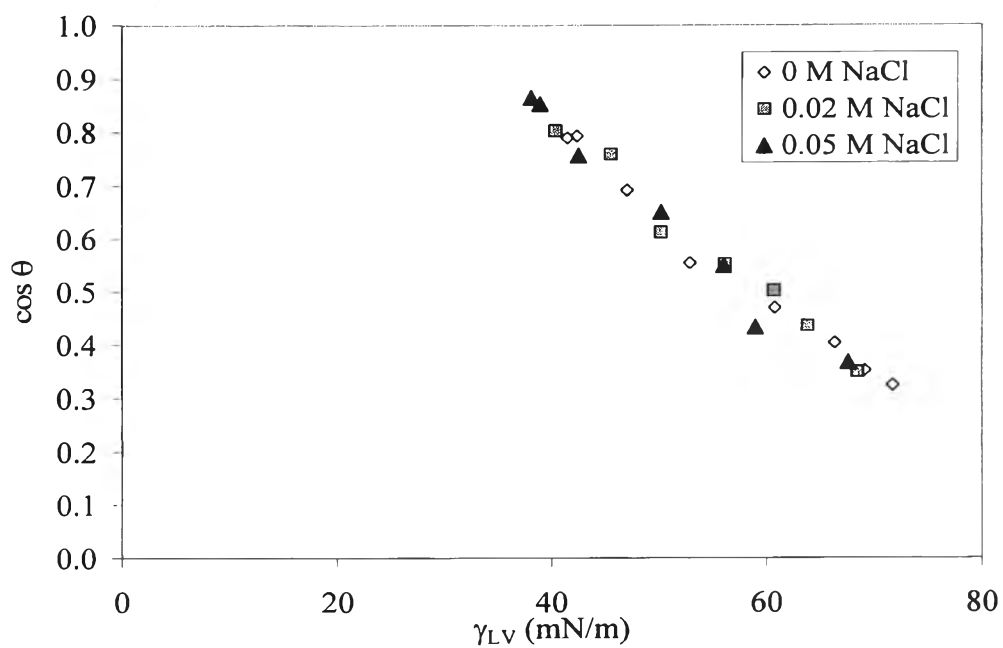**Figure 4.43** Contact angle of NaOBS on PS as a function of its liquid/vapor surface tension.

Figure 4.44 Contact angle of NaOBS on PET as a function of its liquid/vapor surface tension.

4.6 The Liquid/Vapor Surface Tension and CMC of Triton X-100

The liquid/vapor surface tension (γ_{LV}) of Triton X-100 solutions is plotted as a semi-logarithmic function of its concentration as shown in Figure 4.45. The liquid/vapor surface tension (γ_{LV}) decreases with Triton X-100 concentration until reaching CMC at about 240 μM.
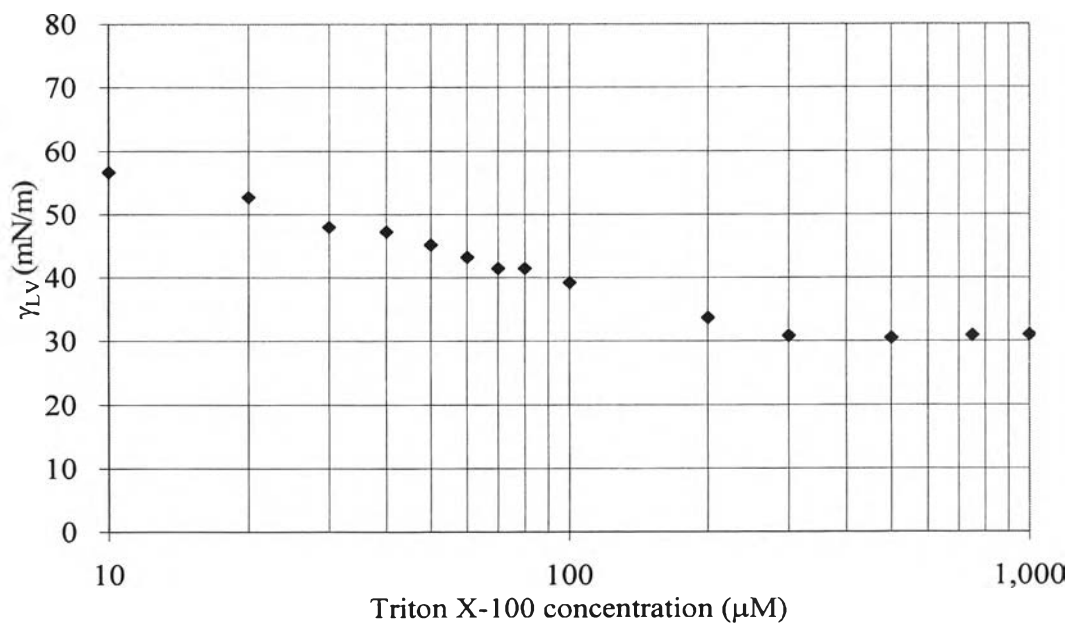

Figure 4.45 Liquid/vapor surface tension as a function of Triton X-100 concentration.

4.7 Adsorption of Triton X-100 and Its Wetting on Plastics

4.7.1 Adsorption Isotherm of Triton X-100

The adsorption isotherms of Triton X-100 on HDPE, PS, and PET are shown in Figure 4.46. The adsorption increases with surfactant concentration until reach plateau at about CMC.
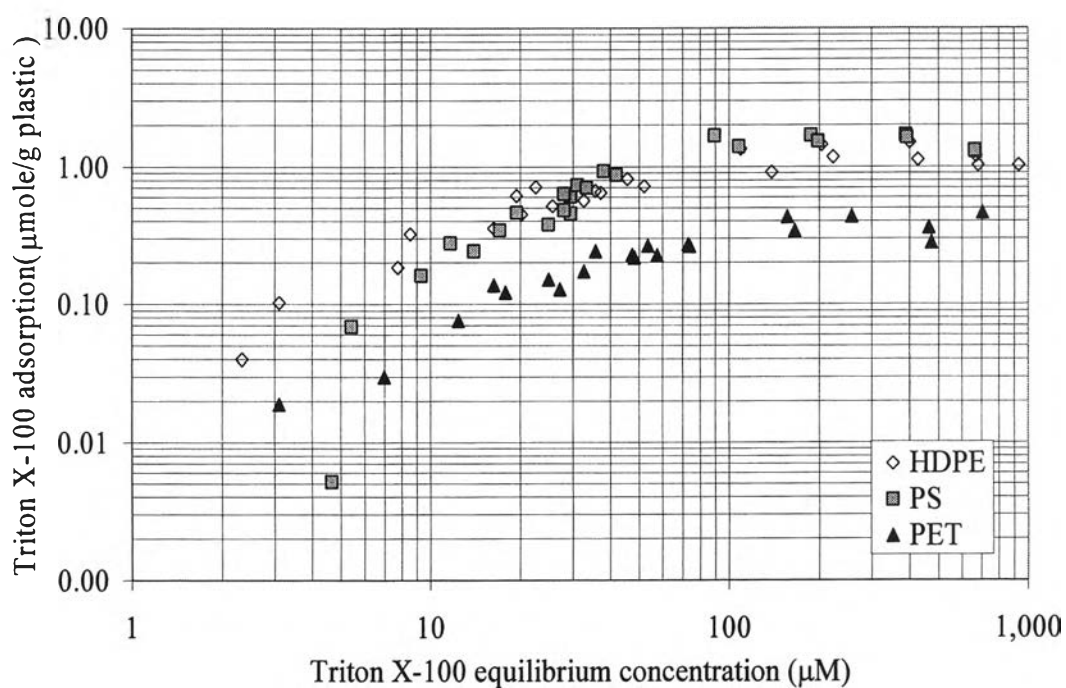

Figure 4.46 Adsorption isotherm of Triton X-100 on plastics.

4.7.2 Contact Angle of Triton X-100 Solution on Plastics

The static contact angles of Triton X-100 solutions are shown in Figure 4.47. The contact angles decreases notably with increasing Triton X-100 concentration until becoming nearly constant above the CMC. The contact angles on different plastics at the same surfactant concentration are in the same order as found from CPC and NaOBS:
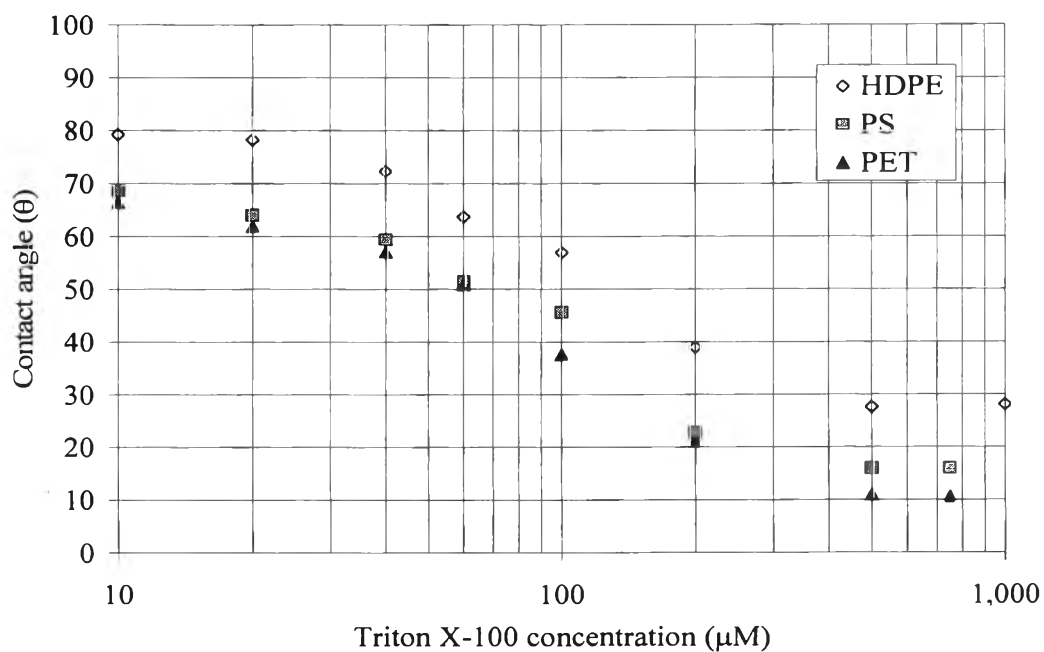

Figure 4.47 Contact angle of Triton X-100 solution on plastics with varying Triton X-100 concentration.

4.7.3 Wetting Enhancement by Triton X-100

As observed in the case of CPC and NaOBS, Figure 4.48 does not show the linear relationship that intercepts at zero. Both Figures 4.48 - 4.49 suggest that (γ_{SV}-γ_{SL}) is not constant and γ_{SL} should be a function of surfactant concentration. Figure 4.50 clearly shows this correlation as γ_{SL} decrease with surfactant concentration. The solid/liquid interfacial tension reaches the minimum value at the CMC and decrease no further beyond this point. Figure 4.51 also points up that the reduction of γ_{SL} is caused by Triton X-100 adsorption on plastic surface.
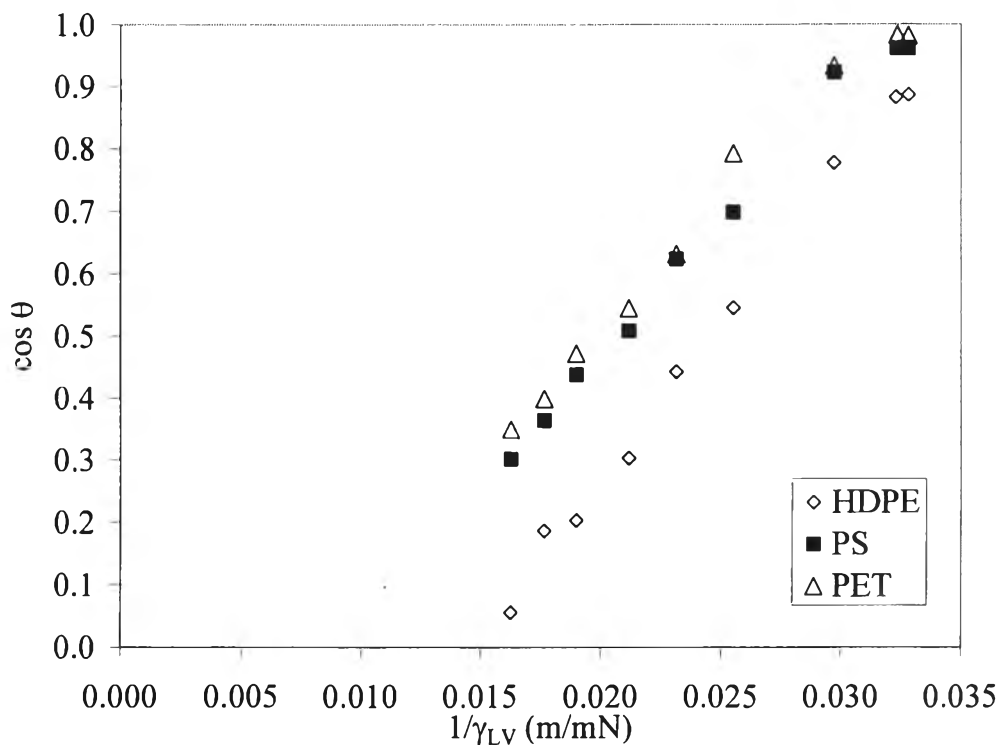

Figure 4.48 Contact angle on plastics related to inversion of liquid/vapor surface tension of Triton X-100 solution.
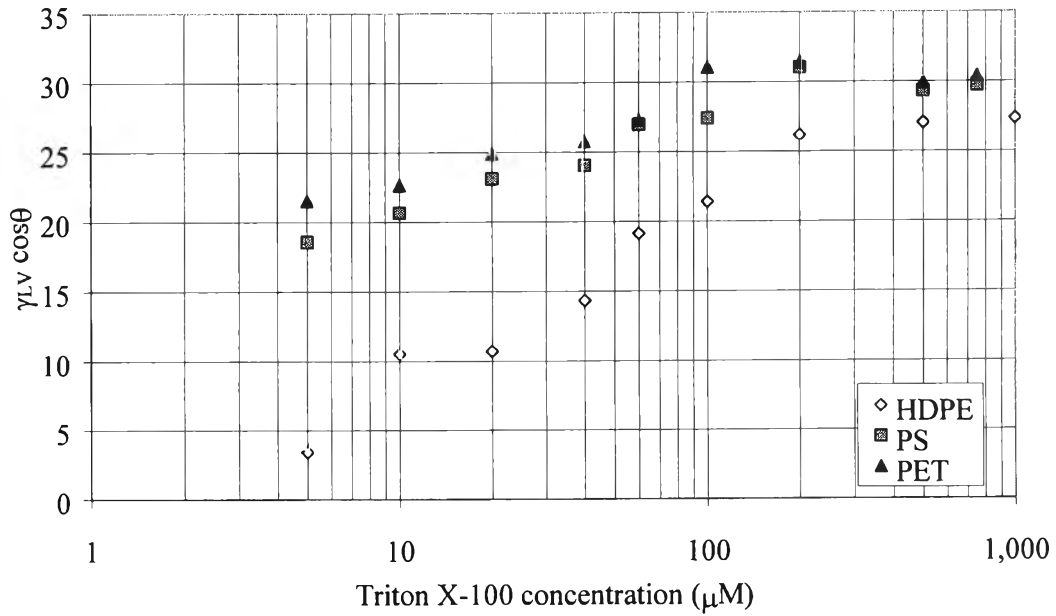
Figure 4.49 $\gamma_{LV} \cos \theta$ on plastics related to equilibrium concentration of Triton X-100 solution.
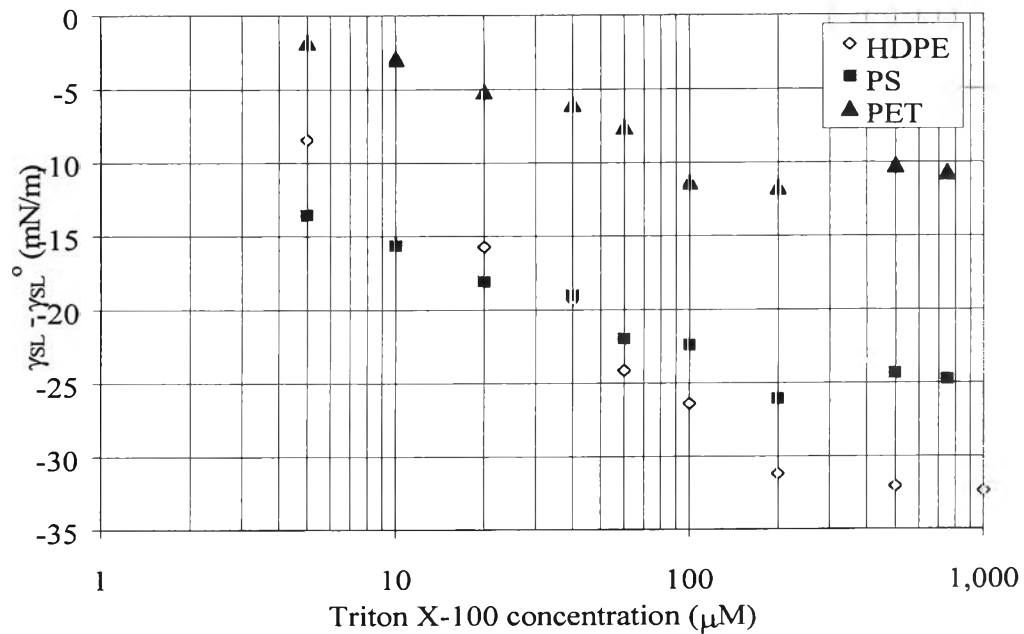

Figure 4.50 Relative solid/liquid interfacial tension of plastics as a function of Triton X-100 concentration.
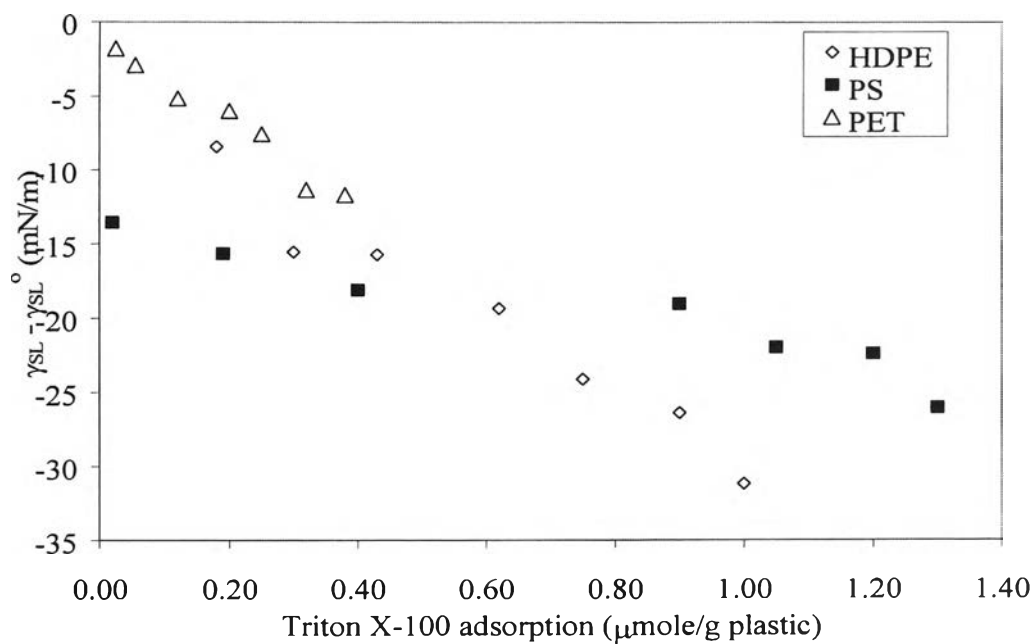
Figure 4.51 Relative solid/liquid interfacial tension of plastics as a function of Triton X-100 adsorption.