

## CHAPTER IV

### RESULTS AND DISCUSSION

The adsorption isotherms of the various surfactant-solid combinations were studied. Cetylpyridinium chloride (CPC), octylbenzenesulfonate sodium salt (NaOBS) and polyoxyethylene octyl phenyl ether (OPEO<sub>10</sub>) are respectively representatives for cationic, anionic and nonionic surfactant. Polytetrafluoroethylene (PTFE), polyvinylchloride (PVC) and polycarbonate (PC) were used as polymer substrate. All experiments were done at difference salt concentrations which are 0, 0.02 and 0.05 M of NaCl. Moreover, the liquid/vapor surface tension and the contact angle of surfactant solutions on PTFE, PVC and PC were also measured.

#### 4.1 Contact Angle of Water and Specific Surface Area of Plastics

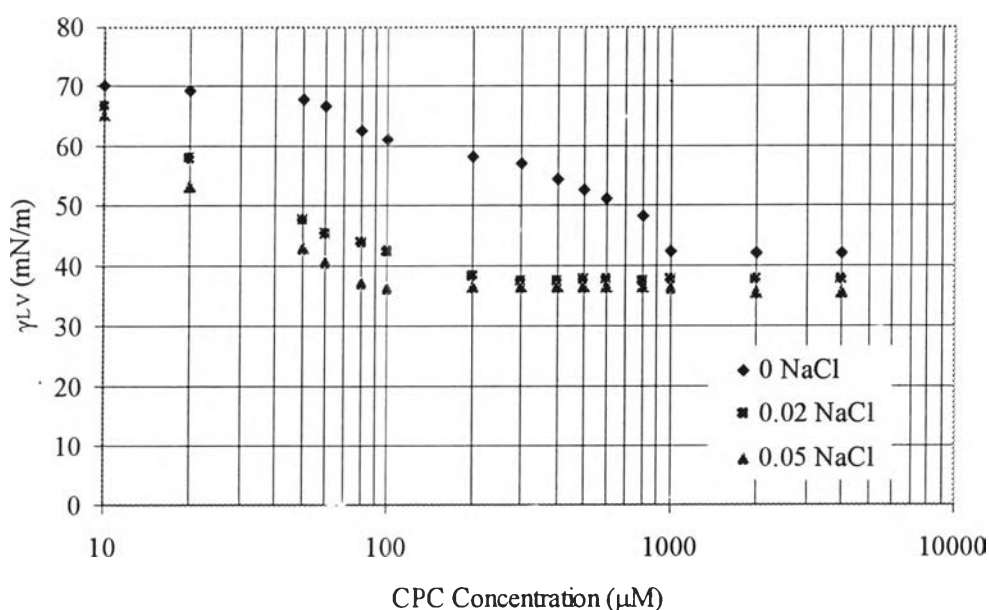
Table 4.1 presents the contact angle of water on PTFE, PVC and PC, and the specific surface area of these plastics. From Table 4.1, the water contact angle of PTFE is highest and followed by PVC and PC respectively. This indicates that PTFE is more hydrophobic than PVC and PC, and PC is the most hydrophilic among these three plastics.

**Table 4.1** The contact angle of water and the specific surface area of PTFE, PVC and PC

Plastics	Contact angle of water (degree)	Specific surface area (m <sup>2</sup> /g)
PTFE	102.5	13.00
PVC	84.9	2.84
PC	73.5	3.98

## 4.2 The Surface Tension and CMC of CPC

Figure 4.1 shows the relation between CPC surface tension and CPC concentration at different ionic strength. The liquid/vapor surface tension decreased with increasing surfactant concentration and constant after reaching the critical micelle concentration (CMC) which can be determined as the break point of the plot. The CMC of CPC solution is 950  $\mu\text{M}$ . From Figure 4.1, the CMC of CPC solutions decreased to 130 and 80  $\mu\text{M}$  as the salt concentration increased to 0.02 and 0.05, respectively.



**Figure 4.1** CPC solution surface tension as a function of its concentration at various salt concentration.

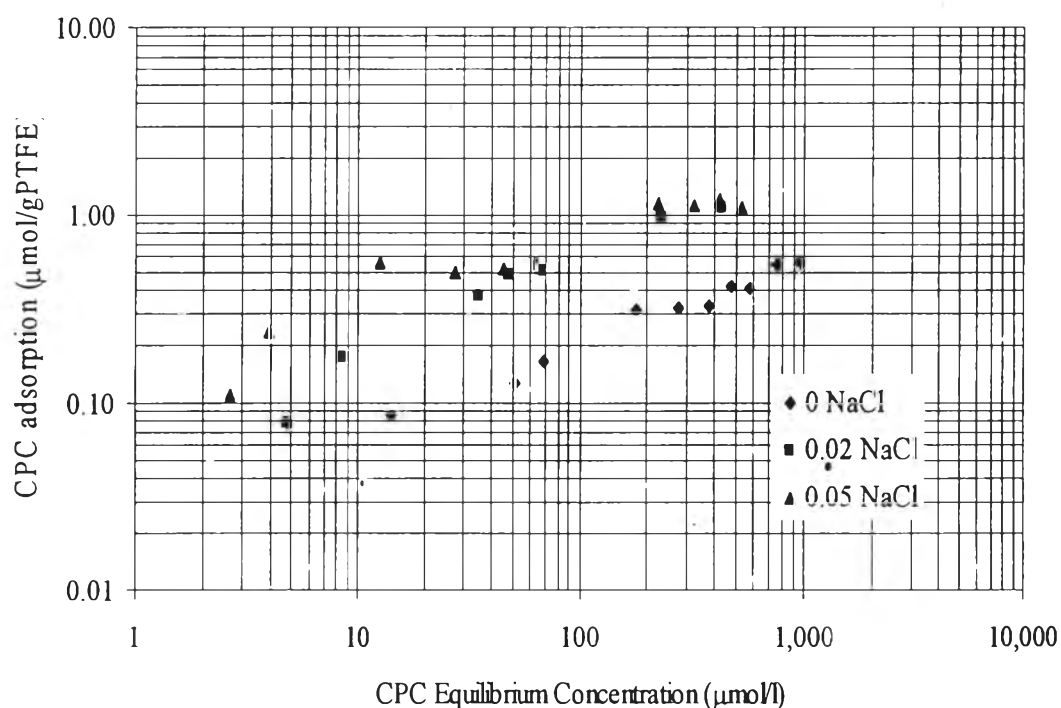
## 4.3 CPC Adsorption and Wetting on PTFE, PVC and PC

### 4.3.1 Adsorption Isotherms of CPC

The adsorption isotherms of CPC on PTFE, PVC and PC with varying salt concentrations are showed in Figure 4.2, Figure 4.3 and Figure 4.4 respectively. The isotherms are the relationship between the amount of adsorbed CPC per gram of plastics and the equilibrium concentration of CPC solution. It can be observed that

the CPC is gradually adsorbed more as the CPC concentration is increased before the critical micelle concentration (CMC) is reached. Above the CMC, the CPC adsorption is constant and the isotherms leveled out at the CMC. Moreover, the present of salt reduces the CMC of CPC and also slightly increases the maximum adsorption of CPC on all three plastics.

As shown in Figure 4.2, it can be noted that the slope of the CPC adsorption isotherms on PTFE is about 1, which indicates that there is no lateral interaction of CPC adsorption on PTFE. However, for CPC adsorption on PVC and PC (Figure 4.3 and 4.4), the typical S-shaped adsorption isotherms for hydrophilic surface are observed for the zero salt. This might because both PVC and PC are relatively high surface energy, when compare with PTFE. When there is salt present in the systems, the adsorption isotherms of CPC on PVC and PC are shifted to the left, probably due to the effect of salt that reduces the electrostatic repulsion between the CPC head group.



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

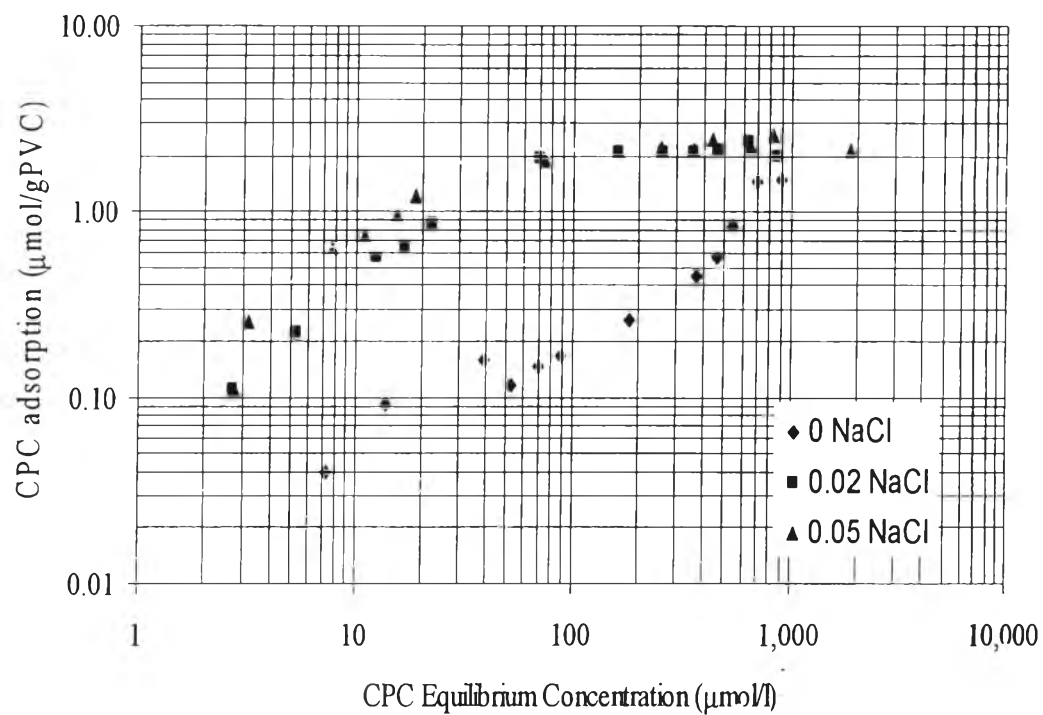


Figure 4.3 Adsorption isotherms of CPC on PVC.

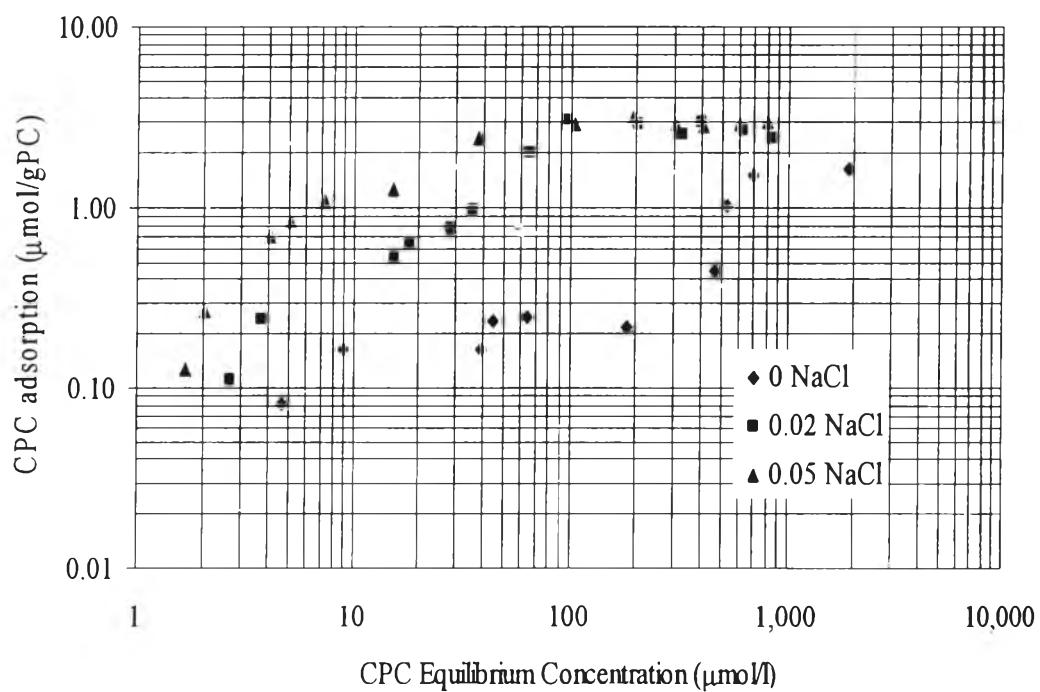
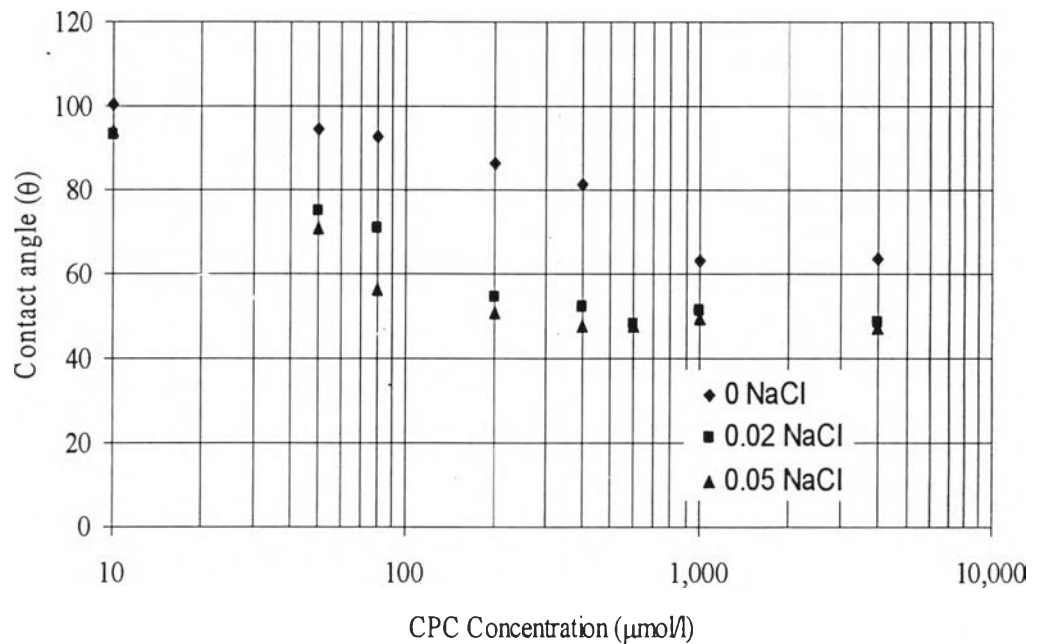


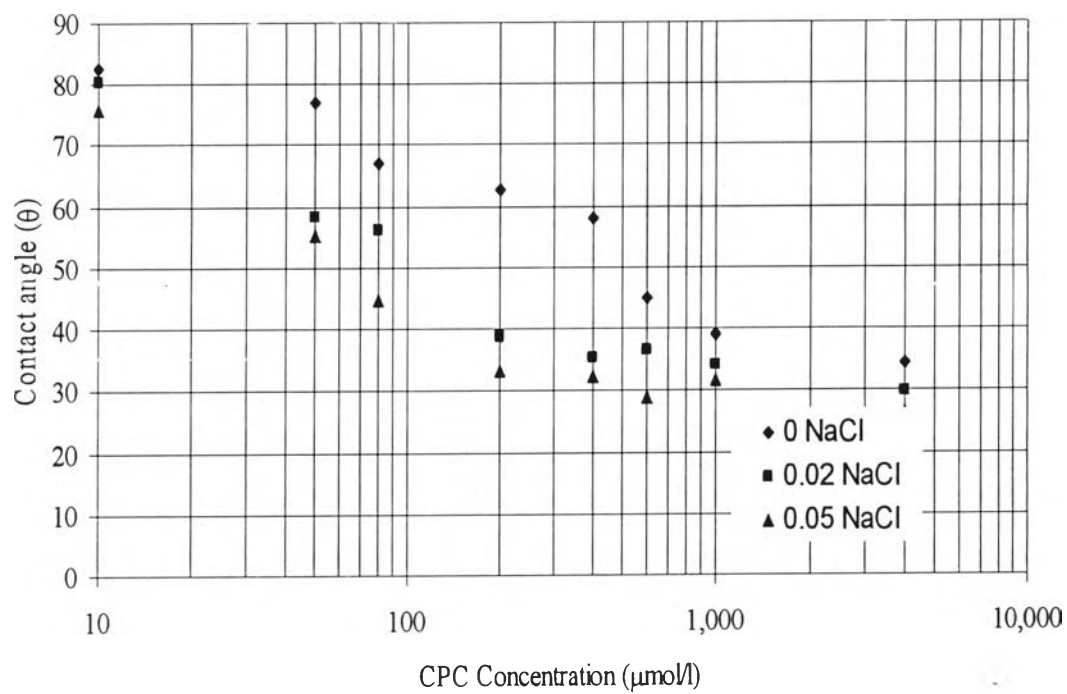
Figure 4.4 Adsorption isotherms of CPC on PC..

#### 4.3.2 Contact Angle of CPC Solution on Plastics

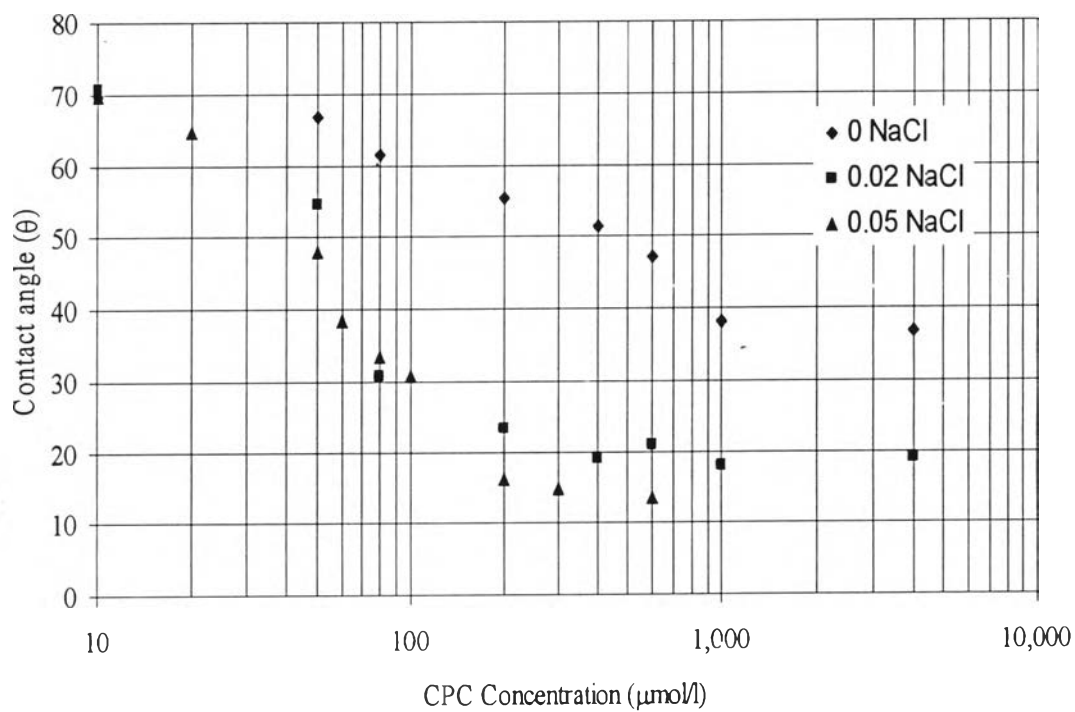
Contact angle of CPC solutions at various concentration on PTFE, PVC and PC are showed in Figure 4.5, Figure 4.6 and Figure 4.7 respectively. In all cases, the contact angle is decreased when CPC concentration is increased, and then become nearly constant. Moreover, a comparison of contact angle for CPC solutions on studied plastics reveals that follows the order PTFE > PVC > PC corresponding to the degree of hydrophobicity of plastics. Furthermore, the addition of NaCl leads to a decrease in the contact angle. The results show that an increase in NaCl concentration, increasing ionic strength, produces a lower contact angle at the same CPC concentration.



**Figure 4.5** Contact angle of CPC solution on PTFE at various NaCl concentrations.



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



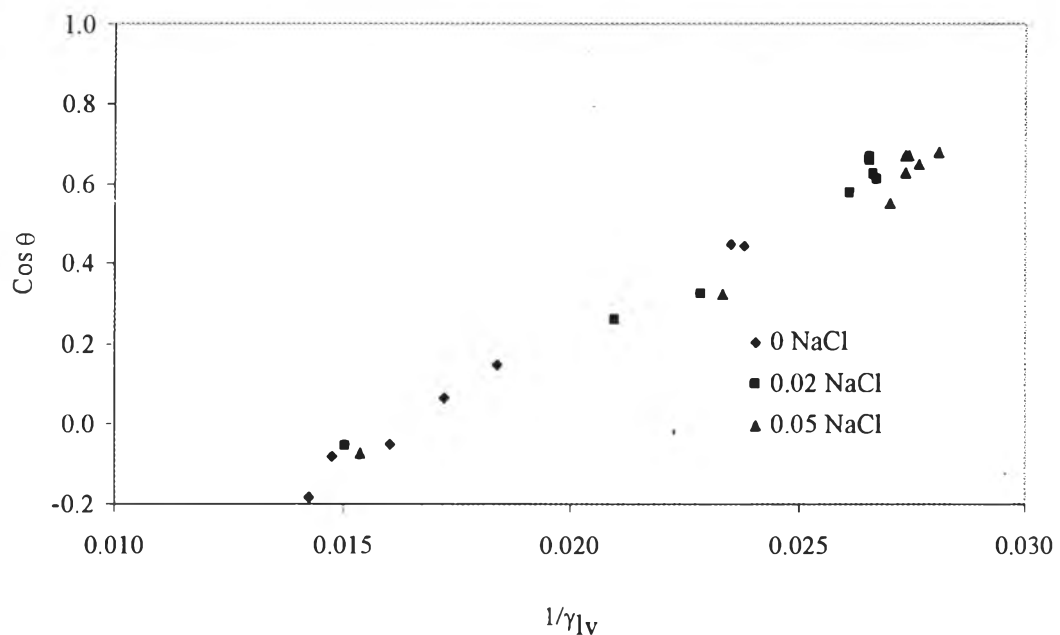
**Figure 4.7** Contact angle of CPC solution on PC with varying NaCl concentration.

### 4.3.3 Wetting Enhancement by CPC

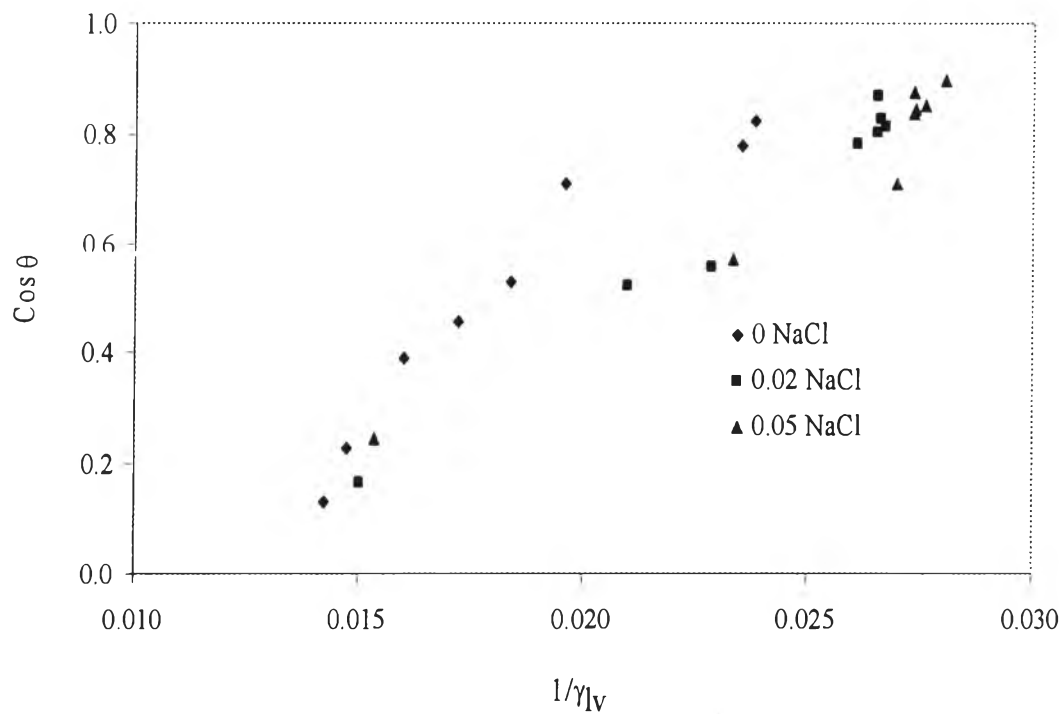
According to Young's equation, the wetting behavior of a liquid was expressed in the following relation:  $\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL}$ . However, it is difficult to measure  $\gamma_{SL}$  and  $\gamma_{SV}$  directly. Therefore, to understand the wettability of surfactant solution, the whole term  $(\gamma_{SV} - \gamma_{SL})$  should be considered.

If the values of  $\gamma_{SL}$  and  $\gamma_{SV}$  are constant, the plots between  $\cos\theta$  and the inversion of liquid/vapor surface tension of CPC solution,  $1/\gamma_{LV}$ , should be straight line and intercept at zero. However, Figure 4.8, Figure 4.9 and Figure 4.10 show that these plots do not intercept at zero.

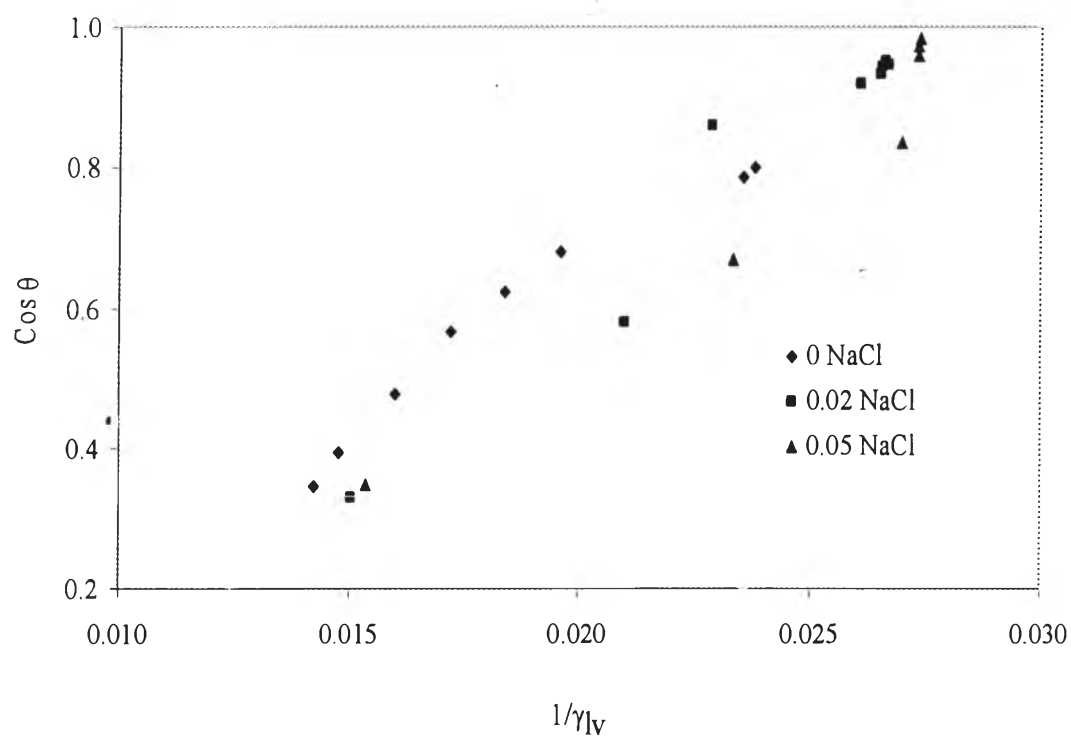
The term  $(\gamma_{LV} \cos\theta)$  is not constant but also varies with CPC concentration which are represent by Figure 4.11 – Figure 4.13. This term increases moderately with increasing CPC concentration. Moreover, for nonvolatile surfactants,  $\gamma_{SV}$  does not depend on surfactant concentration since it is usually assumed that the transfer of surfactants to the solid/vapor interface is impossible. Consequently  $\gamma_{SL}$  is not constant but varies with CPC concentration.



**Figure 4.8** Contact angle on PTFE related to inversion liquid/vapor surface tension of CPC solution.

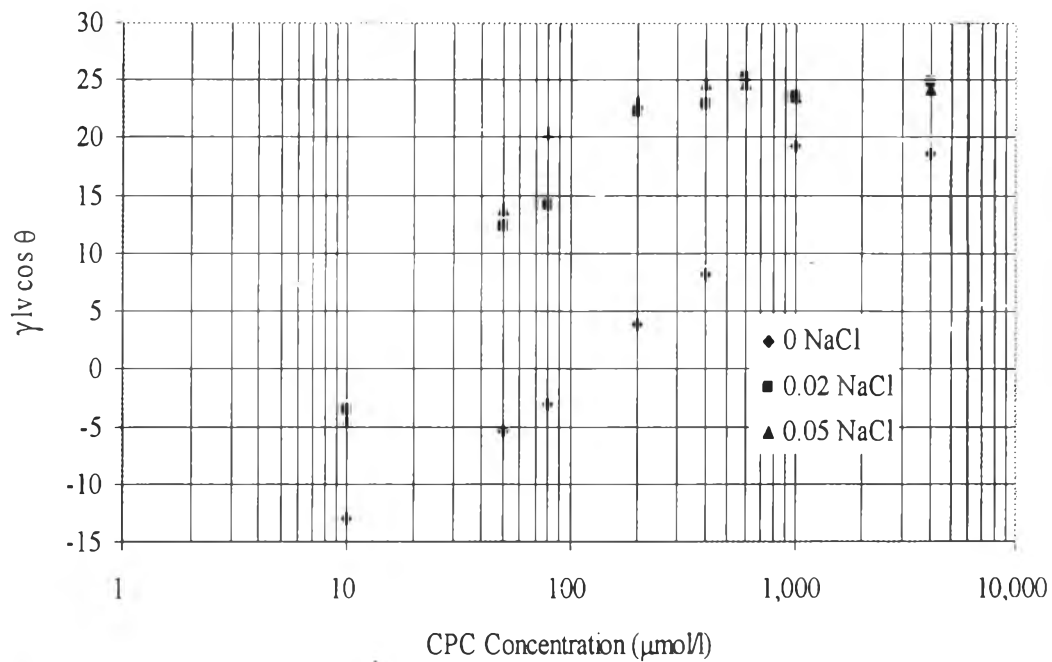


**Figure 4.9** Contact angle on PVC related to inversion liquid/vapor surface tension of CPC solution.

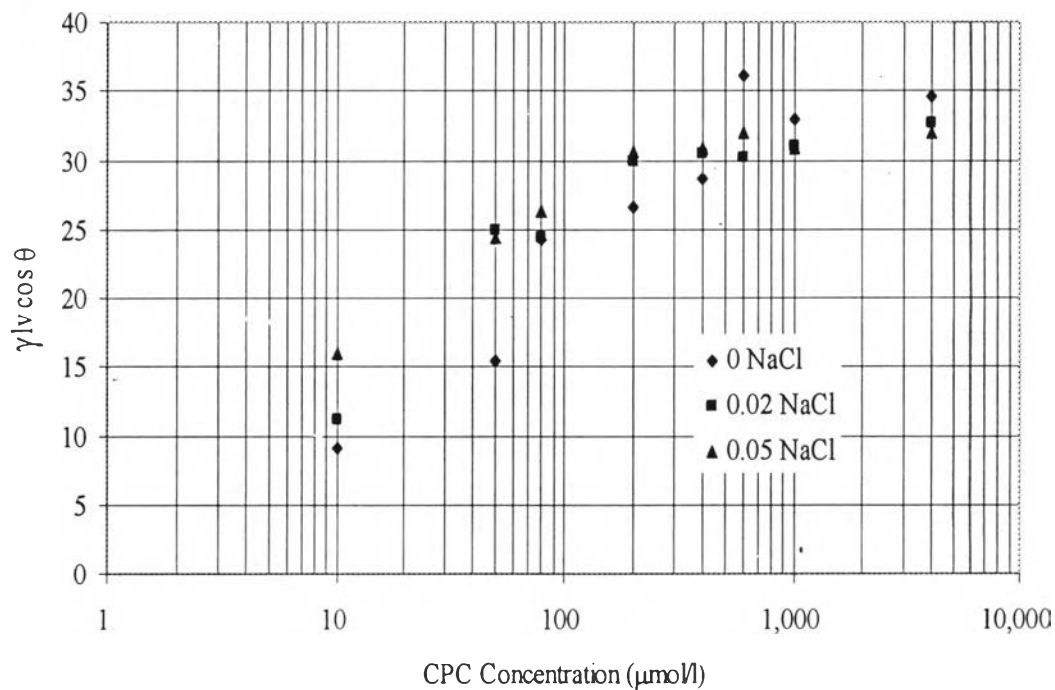


**Figure 4.10** Contact angle on PC related to inversion liquid/vapor surface tension of CPC solution.

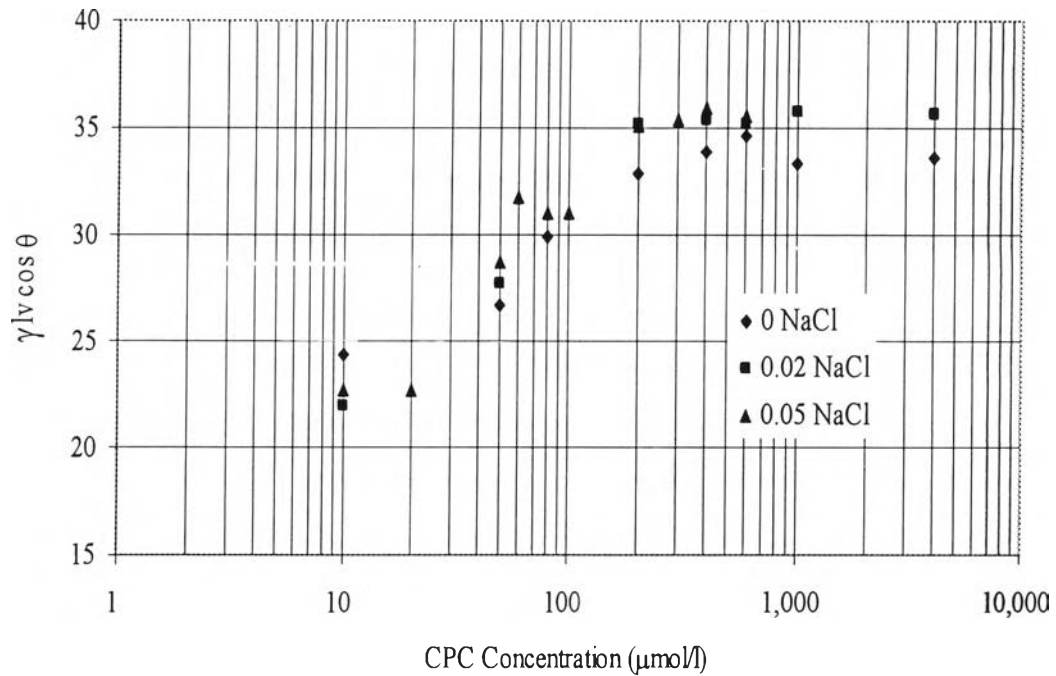




**Figure 4.11**  $\gamma_{LV} \cos \theta$  on PTFE related to CPC concentration.



**Figure 4.12**  $\gamma_{LV} \cos \theta$  on PVC related to CPC concentration.



**Figure 4.13**  $\gamma_{LV} \cos \theta$  on PC related to CPC concentration.

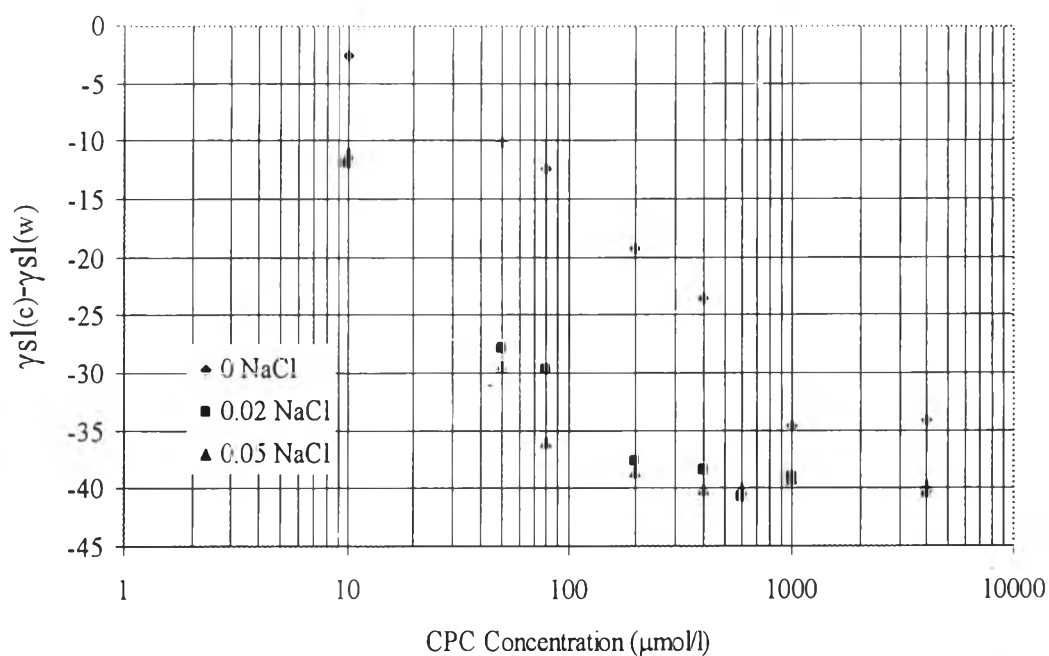
As mentioned above the value of  $\gamma_{SL}$  is difficult to measure directly, however  $\gamma_{SL}$  can be related to CPC adsorption and CPC concentration by using the relative value of the solid/liquid interfacial tension of the surfactant solution at concentration  $c$ ,  $\gamma_{SL}(c)$ , and the solid/liquid interfacial tension at reference state which uses pure water to a reference liquid,  $\gamma_{SL}(w)$ . To estimate this relative value, the Young's equation was used to show that

$$\begin{aligned} \gamma_{LV}(w)\cos \theta(w) - \gamma_{LV}(c)\cos \theta(c) &= \gamma_{SV}(w) - \gamma_{SL}(w) - \gamma_{SV}(c) + \gamma_{SL}(c) \\ &= \gamma_{SL}(c) - \gamma_{SL}(w) \end{aligned} \quad (4.1)$$

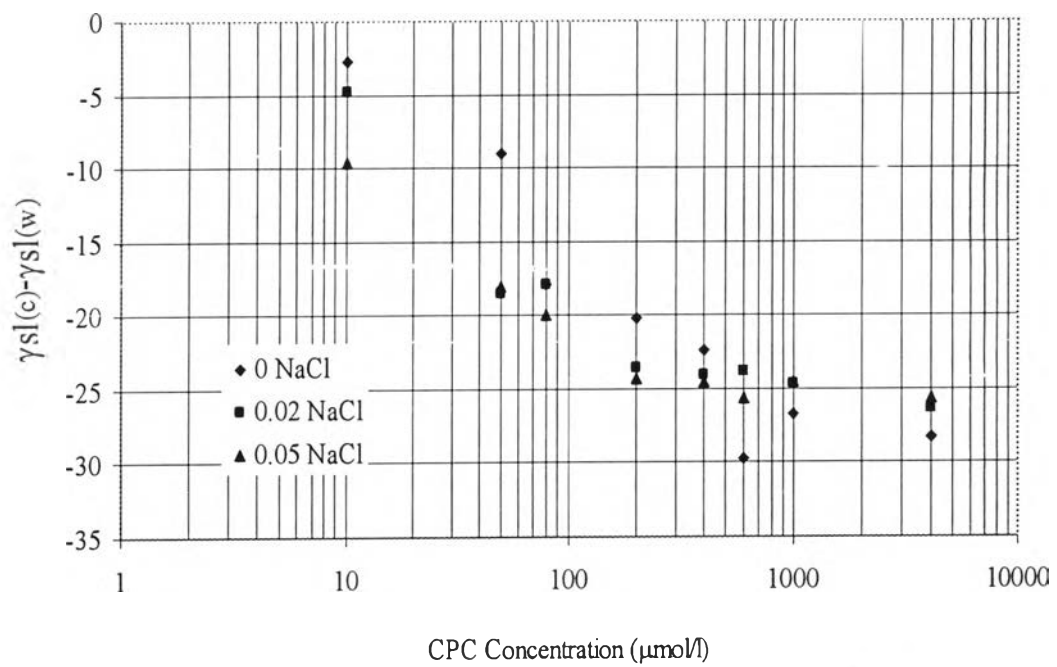
where (c) refers to properties of the surfactant solution at concentration  $c$  and (w) refers to the same value using water (Pyter *et al.*, 1982).

From Figure 14-16, the results indicate that when the concentration of CPC increase this relative interfacial tension,  $\gamma_{SL}(c) - \gamma_{SL}(w)$ , decrease. In addition, at the same concentration it decreases to lower value when the solutions have higher ionic strength. This is in agreement with the adsorption results, high salt results in more CPC adsorbed.

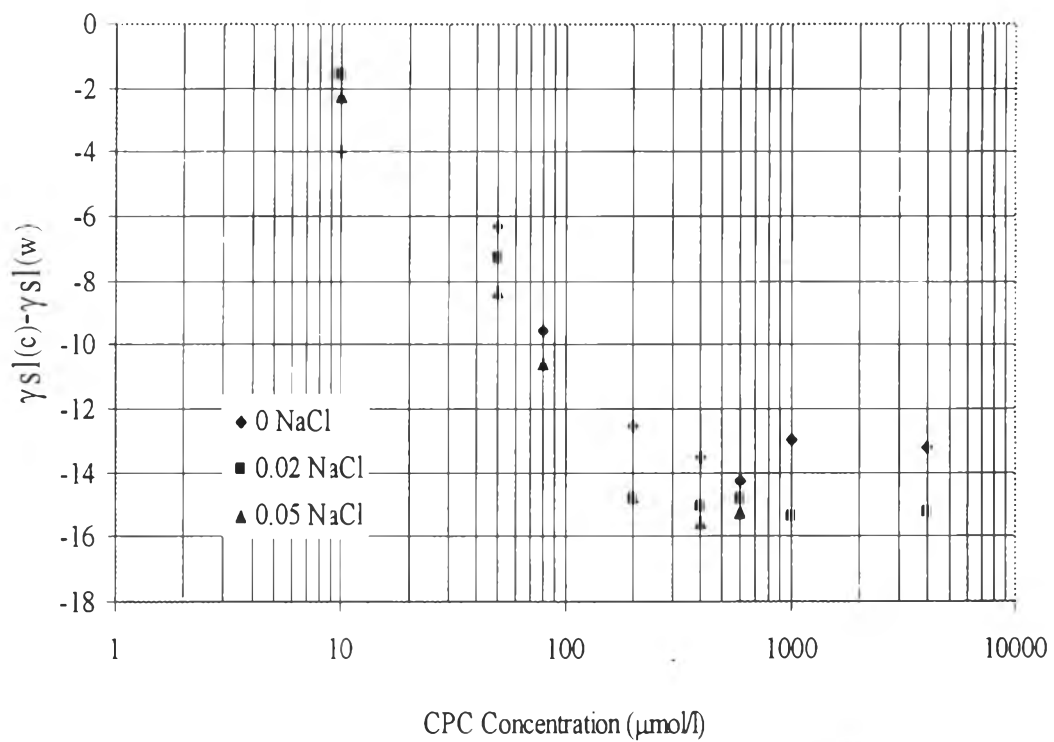
This relative solid/liquid interfacial tension can be related with CPC adsorption that is showed in Figure 4.17-4.19. Correspond to the concentration, the relative value decreases with increasing in adsorbed amount at solid/liquid interface. Therefore it can be seen that the surfactants do not only reduce the liquid/vapor surface tension but also decrease the solid/liquid interfacial tension.



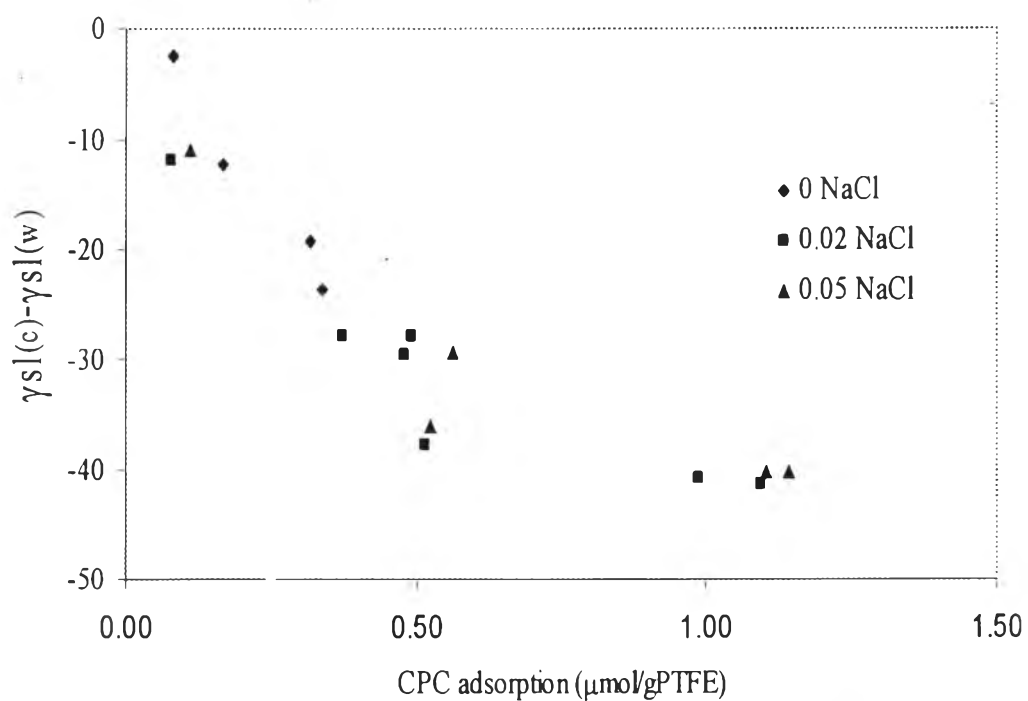
**Figure 4.14** Relative solid/liquid interfacial tension of PTFE as a function of CPC concentration.



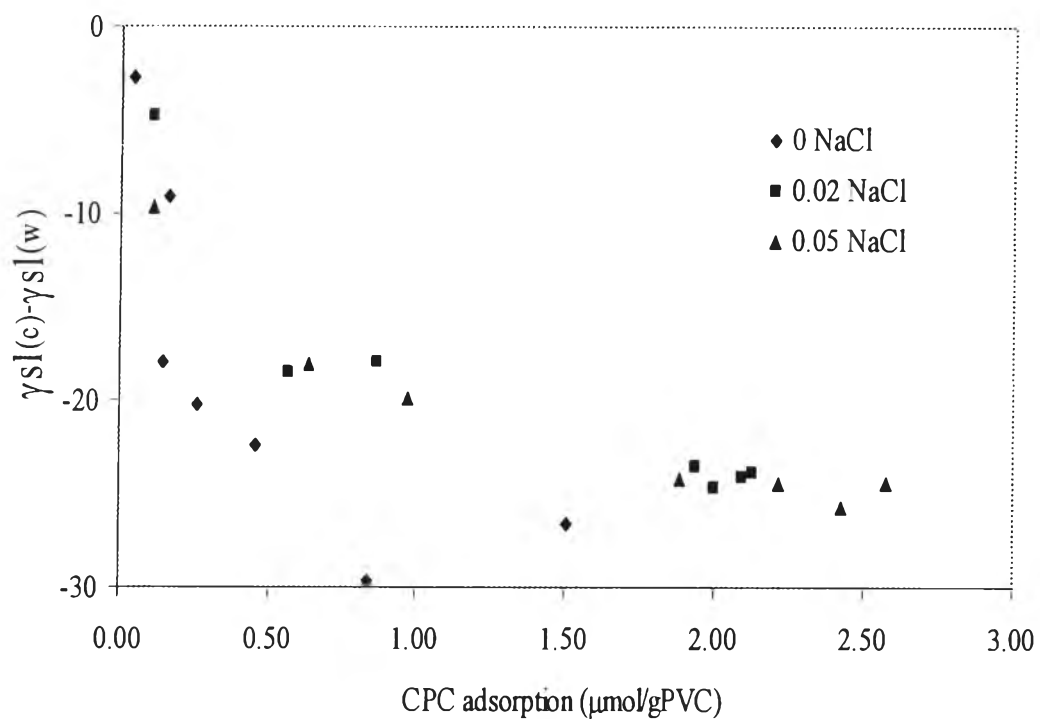
**Figure 4.15** Relative solid/liquid interfacial tension of PVC as a function of CPC concentration.



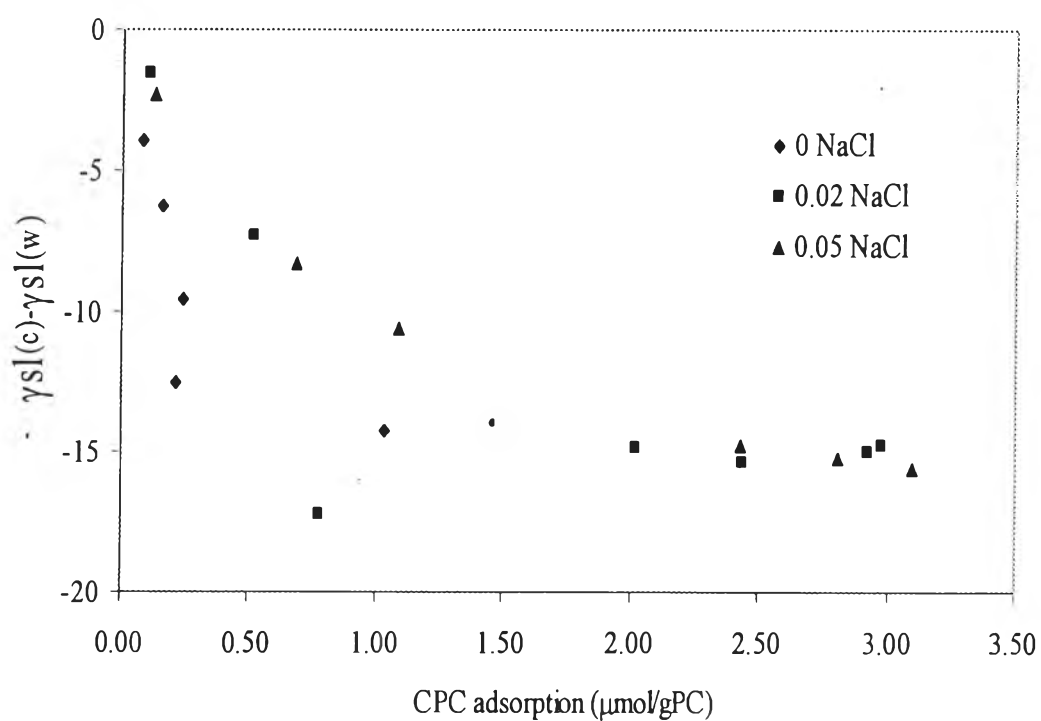
**Figure 4.16** Relative solid/liquid interfacial tension of PC as a function of CPC concentration.



**Figure 4.17** Relative solid/liquid interfacial tension of PTFE as a function of CPC adsorption.



**Figure 4.18** Relative solid/liquid interfacial tension of PVC as a function of CPC adsorption.

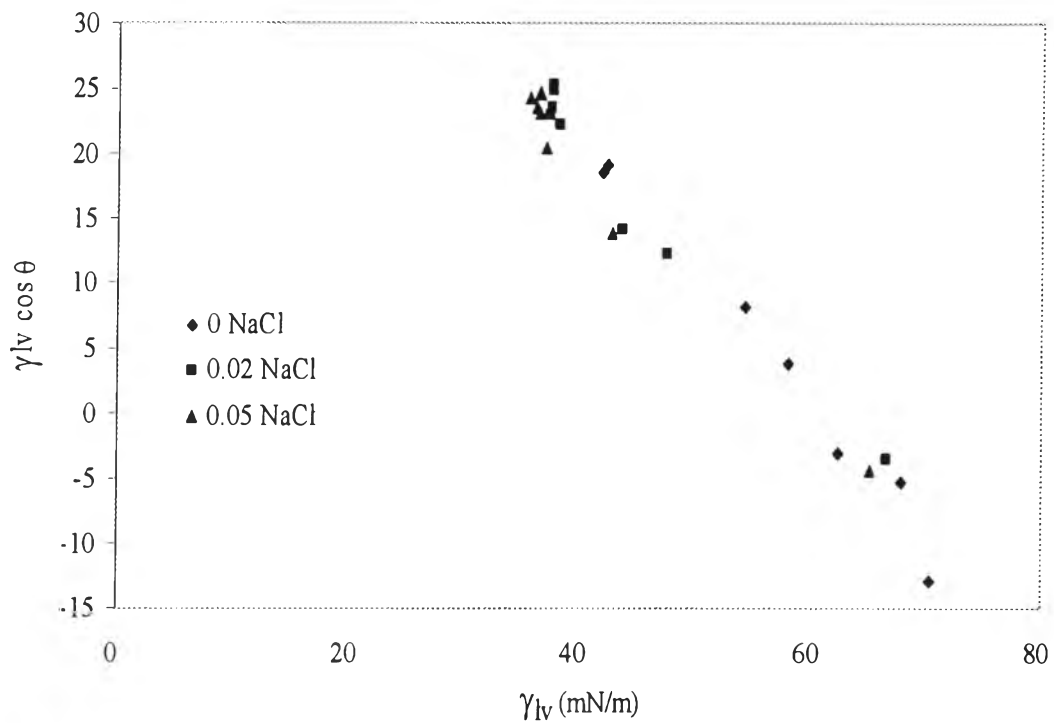


**Figure 4.19** Relative solid/liquid interfacial tension of PC as a function of CPC adsorption.

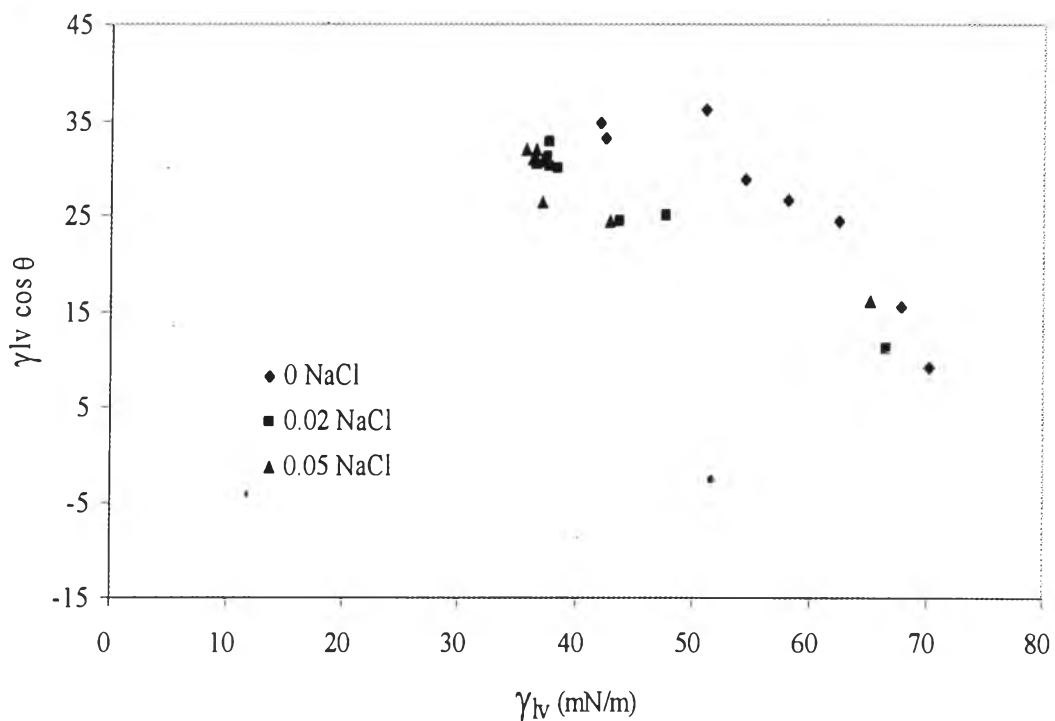
Moreover from Young's equation, the adsorption of surfactant can be related to equilibrium wetting. Figures 4.20 - 4.22, the adhesion tension plots, illustrate the adhesion tension,  $\gamma_{LV}\cos\theta$ , related to liquid/vapor surface tension of CPC solution. If  $\Gamma_{sv}$  for a surfactant is assumed to be zero, the slope of adhesion tension plot should be the ratio of surface excess concentration at solid/liquid to liquid/vapor interface.

In the case of PTFE, these plots show the straight line with slope of about -1. The results indicate that  $\Gamma_{SL}$  and  $\Gamma_{LV}$  are equal. It indicates that the surfactants can adsorb at the solid/liquid interface as well as at the liquid/vapor surface. The possible reason is due to the nature of PTFE surface can be considered as strong hydrophobic. Therefore, it can be suggested that the nature of solid/liquid interface and liquid/vapor surface are similar and the presence of salt does not considerably affect the wettability of surfactant solution that have the same  $\gamma_{LV}$ . From this reason, the plots between  $\cos\theta$  and  $\gamma_{LV}$ , Zisman's plots, do not show the deviation represented by Figure 4.23.

Contrary to PTFE, PVC and PC surfaces have considerably higher surface area. The adsorption of surfactants at the liquid/vapor and solid/liquid interfaces is different because of the different in the nature between these interfaces. It can be seen in Figure 4.21 and Figure 4.22 that the slope is being less negative which indicates that the  $\Gamma_{SL}$  is less than  $\Gamma_{LV}$  as the solid become more polar. Moreover, the CPC solutions varying with NaCl concentration do not produce the same contact angle at the same  $\gamma_{LV}$ . It produces smaller contact angle when the CPC solution has less ionic strength as depicted in Figure 4.24 and Figure 4.25. This deviation appears since NaCl cannot allow surfactants to adsorb more at the solid/liquid interface as well as at liquid/vapor interface. Hence, the  $\gamma_{SL}$  does not be reduced as effectively as  $\gamma_{LV}$  resulting in the deviation of Zisman's plot.

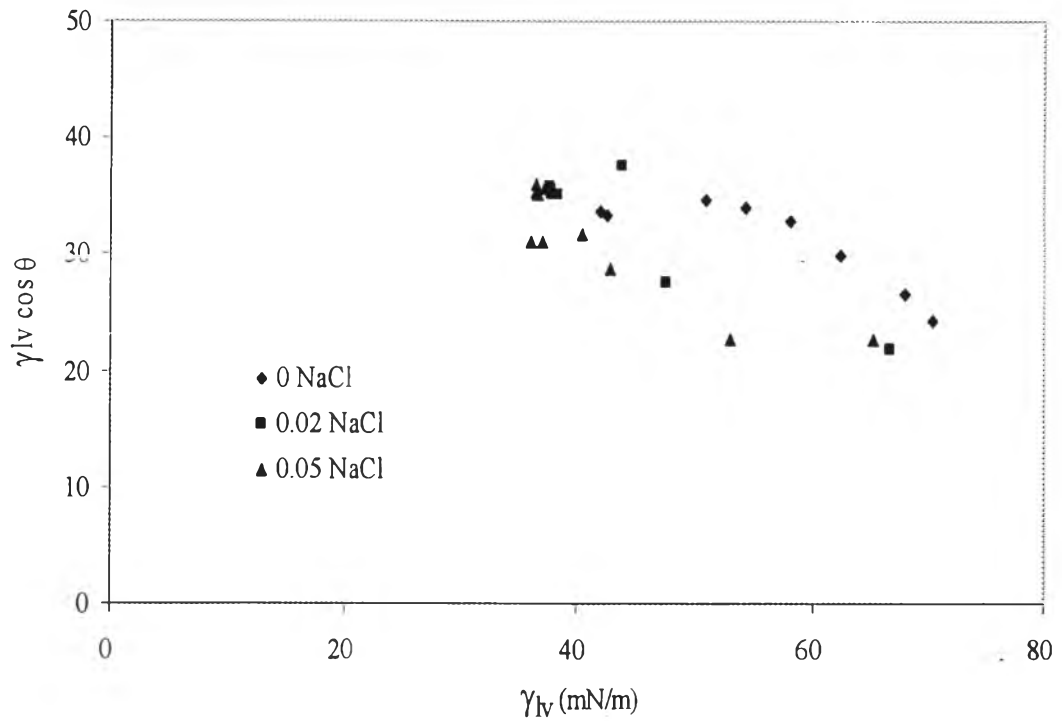


**Figure 4.20** Adhesion tension plot of CPC solution on PTFE.

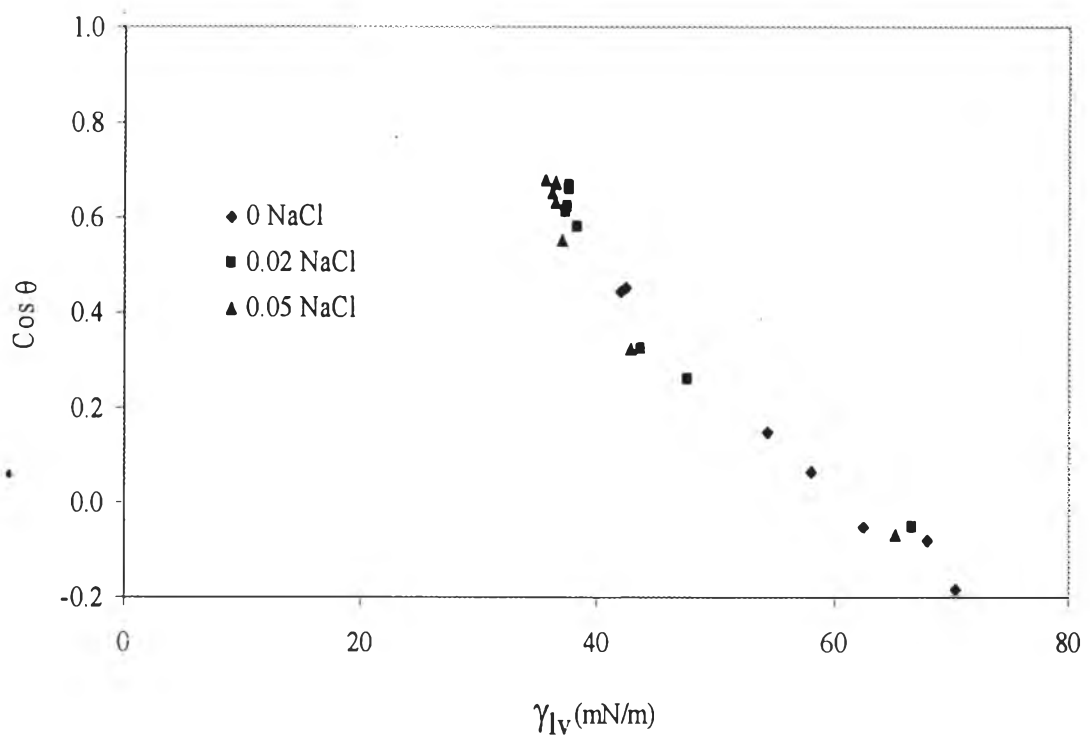


**Figure 4.21** Adhesion tension plot of CPC solution on PVC.

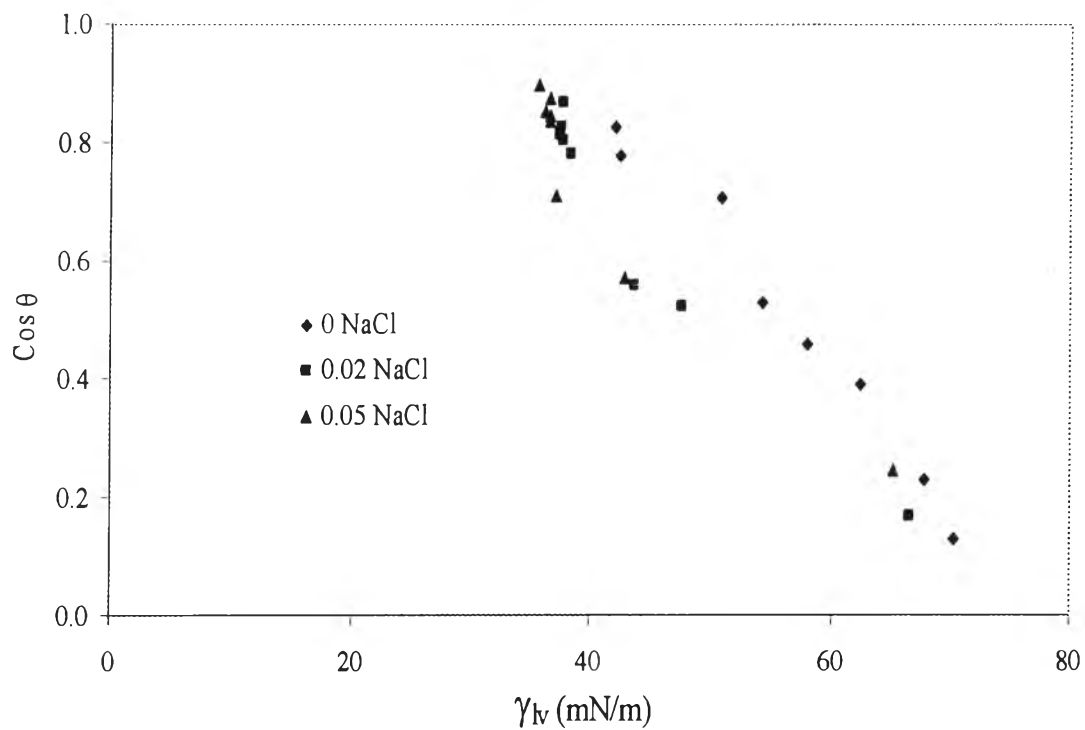




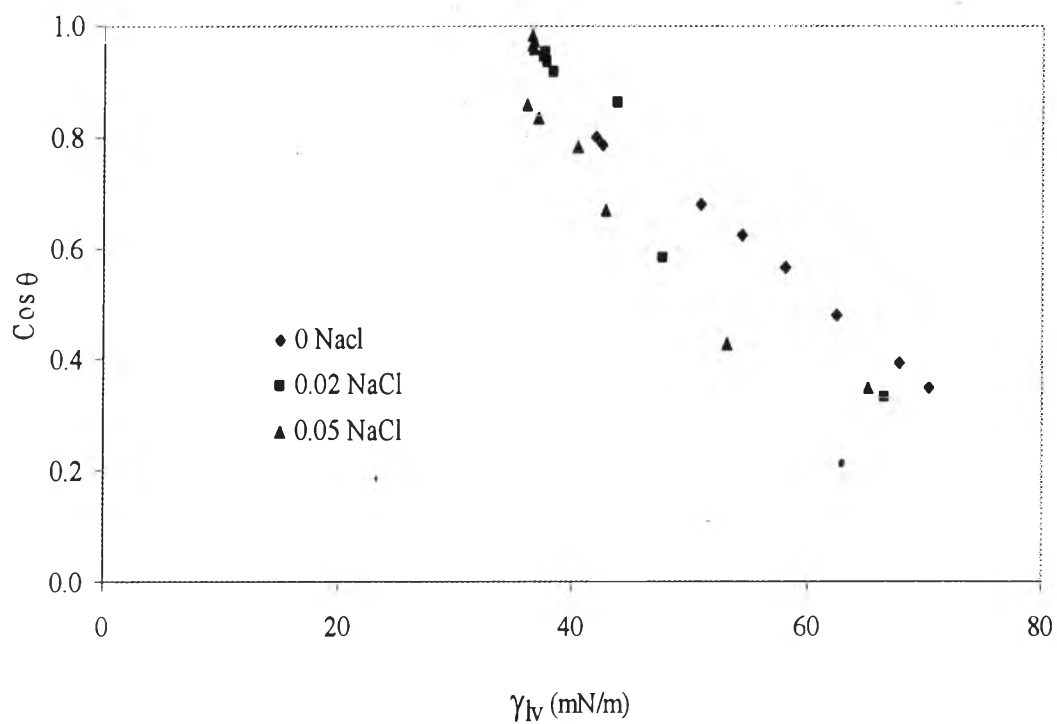
**Figure 4.22** Adhesion tension plot of CPC solution on PC.



**Figure 4.23** Contact angle of CPC on PTFE as a function of its  $\gamma_{LV}$ .



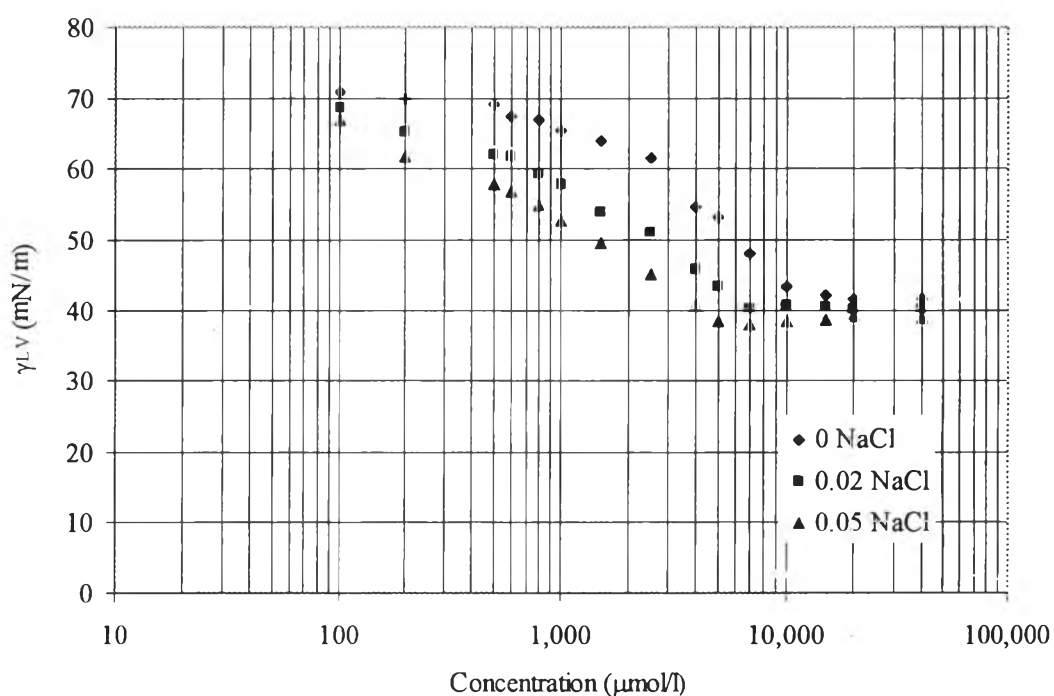
**Figure 4.24** Contact angle of CPC on PVC as a function of its  $\gamma_{LV}$ .



**Figure 4.25** Contact angle of CPC on PC as a function of its  $\gamma_{LV}$ .

#### 4.4 The Surface Tension and CMC of NaOBS

Figure 4.4 shows the plots of the surface tension of NaOBS solution with varying ionic strength. The surface tension decreased with increasing surfactant concentration and constant after reaches the CMC that is the break point of the plot. The CMC of NaOBS solution is 10000  $\mu\text{M}$  which is corresponding to literature data (10000  $\mu\text{M}$ , Dao *et al.*, 1998). From Figure 4.4, the CMC of NaOBS solutions decreased to 7000 and 5000  $\mu\text{M}$  as the salt concentration increased to 0.02 and 0.05, respectively.

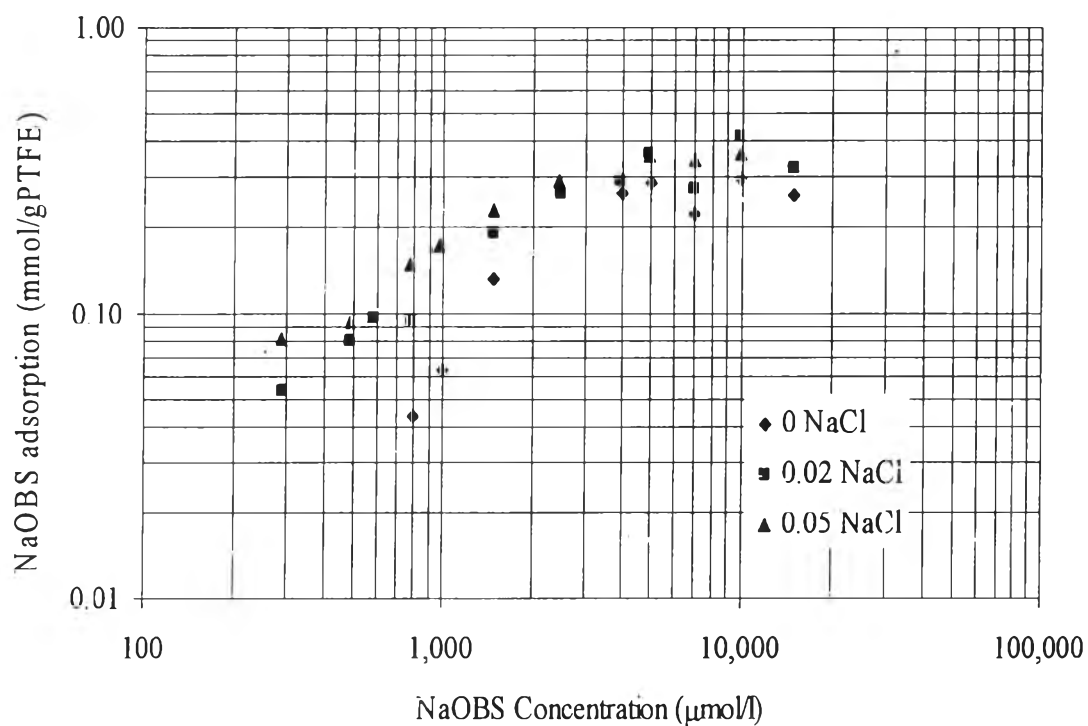


**Figure 4.26** NaOBS surface tension as a function of its concentration at various salt concentration.

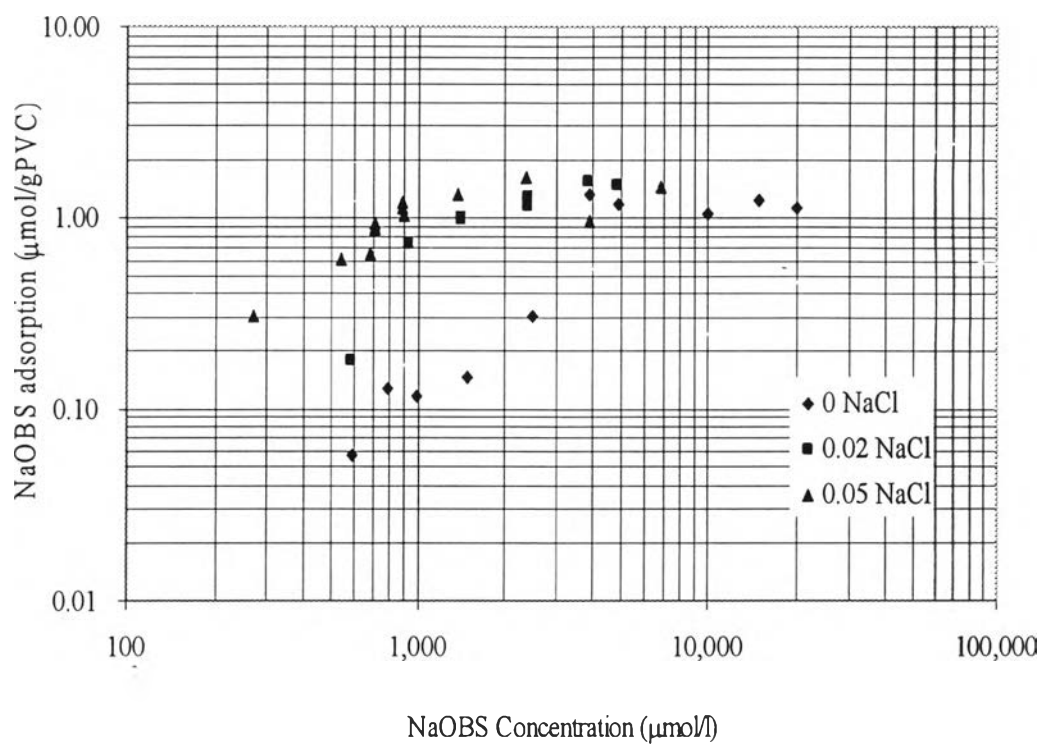
## 4.5 NaOBS Adsorption and Wetting on PTFE, PVC and PC

### 4.5.1 Adsorption Isotherms of NaOBS

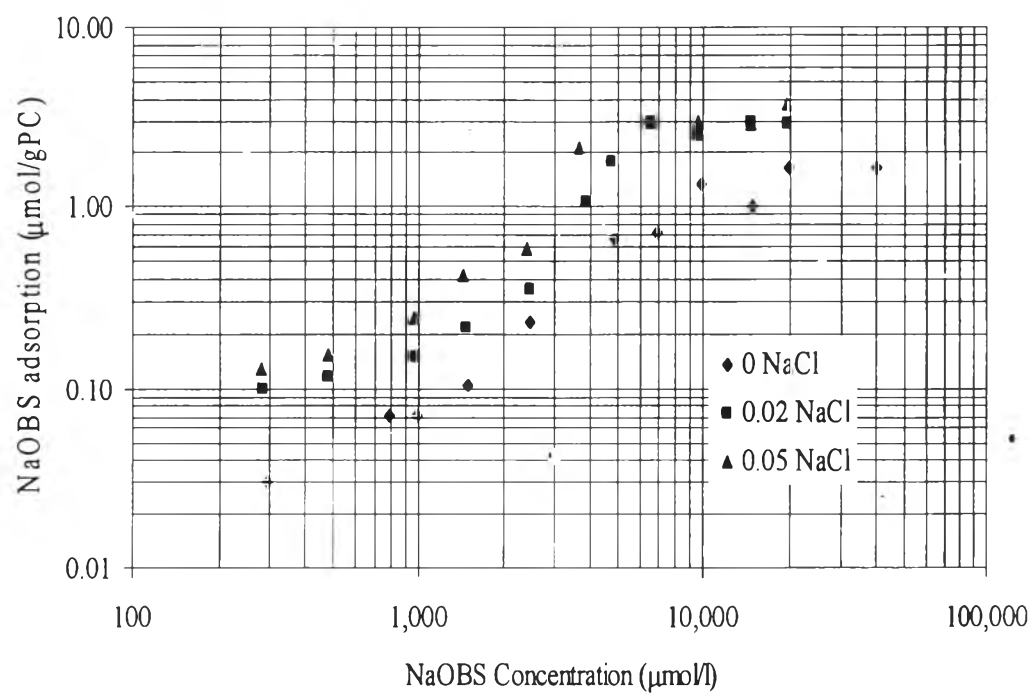
The adsorption isotherms of NaOBS on PTFE, PVC and PC with varying salt concentrations are respectively showed in Figure 4.27, Figure 4.28 and Figure 4.29. It can be observed that the NaOBS is gradually adsorbed more as its concentration is increased before the critical micelle concentration (CMC) is reached. Above the CMC, the NaOBS adsorption is constant and the isotherms leveled out at the CMC. Moreover, the present of salt reduces the CMC of NaOBS and also the repulsion between NaOBS head group which resulted in increasing adsorbed amount. However, the adsorption isotherms of NaOBS are similarly as in the case of CPC.



**Figure 4.27** Adsorption isotherms of NaOBS on PTFE.



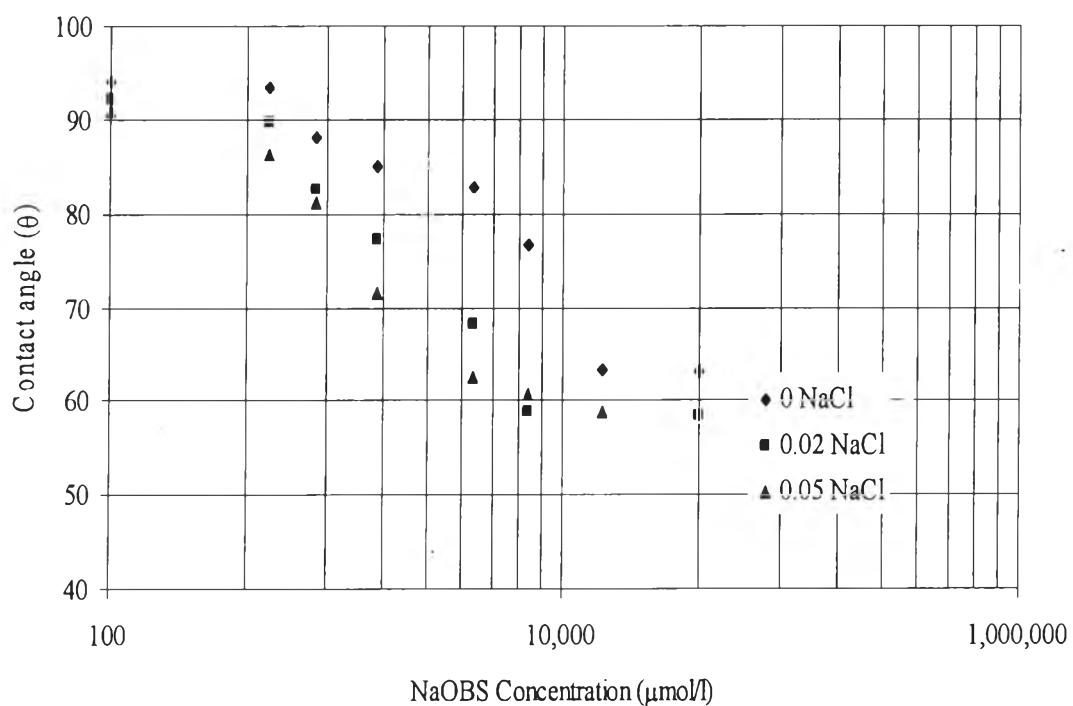
**Figure 4.28** Adsorption isotherms of NaOBS on PVC.



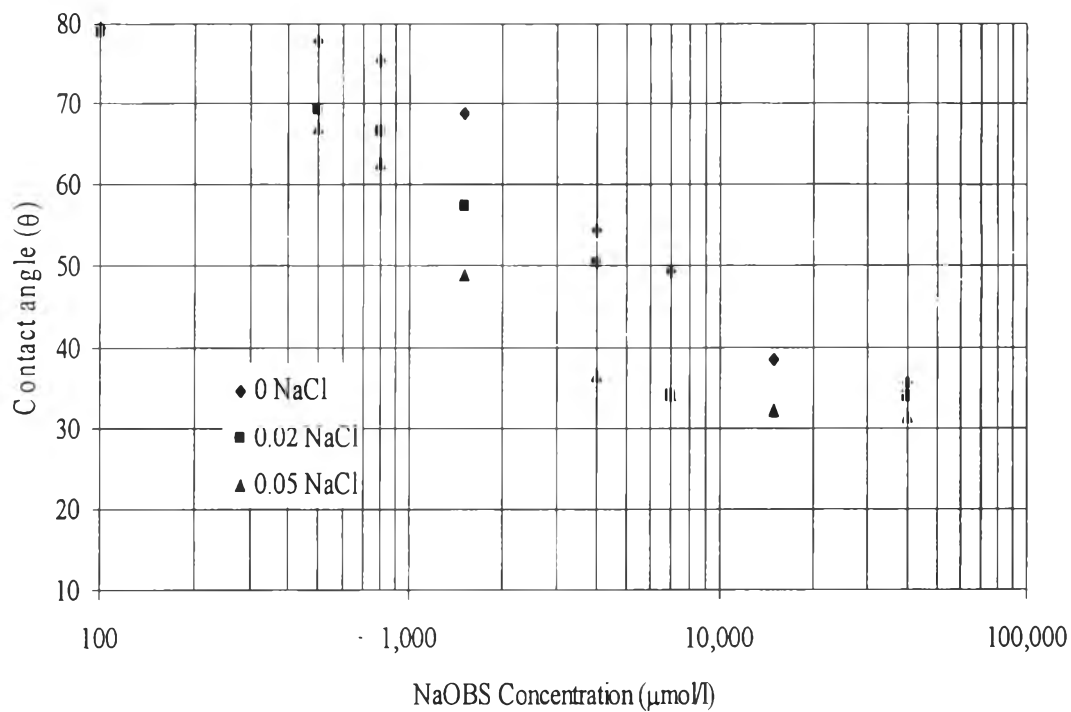
**Figure 4.29** Adsorption isotherms of NaOBS on PC.

#### 4.5.2 Contact Angle of NaOBS Solution on Plastics

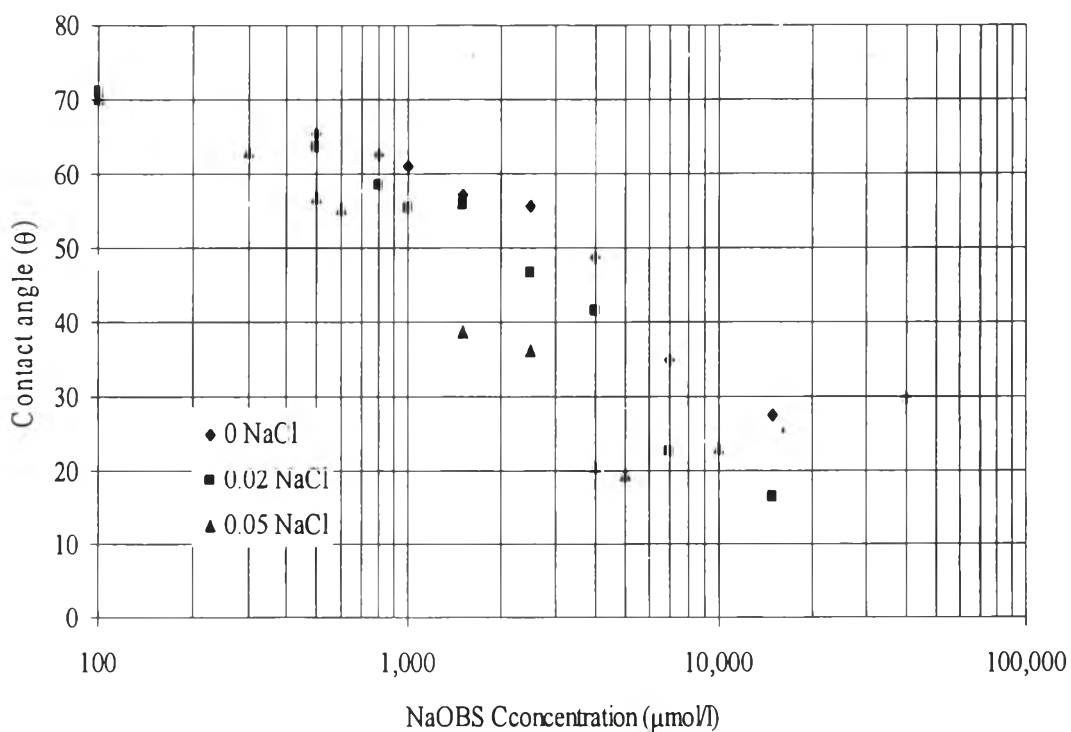
The contact angle of NaOBS solutions on PTFE, PVC and PC are respectively showed in Figure 4.30, Figure 4.31 and Figure 4.32. The contact angle decreases when the concentration of NaOBS increases. A comparison of contact angle of NaOBS solutions reveals the same order as mentioned in the case of CPC case. Moreover, the results show that the NaOBS solutions with high ionic strength create smaller contact angle which is the same as in the case of CPC solutions.



**Figure 4.30** Contact angle of NaOBS solution on PTFE with varying NaCl concentration.



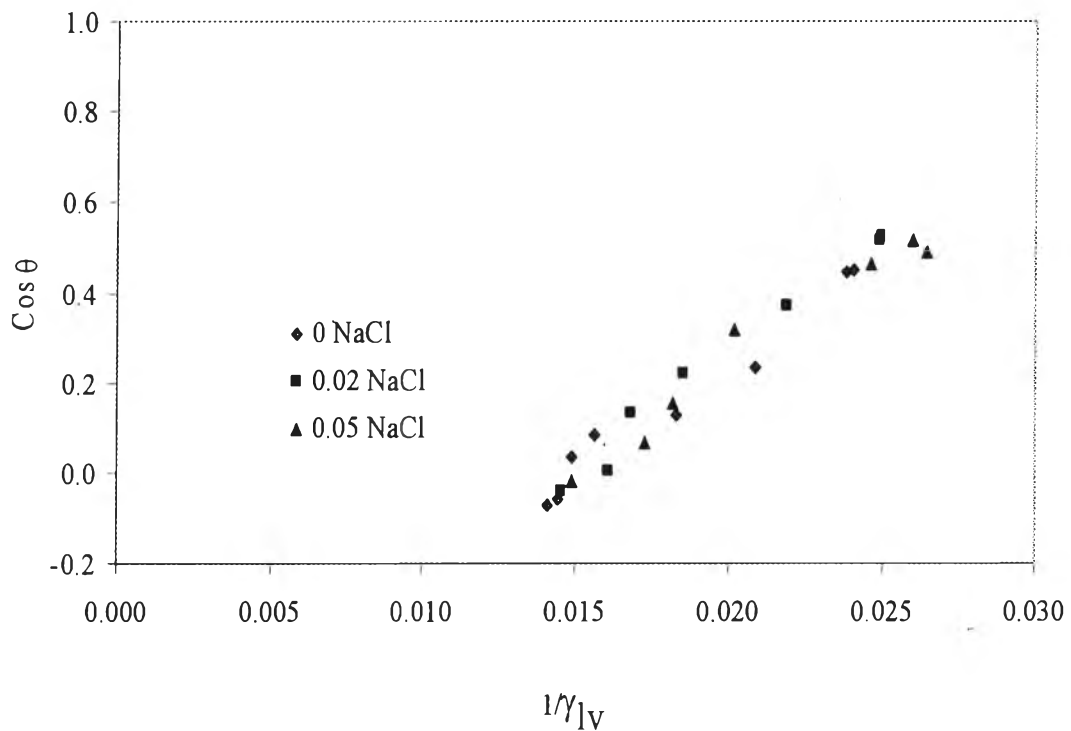
**Figure 4.31** Contact angle of NaOBS solution on PVC with varying NaCl concentration.



**Figure 4.32** Contact angle of NaOBS solution on PC with varying NaCl concentration.

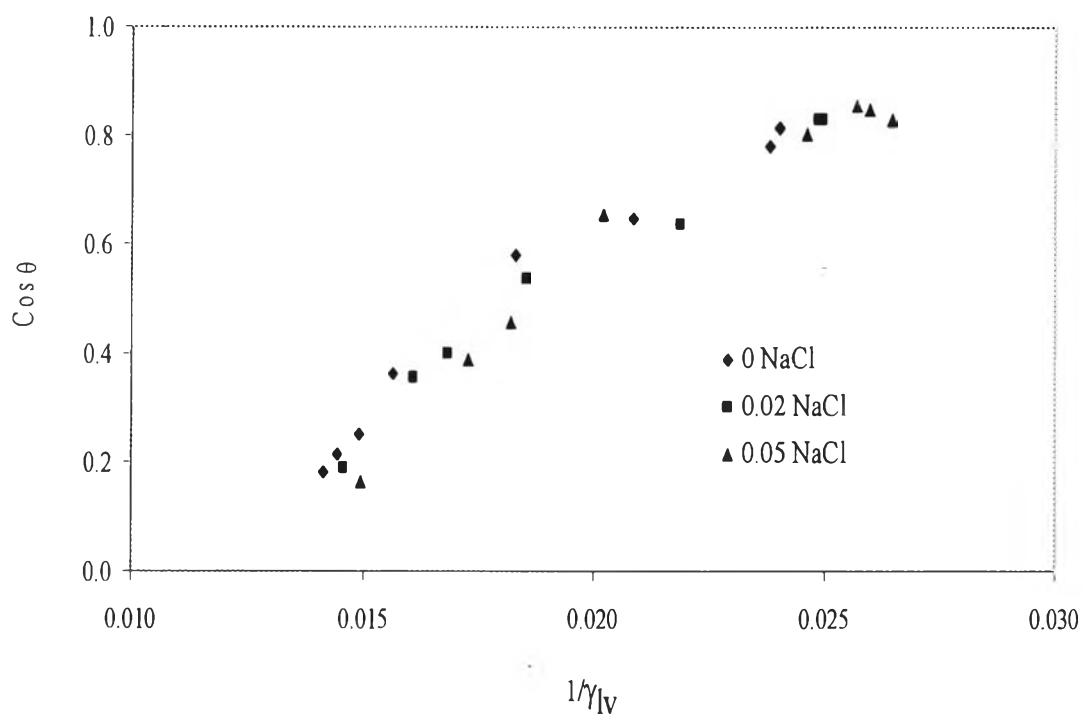
#### 4.5.3 Wetting Enhancement by NaOBS

As mentioned above, if the values of  $\gamma_{SL}$  and  $\gamma_{SV}$  are constant, the plots between  $\cos\theta$  and the inversion of liquid/vapor surface tension of CPC solution,  $1/\gamma_{LV}$ , should be straight line and intercept at zero. However, Figure 4.33 – 4.35 do not show the straight line with intercept at zero so that the solid/liquid interfacial tension,  $\gamma_{SL}$ , should not be constant. Moreover, Figure 4.36-38 indicate that  $\gamma_{LV} \cos\theta$  vary with NaOBS concentration. Therefore, it can be suggested that  $\gamma_{SL}$  should be a function of surfactant concentration.

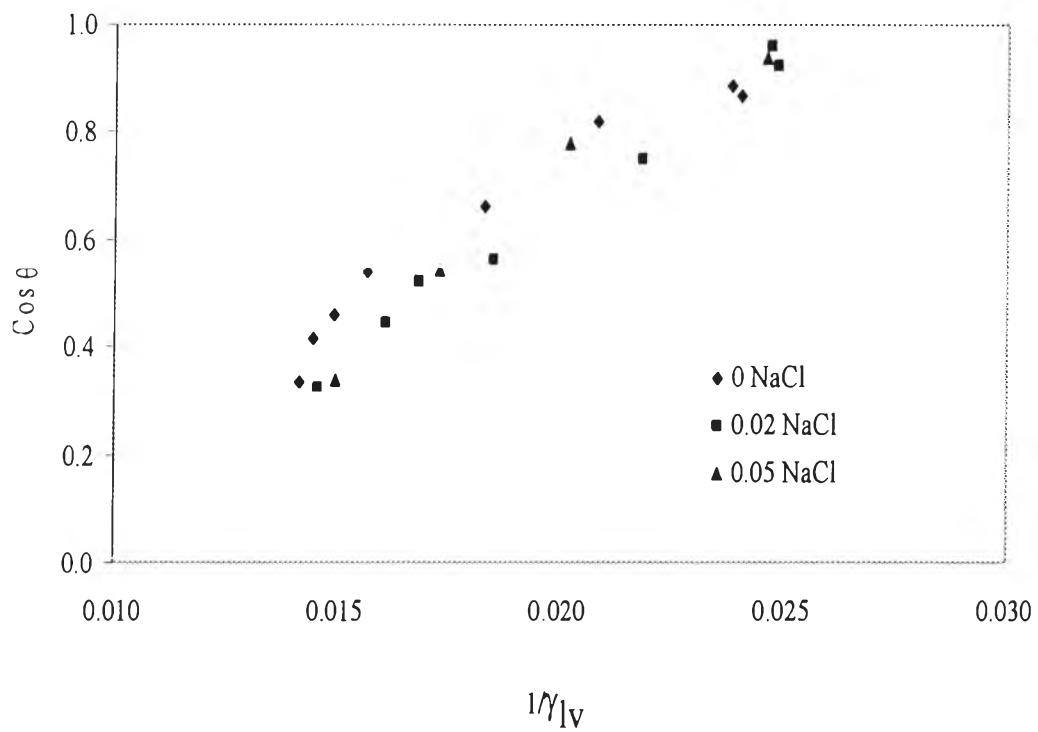


**Figure 4.33** Contact angle on PTFE related to inversion liquid/vapor surface tension of NaOBS solution.





**Figure 4.34** Contact angle on PVC related to inversion liquid/vapor surface tension of NaOBS solution.



**Figure 4.35** Contact angle on PC related to inversion liquid/vapor surface tension of NaOBS solution.

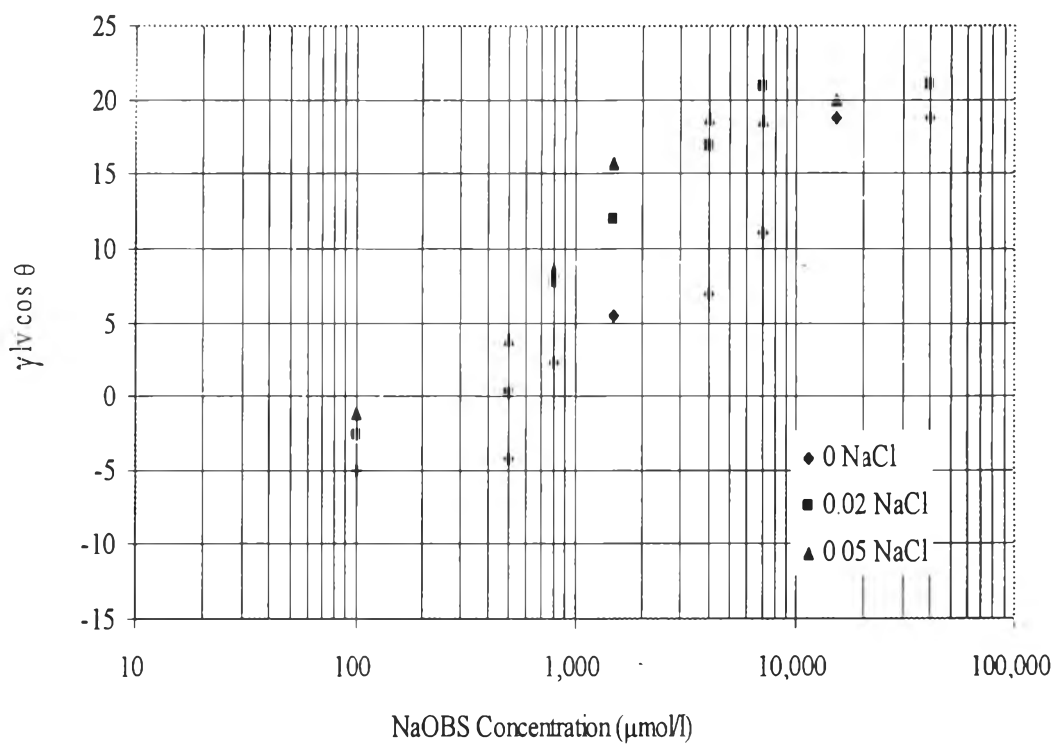


Figure 4.36  $\gamma_{LV} \cos \theta$  on PTFE related to NaOBS concentration.

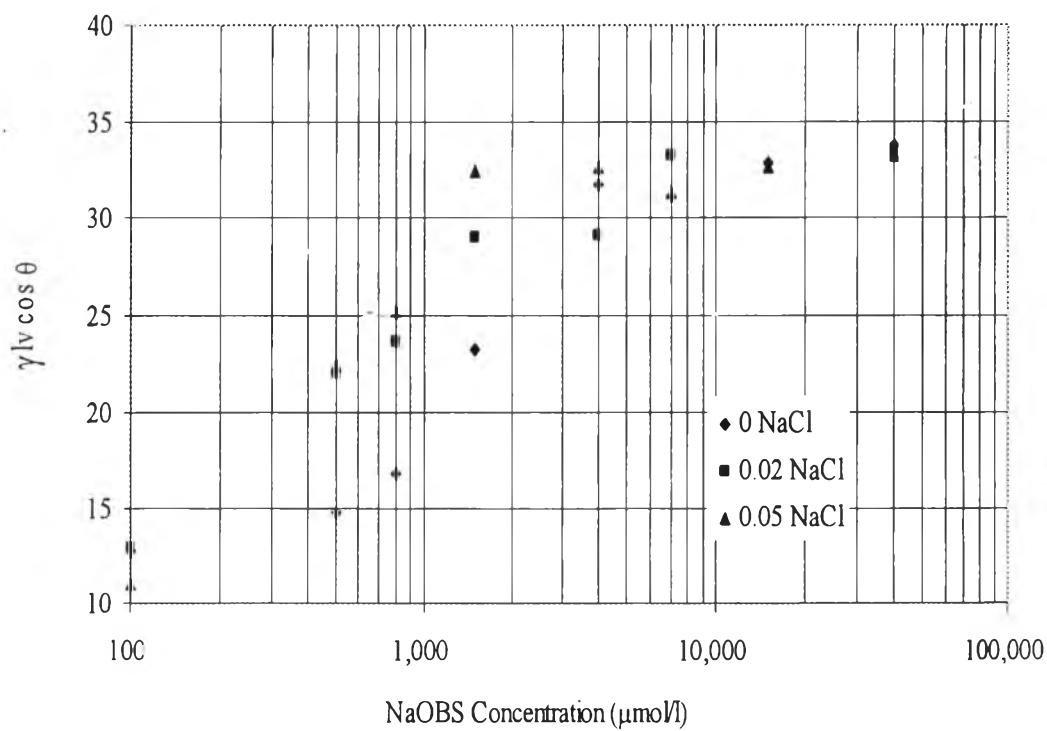
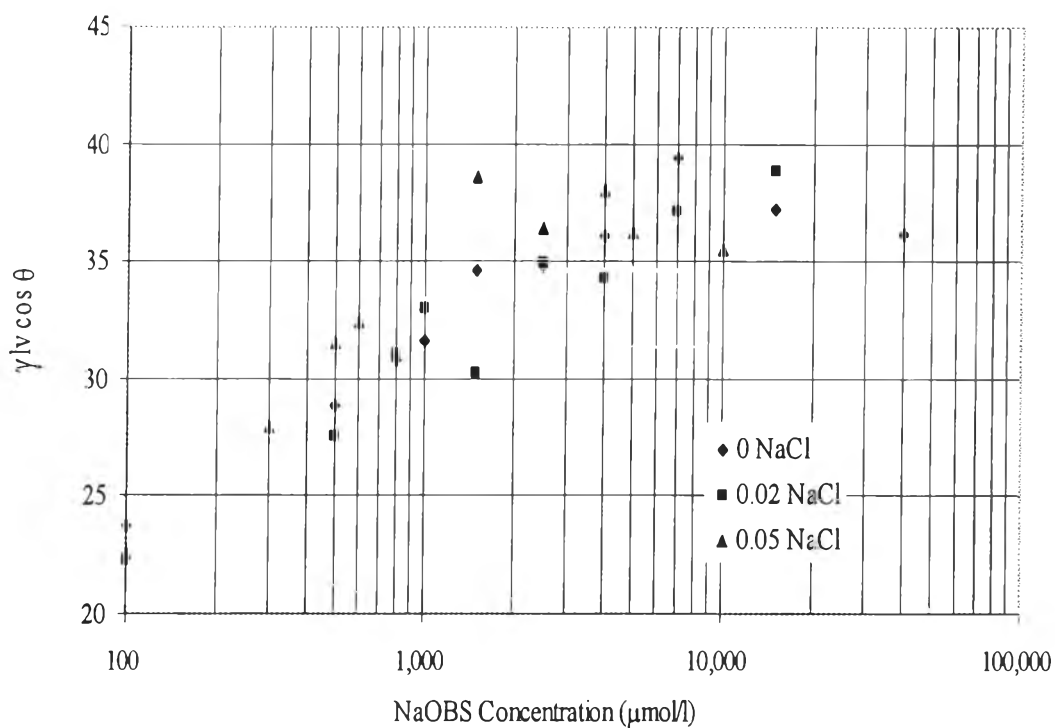


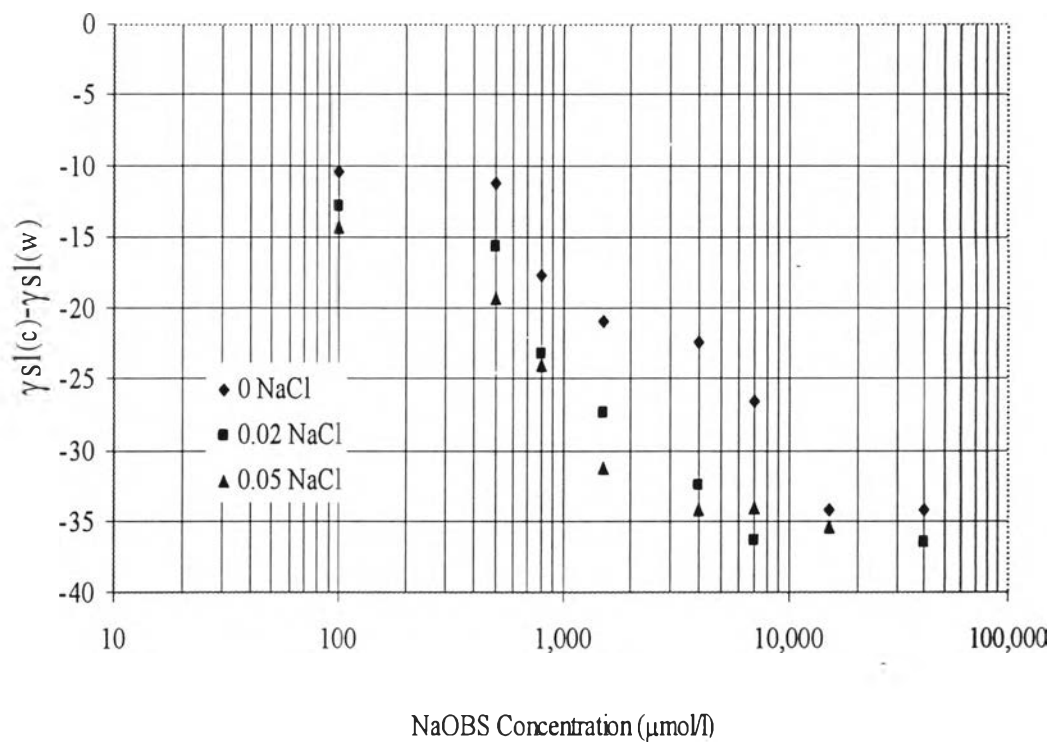
Figure 4.37  $\gamma_{LV} \cos \theta$  on PVC related to NaOBS concentration.



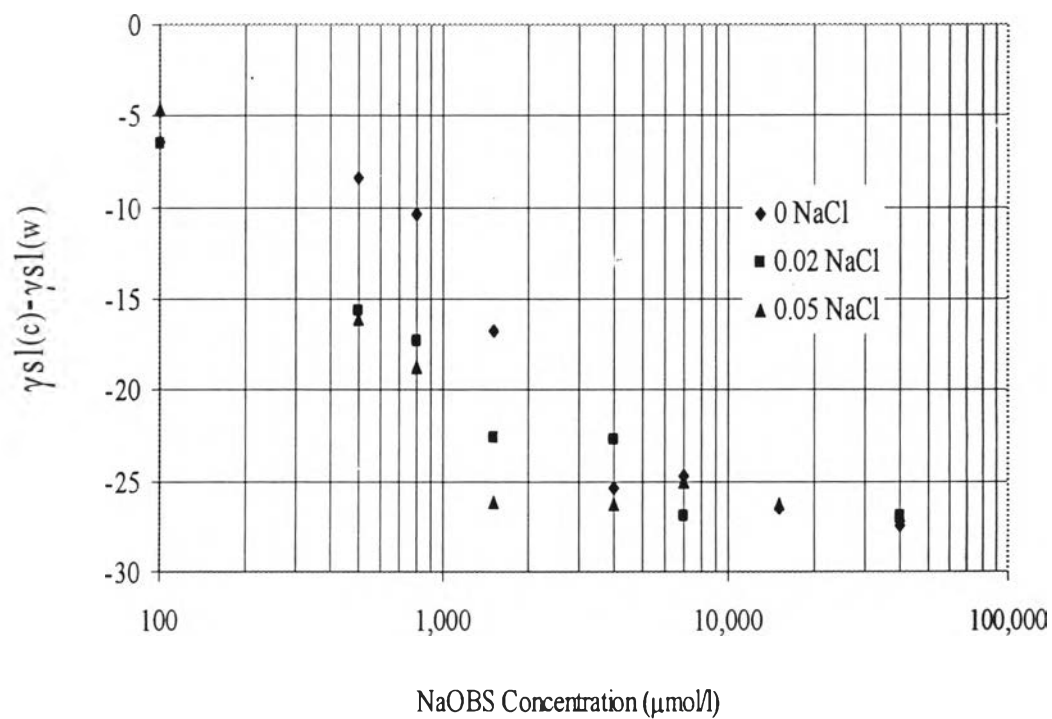
**Figure 4.38**  $\gamma_{LV} \cos \theta$  on PC related to NaOBS concentration.

Figure 4.39-4.41 illustrate the relationship between the relative solid/liquid interfacial tension,  $\gamma_{SL}(c) - \gamma_{SL}(w)$ , and the concentration. This relative value decreases with increasing NaOBS concentration. In addition, at the same concentration, it decreases to lower value when the solutions have more ionic strength that allows more surfactants to adsorb at the solid/liquid interface.

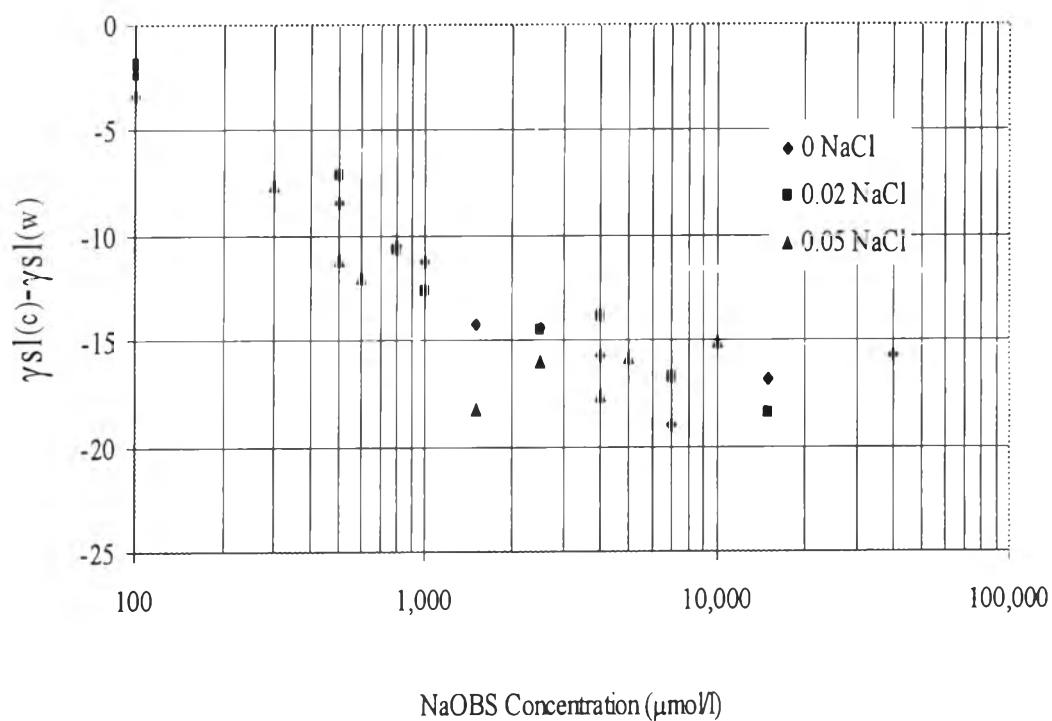
Also, when the relative solid/liquid interfacial tension is related with CPC adsorption it show that the relative value decrease with increasing in adsorbed amount represented by Figure 4.42-4.44. Hence, it can be suggested that the  $\gamma_{SL}$  should be a function of NaOBS adsorption and concentration.



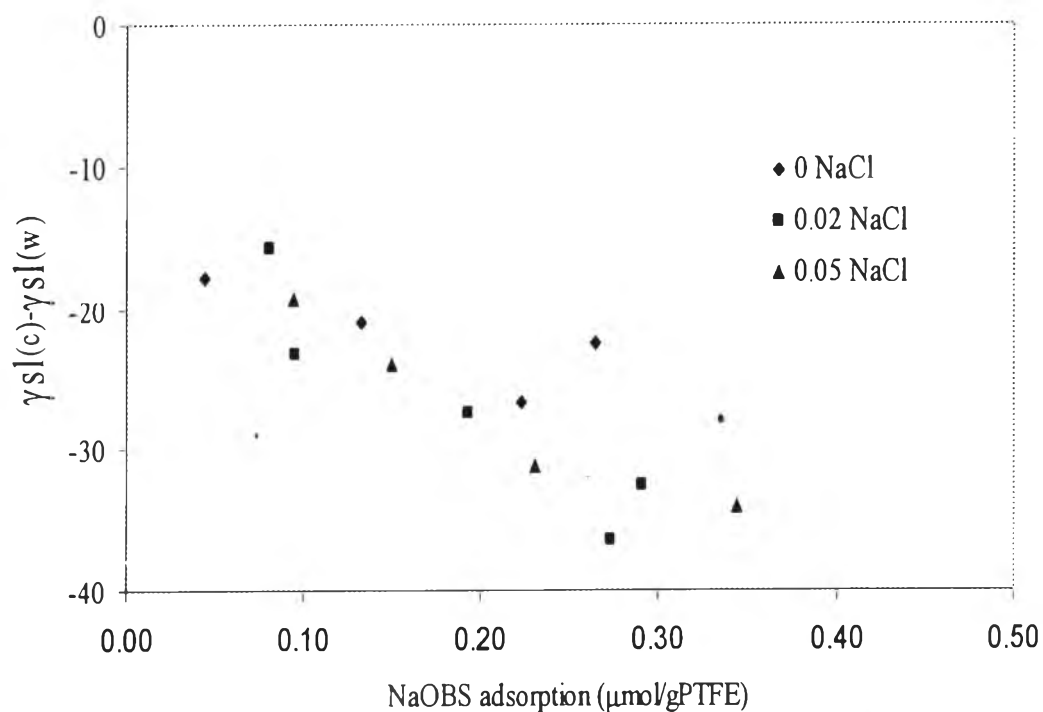
**Figure 4.39** Relative solid/liquid interfacial tension of PTFE as a function of NaOBS concentration.



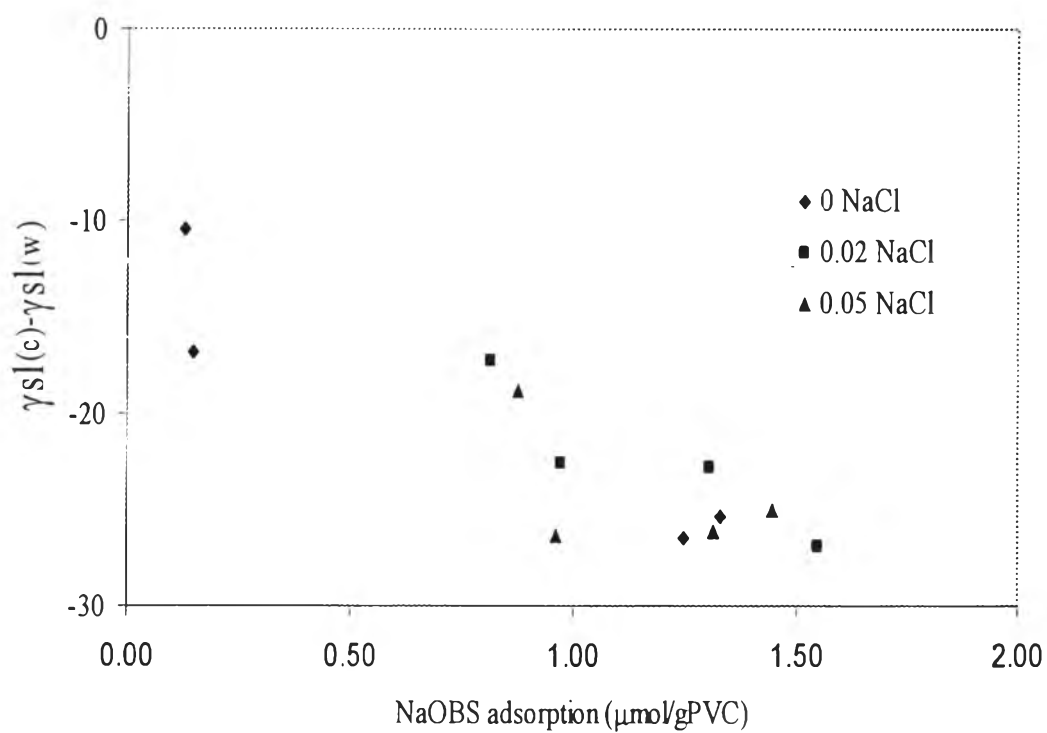
**Figure 4.40** Relative solid/liquid interfacial tension of PVC as a function of NaOBS concentration.



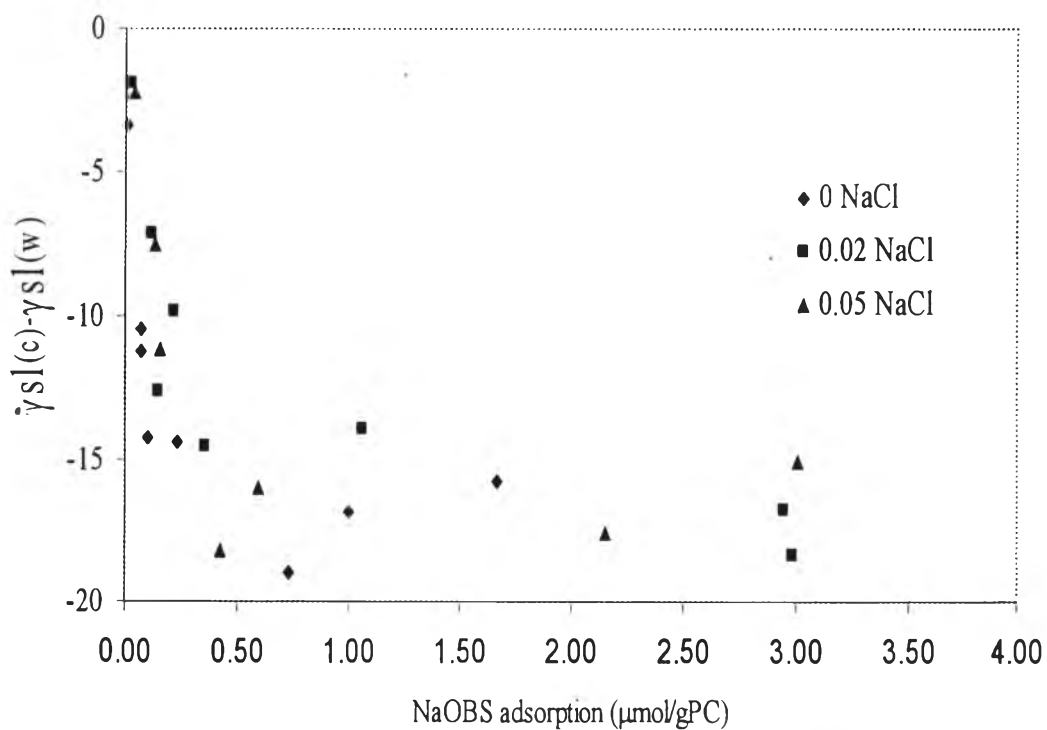
**Figure 4.41** Relative solid/liquid interfacial tension of PC as a function of NaOBS concentration



**Figure 4.42** Relative solid/liquid interfacial tension of PTFE as a function of NaOBS adsorption.



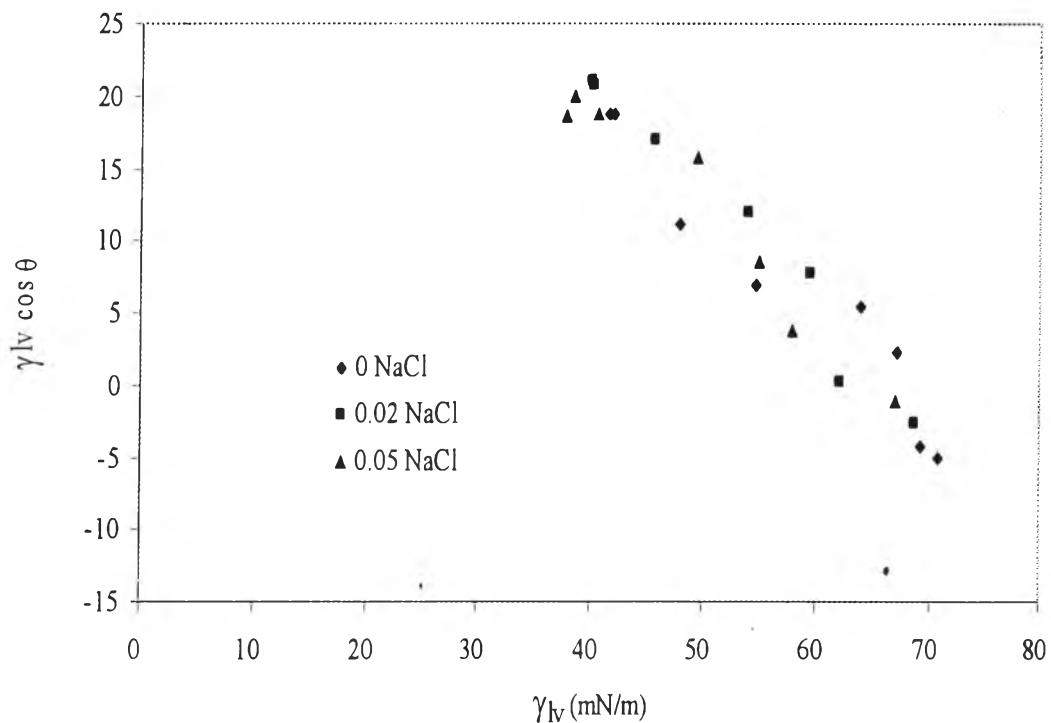
**Figure 4.43** Relative solid/liquid interfacial tension of PVC as a function of NaOBS adsorption.



**Figure 4.44** Relative solid/liquid interfacial tension of PC as a function of NaOBS adsorption.

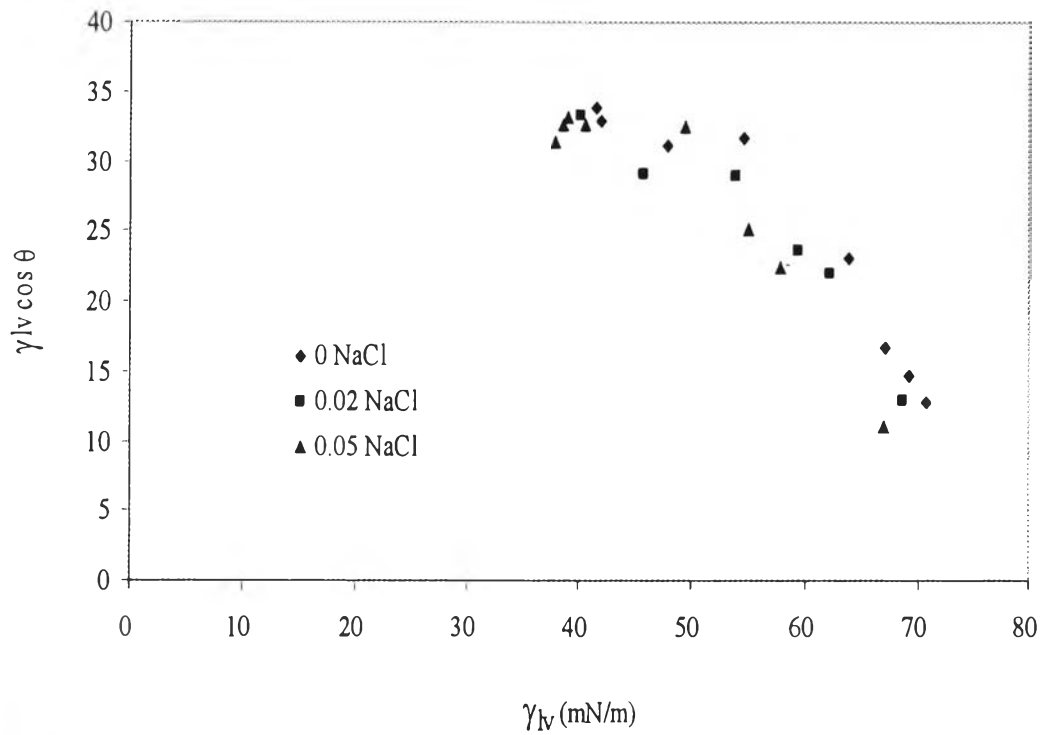
From Figure 4.45-4.47, the adhesion tension plots exhibit the straight line with slope of about -1 in the case of PTFE and give the slope less than 1 for PVC and PC. It can be suggested by the same explanation in CPC case which is the difference between the nature of liquid/vapor and solid/liquid interface.

Contrary to CPC case, the NaOBS solutions varying with NaCl concentration produce almost the same contact angle at the same  $\gamma_{LV}$ , have no deviation in Zisman's plot, which is depicted in Figure 4.48-4.50. The different in the structure of CPC and NaOBS is a likely reason (Supalate, 2004). NaOBS only eight carbon atoms in the hydrophobic tail while CPC has sixteen carbon atoms. Although the solid become more polar NaOBS still has some rooms at the solid/liquid interface. The presence of NaCl can allow surfactant to adsorb more at this interface so that the  $\gamma_{SL}$  would be reduced almost as effectively as  $\gamma_{LV}$ . Hence, the polarity of solid seems to have no effect on contact angle of NaOBS solution.

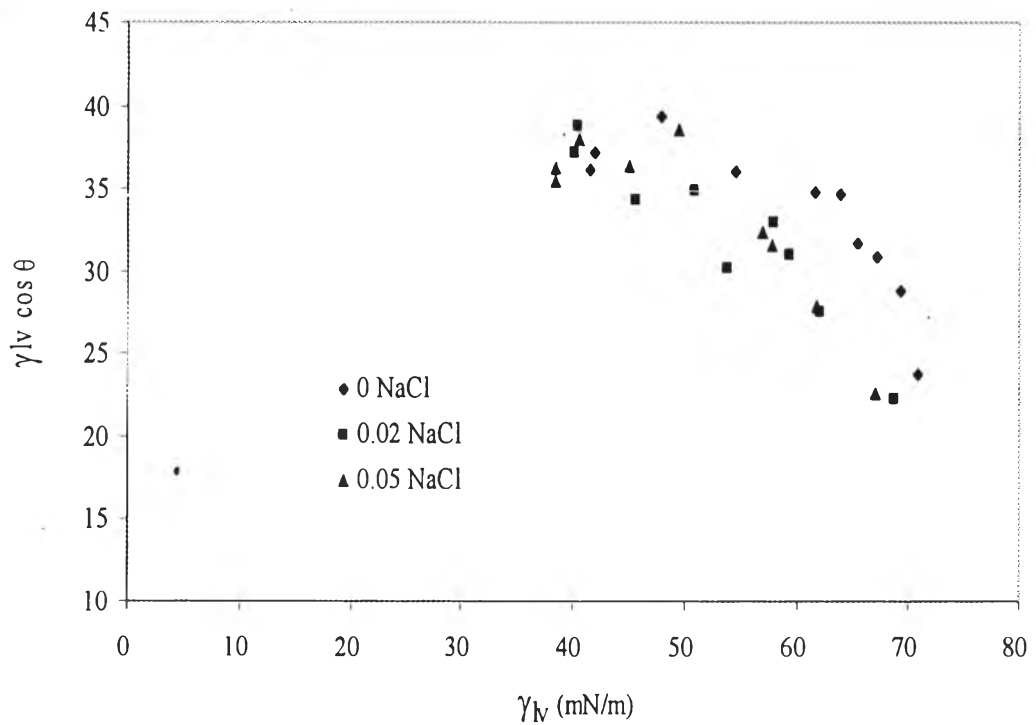


**Figure 4.45** Adhesion tension plot of NaOBS solution on PTFE.

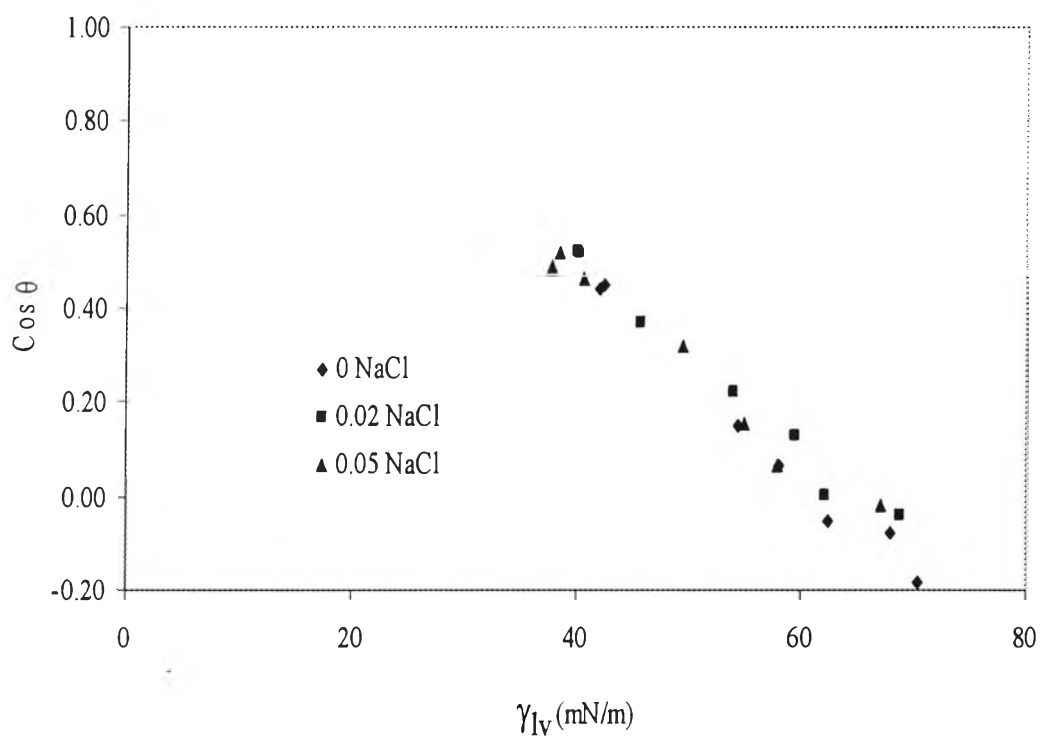




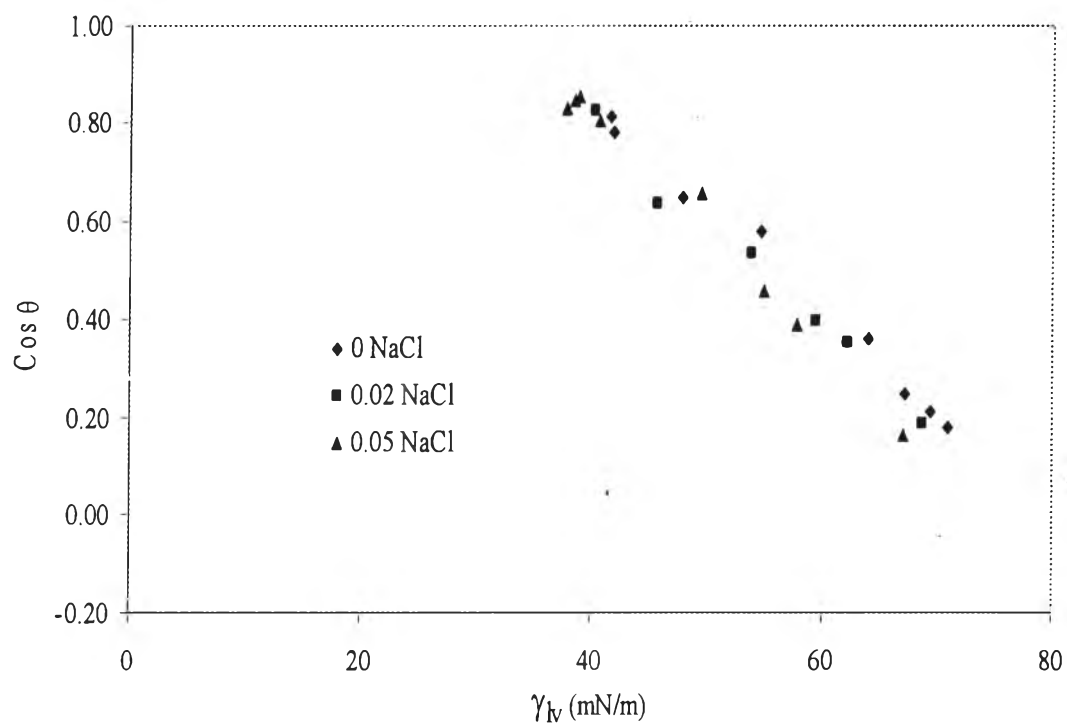
**Figure 4.46** Adhesion tension plot of NaOBS solution on PVC.



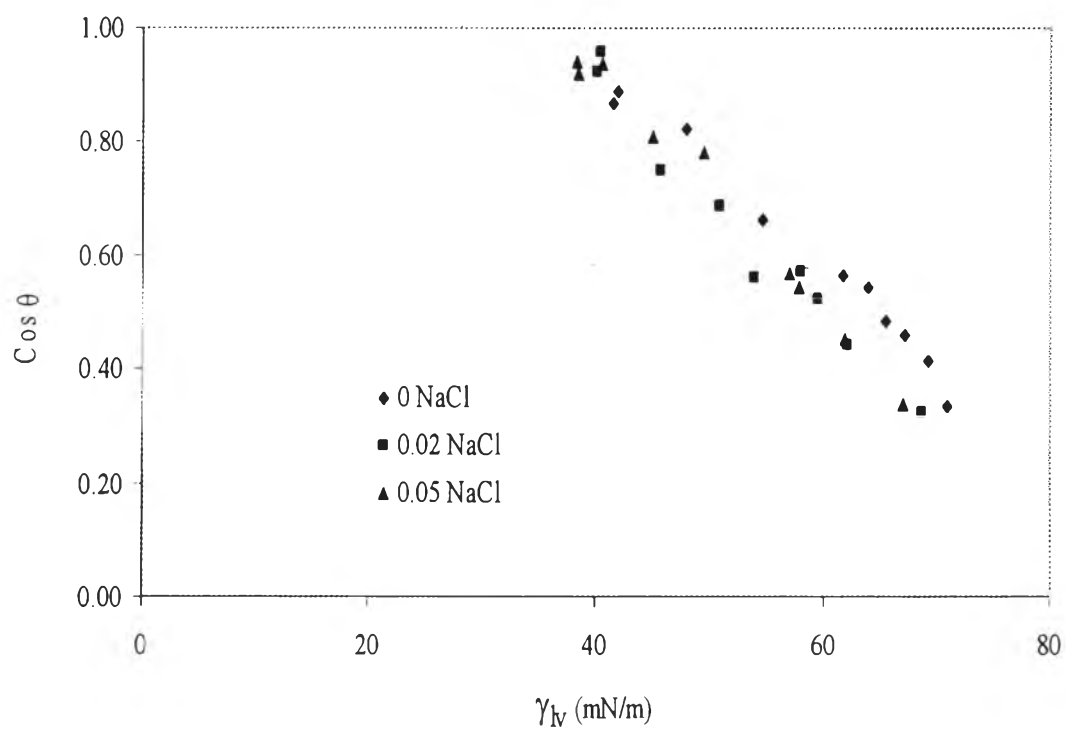
**Figure 4.47** Adhesion tension plot of NaOBS solution on PC.



**Figure 4.48** Contact angle of NaOBS on PTFE as a function of its  $\gamma_{LV}$ .



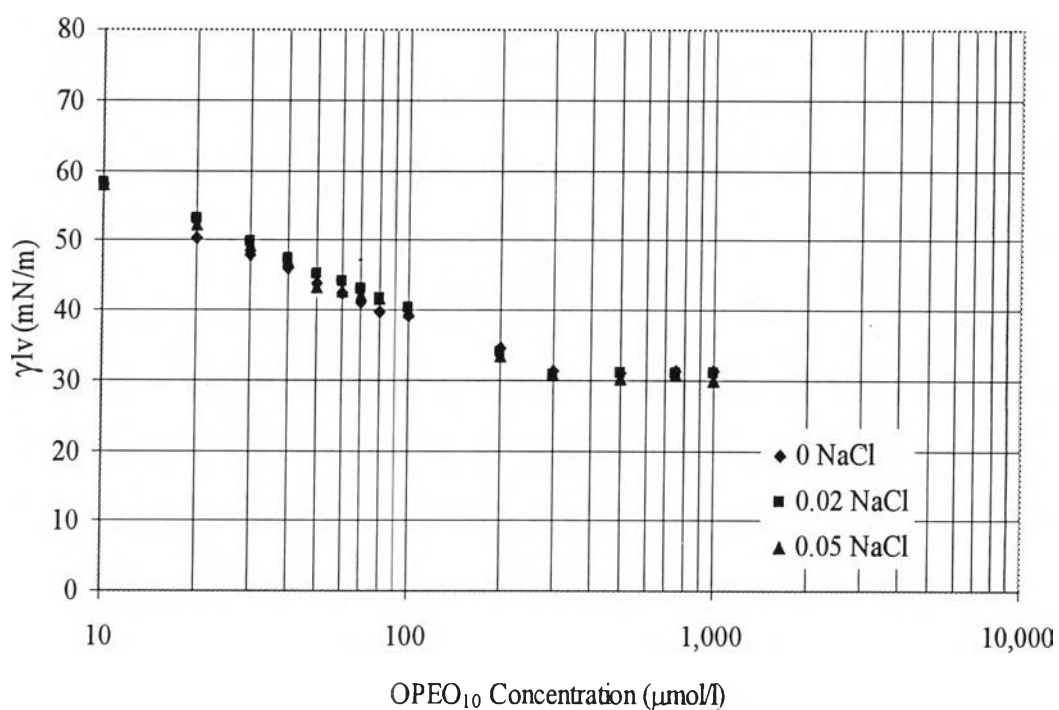
**Figure 4.49** Contact angle of NaOBS on PVC as a function of its  $\gamma_{LV}$ .



**Figure 4.50** Contact angle of NaOBS on PC as a function of its  $\gamma_{LV}$ .

#### 4.6 The Surface Tension and CMC of OPEO<sub>10</sub>

Figure 4.51 shows the plots of the liquid/vapor surface tension of OPEO<sub>10</sub> solution with varying ionic strength. The liquid/vapor surface tension decreased with increasing surfactant concentration and constant after reach the CMC which is the break point of the plot. The CMC of OPEO<sub>10</sub> solution is 240  $\mu\text{M}$ . From Figure 4.51, there is no effect from the present of NaCl up to the NaCl concentration of 0.05 M.



**Figure 4.51** OPEO<sub>10</sub> surface tension as a function of its concentration at various salt concentration.

## 4.7 OPEO<sub>10</sub> Adsorption and Wetting on PTFE, PVC and PC

### 4.7.1 Adsorption Isotherms of OPEO<sub>10</sub>

The adsorption isotherms of OPEO<sub>10</sub> on PTFE, PVC and PC with varying salt concentrations are showed in Figure 4.52. The isotherms are plotted in the form of the logarithm of the adsorbed amount versus the equilibrium concentration of OPEO<sub>10</sub> solution. The results show a slow rise in the adsorbed amount where an increase in adsorption occurs until before the critical micelle concentration (CMC). Above the CMC the adsorption reaches a constant value which all of the isotherms level out to the plateau at about the CMC region.

As shown in Figure 4.52, it can be noted that the slope of the OPEO<sub>10</sub> adsorption isotherms on PTFE, PVC and PC are about 1, which indicate that there are no lateral interaction of OPEO<sub>10</sub> adsorption on these three plastics.

Only the surfactant concentration at 0 M of NaCl was used to represent all of the adsorption of OPEO<sub>10</sub> since the preliminary results showed no significant differences in the liquid/vapor surface tension from varying salt concentration.

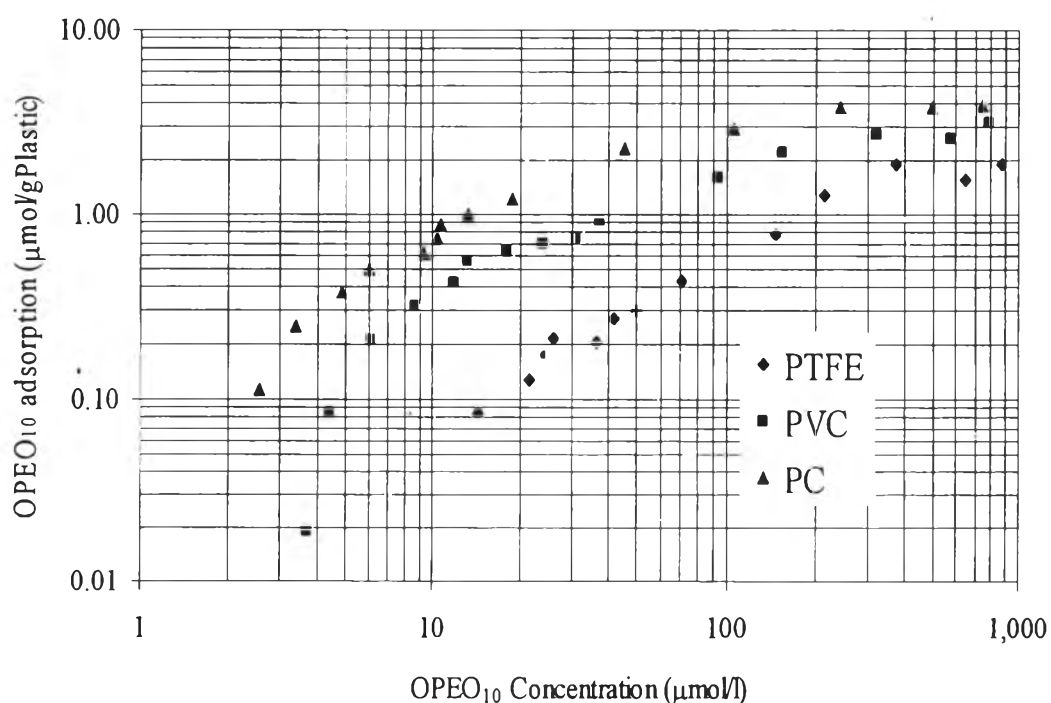
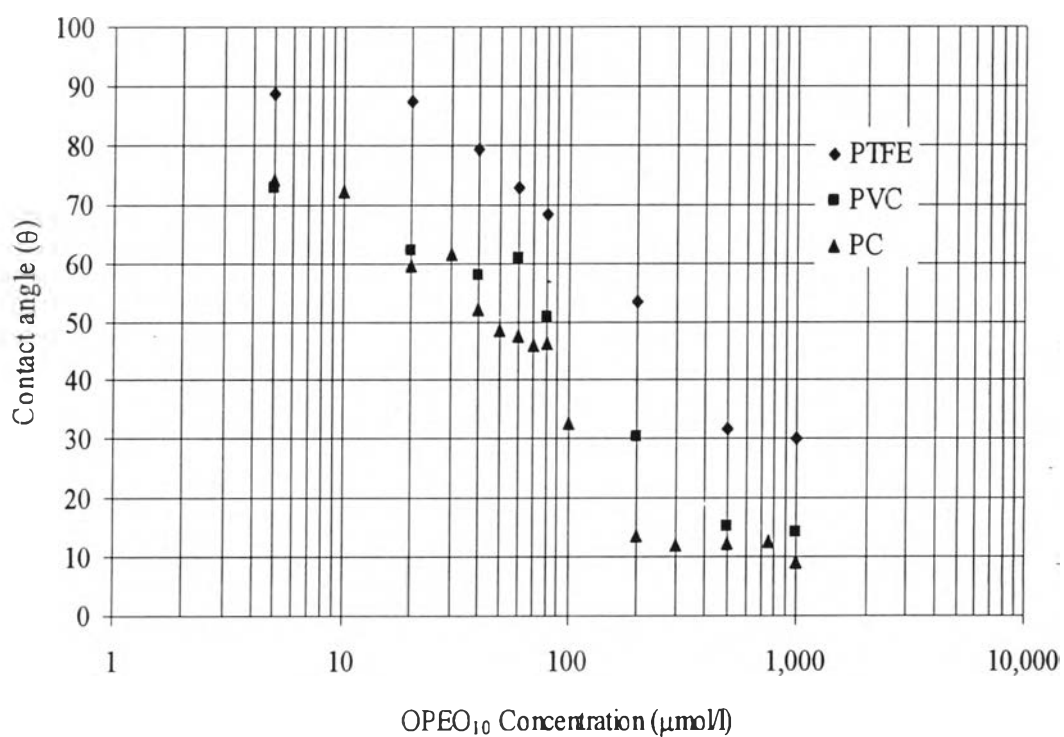


Figure 4.52 Adsorption isotherms of OPEO<sub>10</sub> on PTFE, PVC and PC.

#### 4.7.2 Contact Angle of OPEO<sub>10</sub> Solution on Plastics

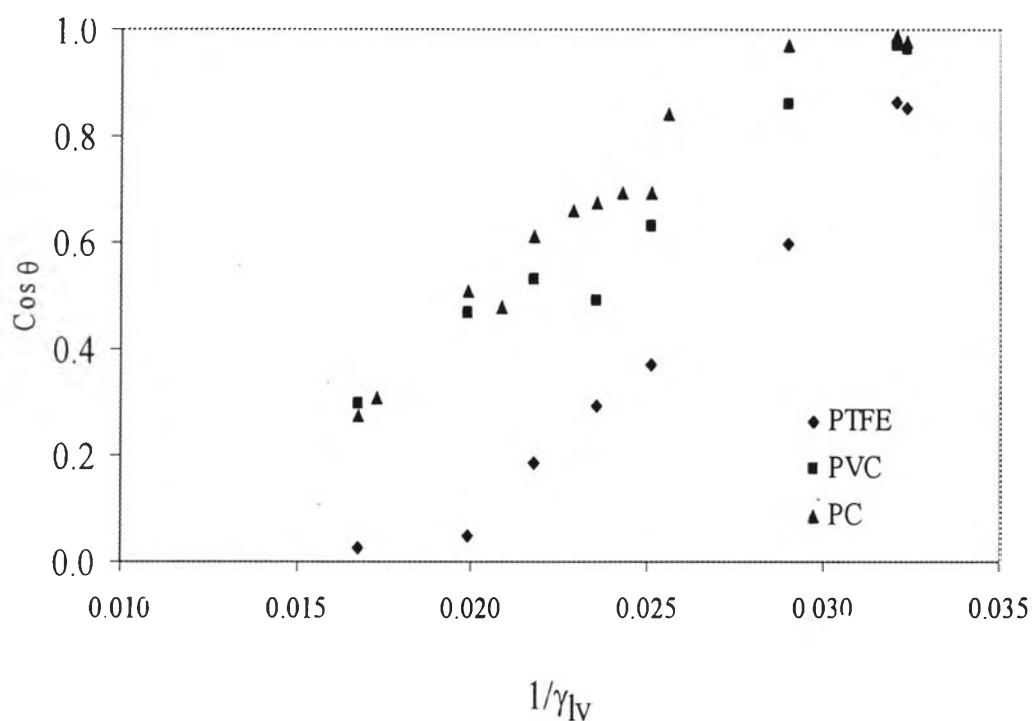
The contact angle of OPEO<sub>10</sub> solutions on PTFE, PVC and PC are depicted in Figure 4.53. In all cases the value of contact angle decreased when OPEO<sub>10</sub> concentration increased and become nearly constant. Moreover, a comparison of contact angle for OPEO<sub>10</sub> solutions that follows the same order, PTFE > PVC > PC, corresponding to CPC and NaOBS cases.



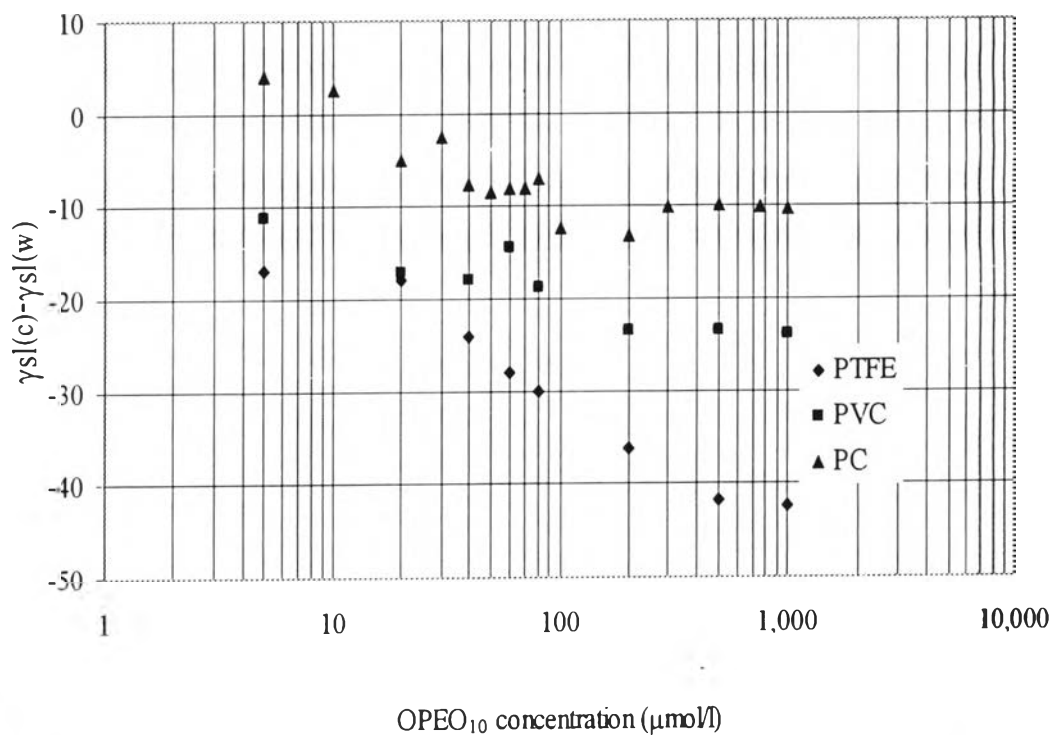
**Figure 4.53** Contact angle of OPEO<sub>10</sub> solution on PTFE, PVC and PC.

### 4.7.3 Wetting Enhancement by OPEO<sub>10</sub>

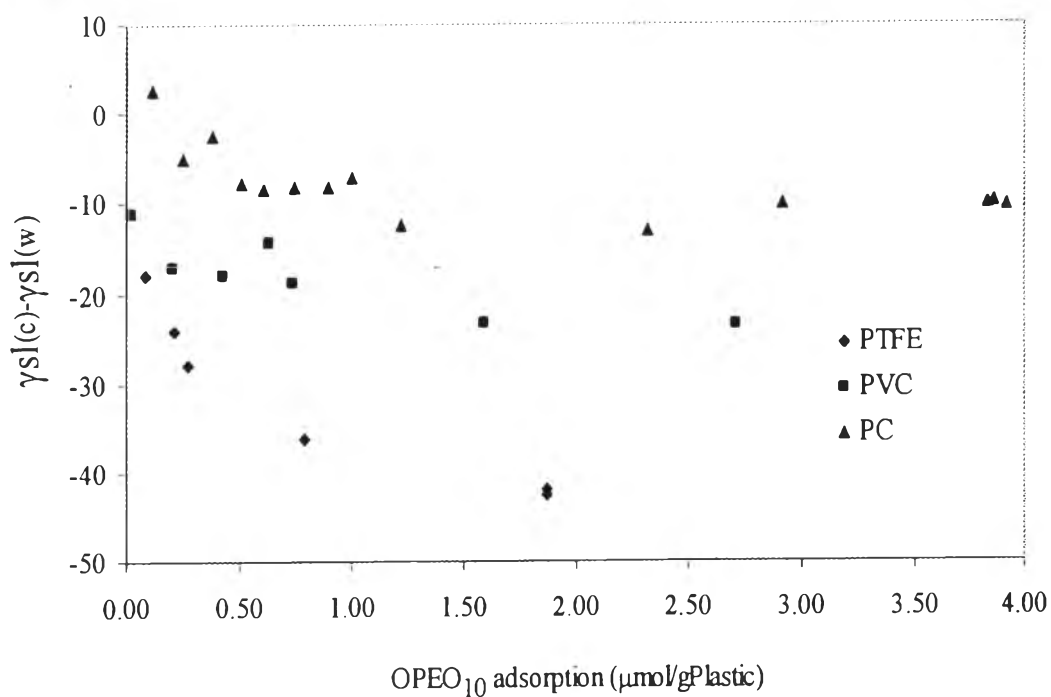
As mentioned in the case of CPC and NaOBS, the  $\gamma_{SL}$  is not constant but is a function of the surfactant concentration and adsorption. Figure 4.54 does not show the linear relation that intercept at zero. In addition, Figure 4.55 and Figure 4.56 also show that the relative interfacial tension decreases with increasing OPEO<sub>10</sub> concentration and OPEO<sub>10</sub> adsorption.



**Figure 4.54** Contact angle on plastics related to inversion liquid/vapor surface tension of OPEO<sub>10</sub> solution.



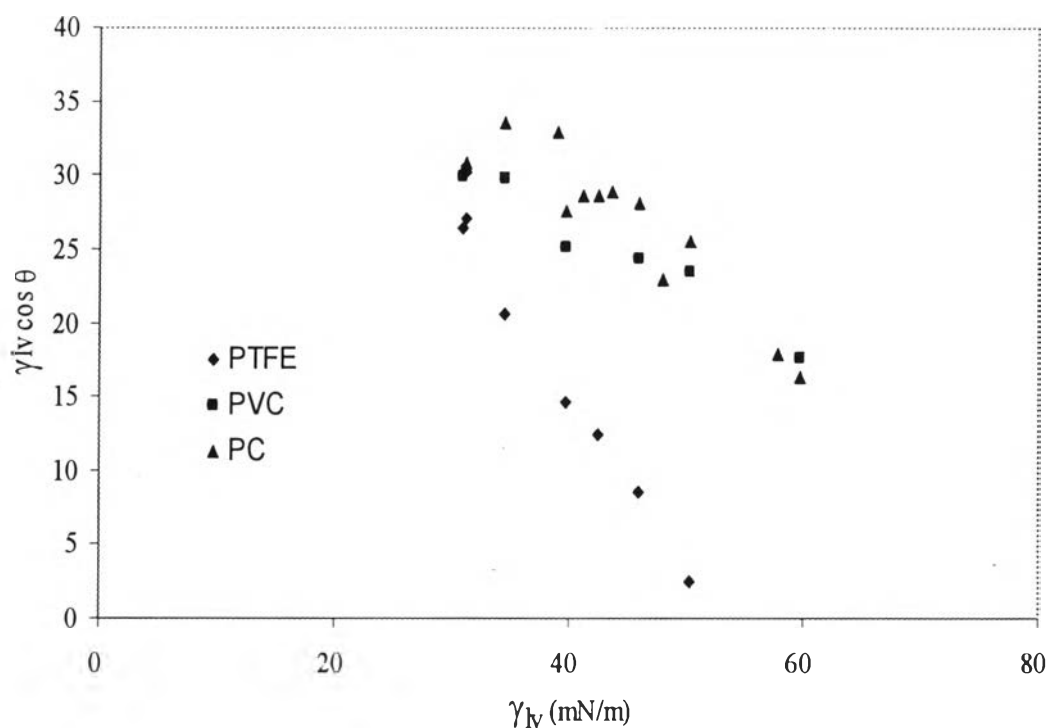
**Figure 4.55** Relative solid/liquid interfacial tension of plastics as a function of OPEO<sub>10</sub> concentration.



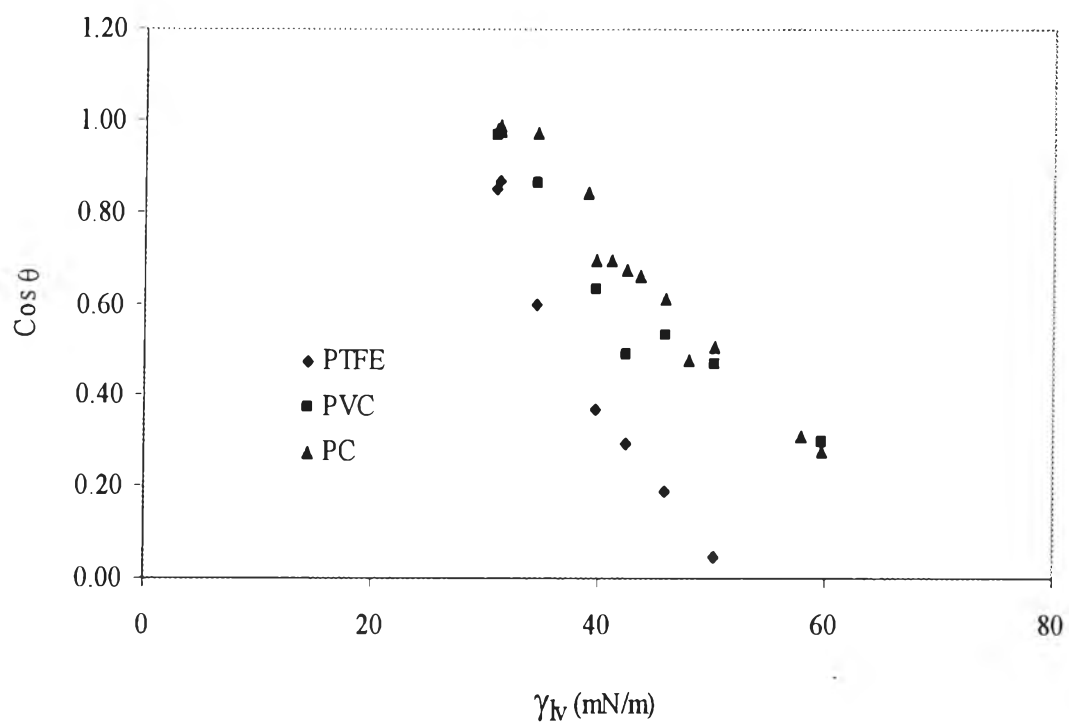
**Figure 4.56** Relative solid/liquid interfacial tension of plastics as a function of OPEO<sub>10</sub> adsorption.



The adhesion tension plots of OPEO<sub>10</sub> show a slope of about -1 in the case of PTFE, PVC and PC which are exhibited in Figure 4.57. It indicates that the adsorbed amount at the solid/liquid interface is almost equal at liquid /vapor surface. Moreover, Zisman's plots of OPEO<sub>10</sub>, Figure 4.58, still show the rectilinear relation between the  $\cos\theta$  and the liquid/vapor interfacial tension.



**Figure 4.57** Adhesion tension plot of OPEO<sub>10</sub> solution on plastics



**Figure 4.58** Contact angle of OPEO<sub>10</sub> on plastics as a function of its  $\gamma_{LV}$ .