

CHAPTER IV

RESULTS AND DISCUSSION

The adsorption isotherms and contact angle measurements of CPC, NaOBS and OPEO₁₀ were done on three plastic surfaces; PMMA, ABS and Nylon6,6. For CPC and NaOBS, the experiments were done with varying salt concentrations: 0, 0.02, and 0.05 M of NaCl. In addition, the liquid/vapor surface tension and CMC of CPC and NaOBS solutions at different salt concentration were also measured.

4.1 Properties of Plastics

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

Table 4.1 Properties of plastics

Plastics	Contact angle of water (degree)	Specific surface area (m ² /g)
PMMA	70	2.1
ABS	65	6.0
Nylon6,6	64	8.7

From the table, the water contact angles of three plastics are similar which exhibit the small difference in the degree of hydrophobicity. For the specific surface area, generally the specific surface area of plastic is quite low, it is usually lower than 20 m²/g. Moreover, the specific surface areas of three plastics are in the vicinity which indicate that the surface area has no effect in the adsorption amount of each surfactant.

4.2 The Liquid/Vapor Surface Tension and CMC of CPC

Figure 4.1 shows the relation between the liquid/vapor surface tension (γ_{LV}) and the equilibrium concentration of CPC solutions as a semi-logarithmic function. It performed that the γ_{LV} was decreased with increasing surfactant concentration. At the same CPC concentration, the presence of NaCl could cause the reduction of the γ_{LV} . The critical micelle concentration (CMC) of solutions was the concentration at the break point of the plot after this point γ_{LV} was constant. The CMC of CPC solution was $950 \mu\text{M}$. As expected, the CMC of CPC was respectively decreased to 150 and $70 \mu\text{M}$ in the present of NaCl at concentration 0.02 M and 0.05 M.

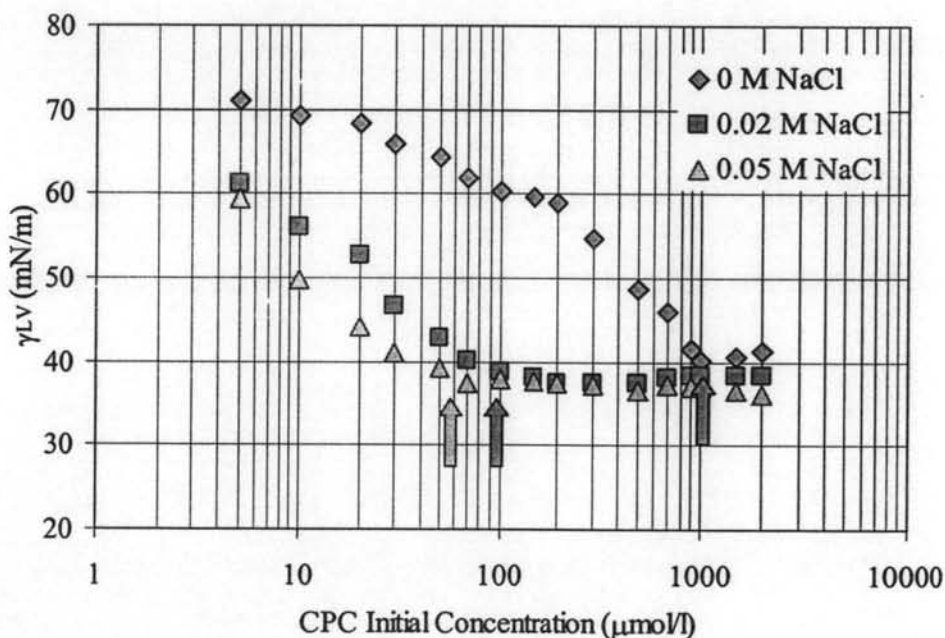


Figure 4.1 Liquid/vapor surface tension as a function of CPC concentration at various salt concentrations.

4.3 Adsorption of CPC and Its Wetting on Plastics

4.3.1 Adsorption Isotherm of CPC

The logarithm of the adsorbed amount was plotted versus the equilibrium concentration of surfactant solution; or so called "the adsorption isotherm". The adsorption isotherms of CPC on PMMA, ABS and Nylon6,6 with varying salt concentrations are shown in Figure 4.2, Figure 4.3 and Figure 4.4 respectively. At a low concentration of surfactant, the adsorption slightly increased with surfactant concentration and level out to the plateau at about the CMC region. While the adsorption increased with higher proportional for surfactant solutions with higher ionic strength. Moreover, an increase in the electrolyte concentration caused a slight raise in the adsorbed amount and also shifted the break point to lower concentration. It was observed that the addition of electrolyte had little effect on the adsorption amount of CPC due to the reduction of electrical repulsion between the head groups of adsorbed CPC and allowed more CPC to adsorb onto the surface.

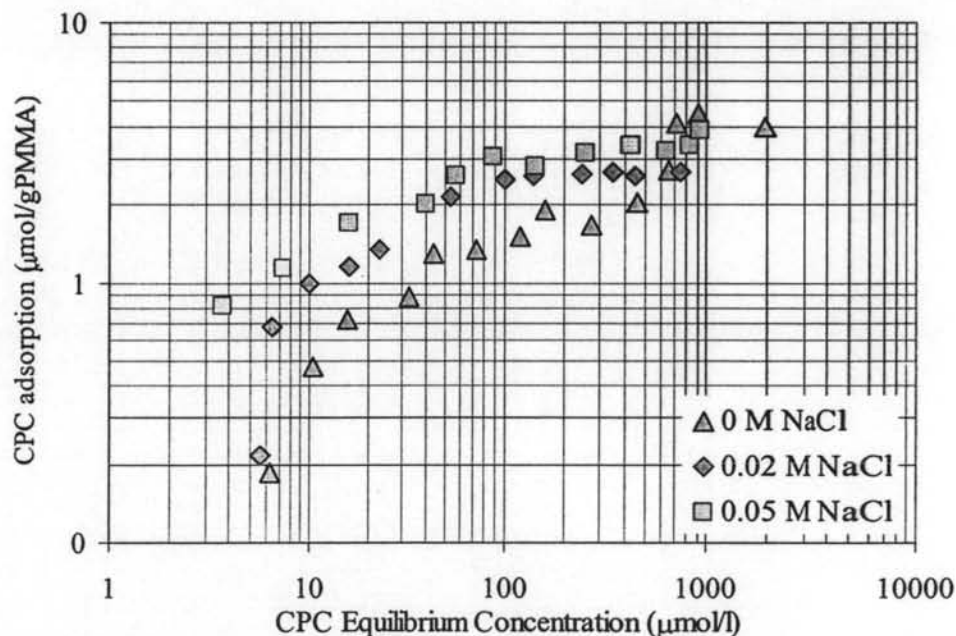


Figure 4.2 Adsorption isotherm of CPC onto PMMA.

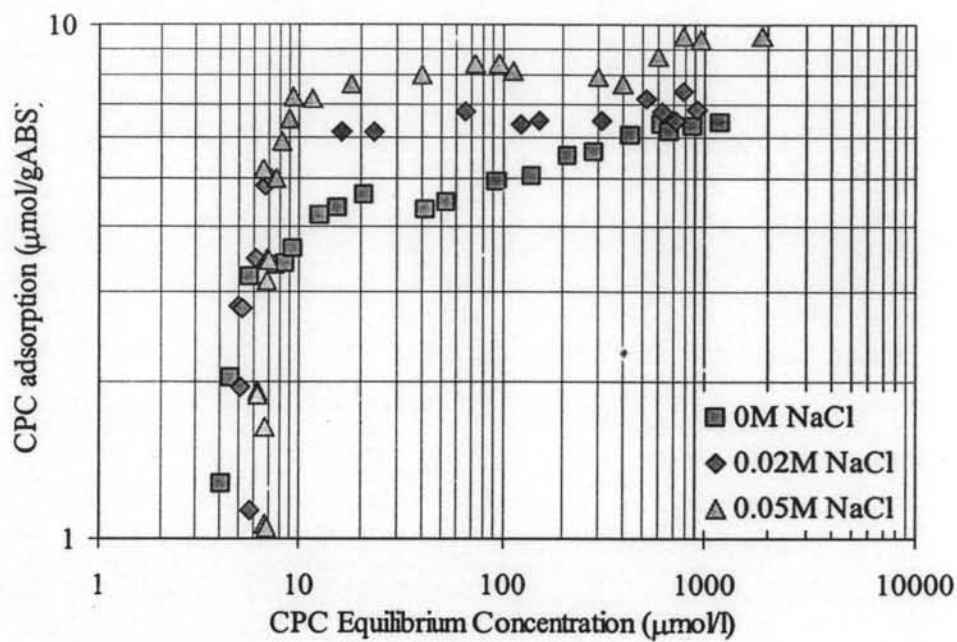


Figure 4.3 Adsorption isotherm of CPC onto ABS.

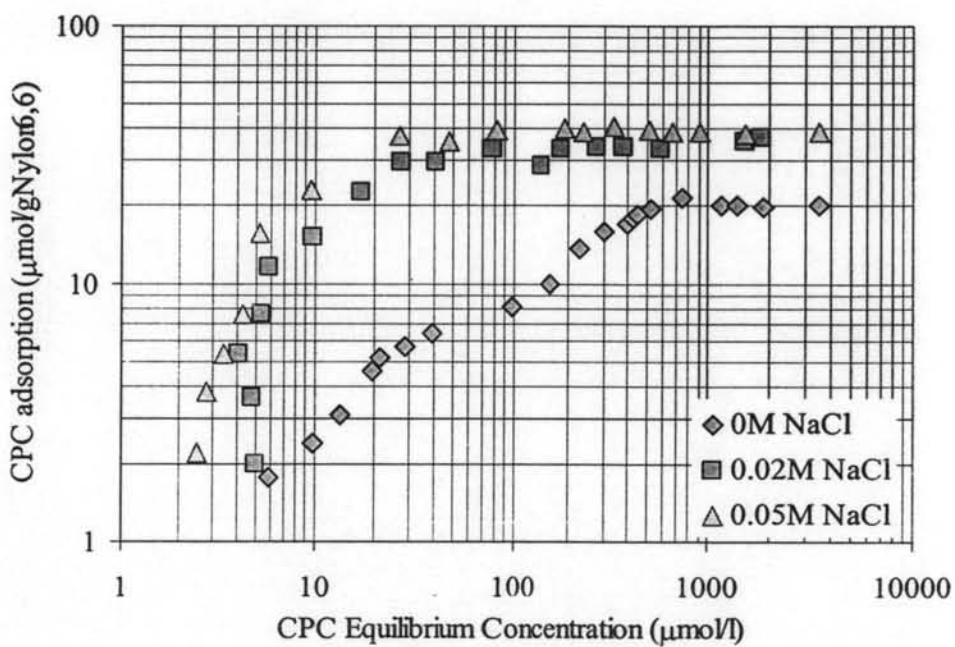


Figure 4.4 Adsorption isotherm of CPC onto Nylon6,6.

4.3.2 Contact Angle of CPC Solution on Plastics

The relations between the static contact angles on PMMA, ABS and Nylon6,6 and concentration of CPC solutions are shown in Figures 4.5 – 4.7. From the plots, the contact angles decreased significantly with increasing CPC concentration and become nearly constant above the CMC. The contact angles of CPC on different plastics were in the vicinity values corresponding to the polarity and hydrophobicity of plastics as shown in Table 4.1. In addition, the presence of NaCl produced smaller contact angle at the same equilibrium CPC concentration. This implied that the addition of NaCl provided better wetting when considered at the same equilibrium concentration. This effect was found to be more pronounced with increasing in the concentration of NaCl

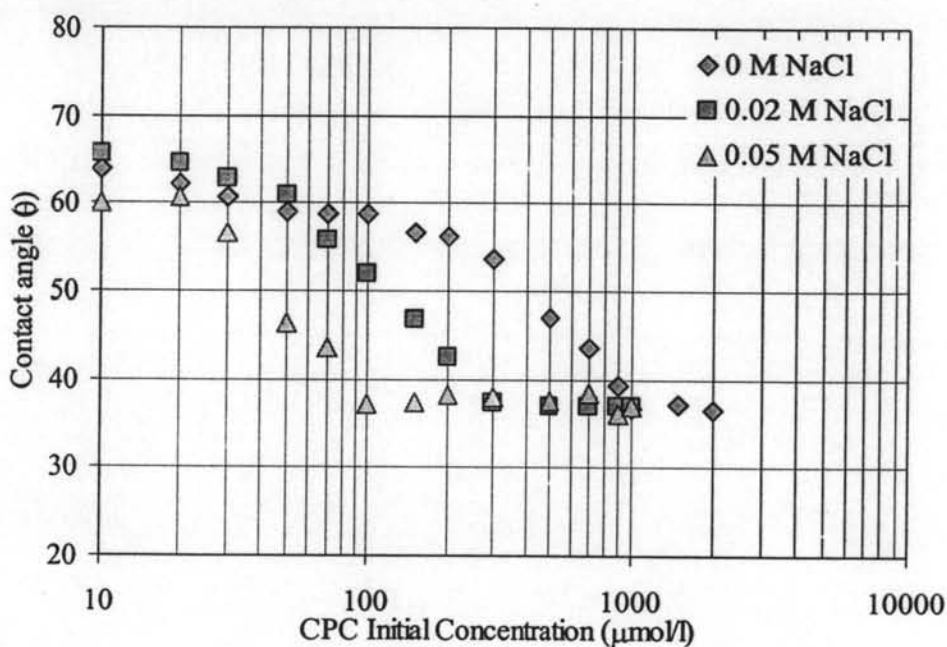


Figure 4.5 Contact angle of CPC solution on PMMA with varying CPC and NaCl concentration.

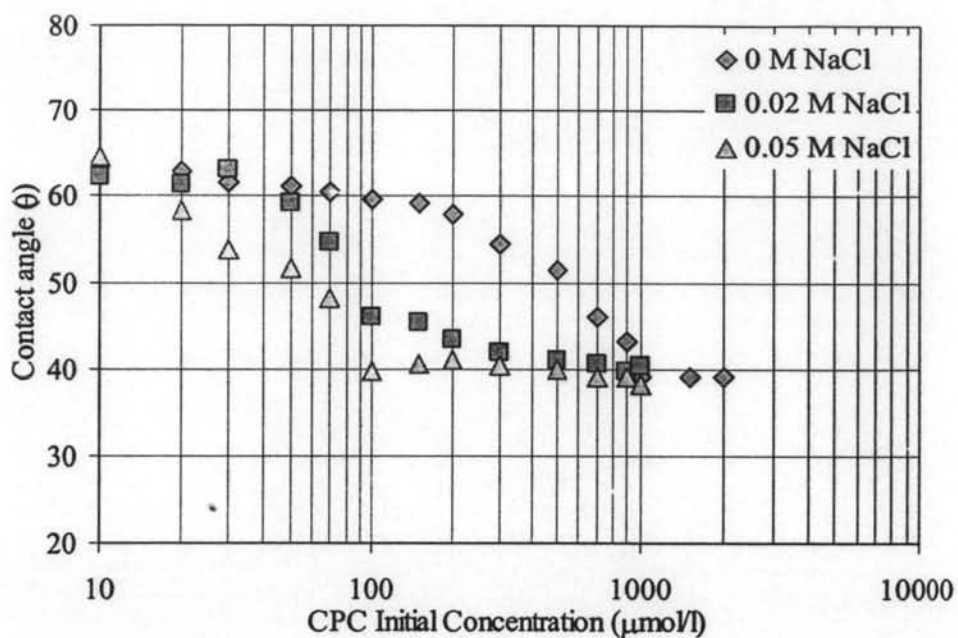


Figure 4.6 Contact angle of CPC solution on ABS with varying CPC and NaCl concentration.

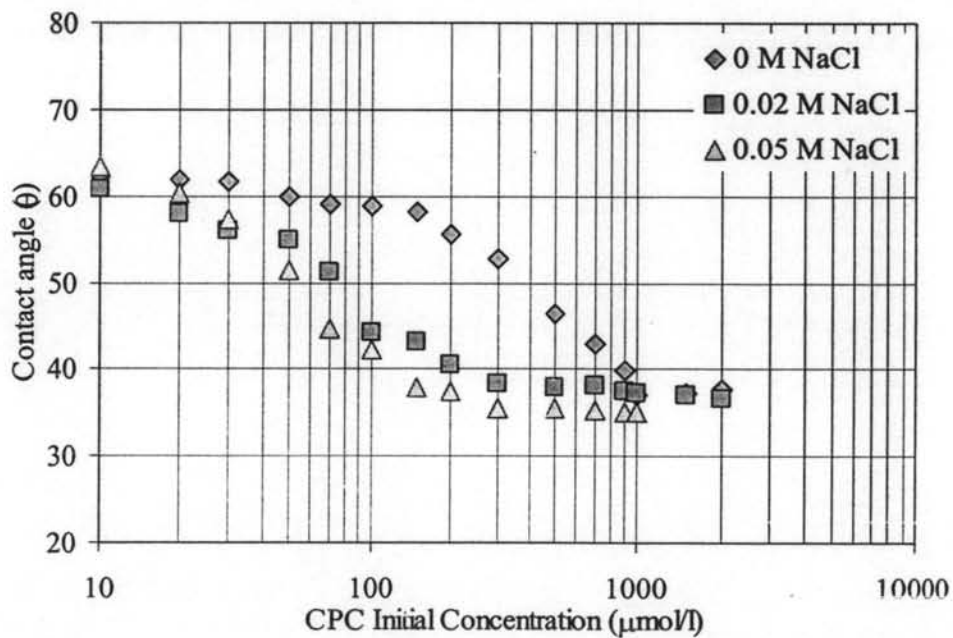


Figure 4.7 Contact angle of CPC solution on Nylon6,6 with varying CPC and NaCl concentration.

4.3.3 Wetting Enhancement by CPC

From Young's Equation, if the relation between $\cos \theta$ and $1/\gamma_{LV}$ was plotted, the plot should be a straight line with the slope of $(\gamma_{SV} - \gamma_{SL})$ and intercepted at the origin. Figures 4.8 – 4.10 show that for pure CPC solution the interceptions were near the origin for all plastics. Nevertheless, the addition of NaCl made the results deviate from this relationship since the intercept values did not equal zero. Hence, it could be suggested that in case of high polar plastics, the γ_{SV} and γ_{SL} were not constant when NaCl was added.

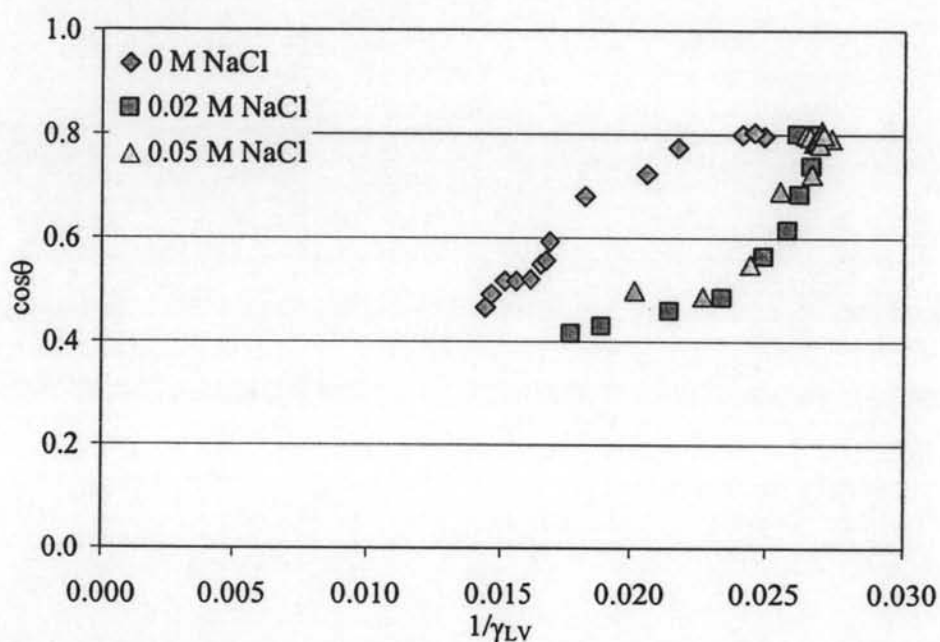


Figure 4.8 Contact angle on PMMA related to inversion of liquid/vapor surface tension of CPC solution.

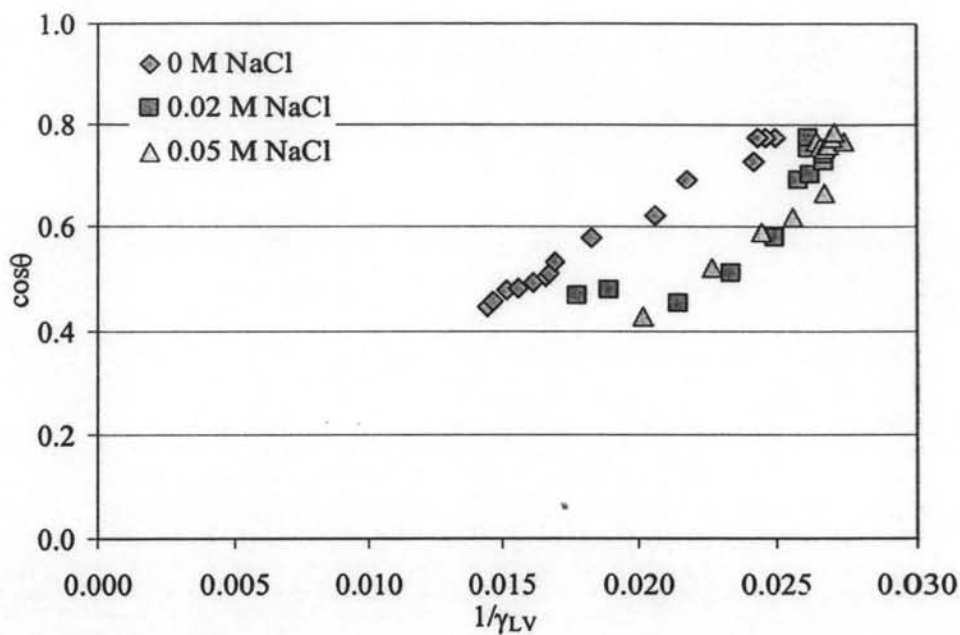


Figure 4.9 Contact angle on ABS related to inversion of liquid/vapor surface tension of CPC solution.

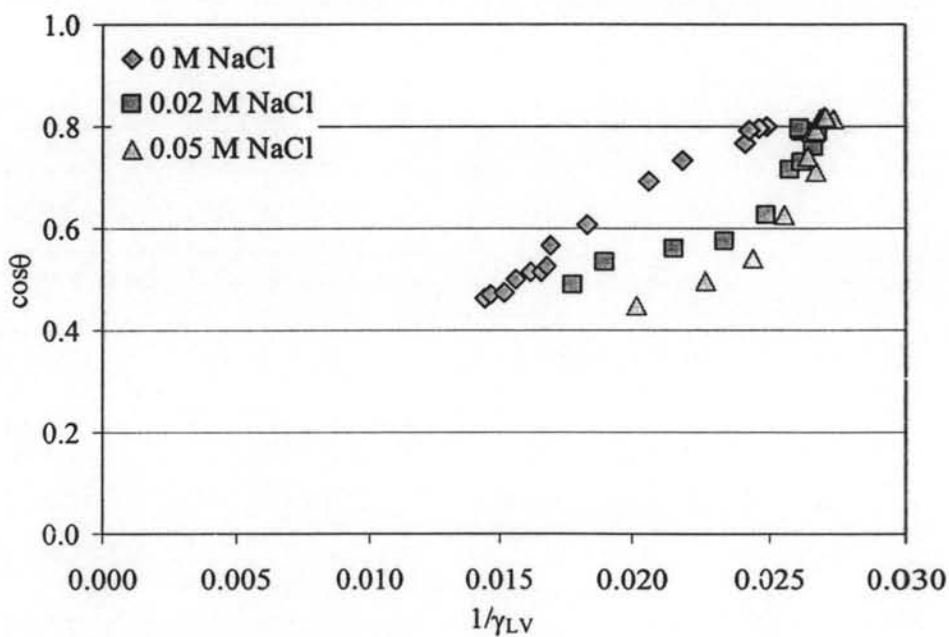


Figure 4.10 Contact angle on Nylon6,6 related to inversion liquid/vapor surface tension of CPC solution.

Another possible way to examine the variation of the $(\gamma_{SV} - \gamma_{SL})$ term is to look at the product of $\cos \theta$ multiply with γ_{LV} (or $\gamma_{LV} \cos \theta$). From Equation 2.1, if $(\gamma_{LV} \cos \theta)$ was constant, the value of $(\gamma_{SV} - \gamma_{SL})$ would be constant. Figures 4.11 – 4.13 show this relationship for pure CPC. In contrast, the addition of NaCl caused the variable of $(\gamma_{LV} \cos \theta)$ with CPC equilibrium concentration.

In practical, the value of the γ_{SV} could be assumed to be independent of the surfactant concentration. Because the dry solid had not been contacted by the solution yet and the transfer of the nonvolatile surfactants to the solid-vapor interface during measurement of contact angles via vapor phase seemed unlikely (Gau and Zografis, 1990). This indicated that the γ_{SL} was constant in case of pure CPC but varied with CPC concentration in the presence of NaCl.

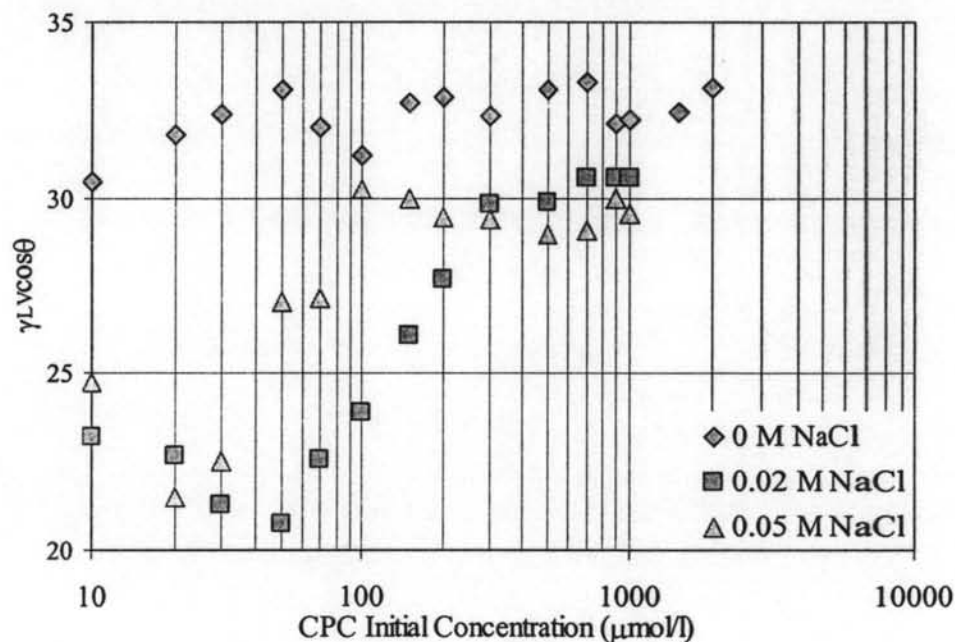


Figure 4.11 $\gamma_{LV} \cos \theta$ on PMMA related to equilibrium concentration of CPC solution.

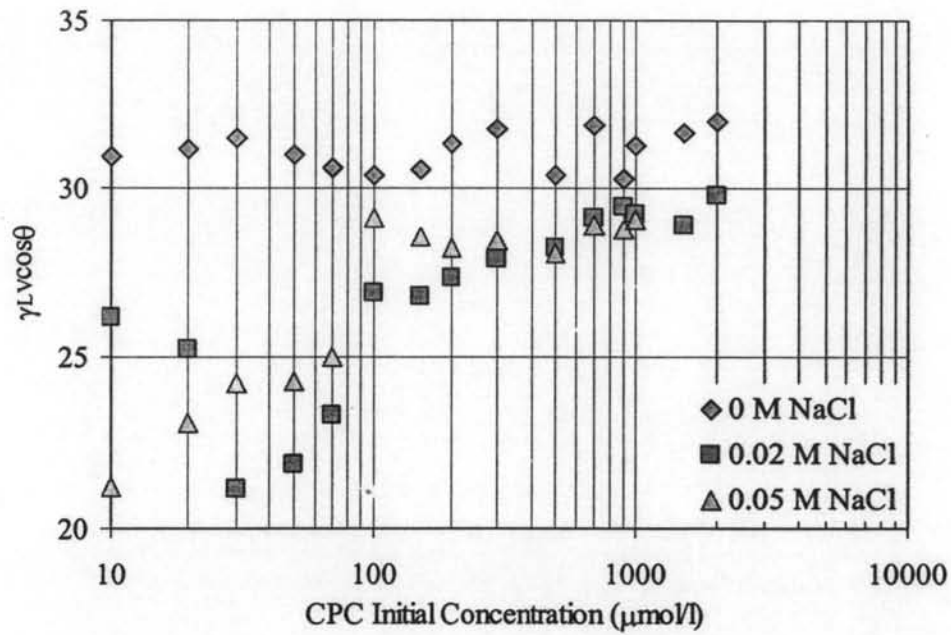


Figure 4.12 $\gamma_{LV} \cos \theta$ on ABS related to equilibrium concentration of CPC solution.

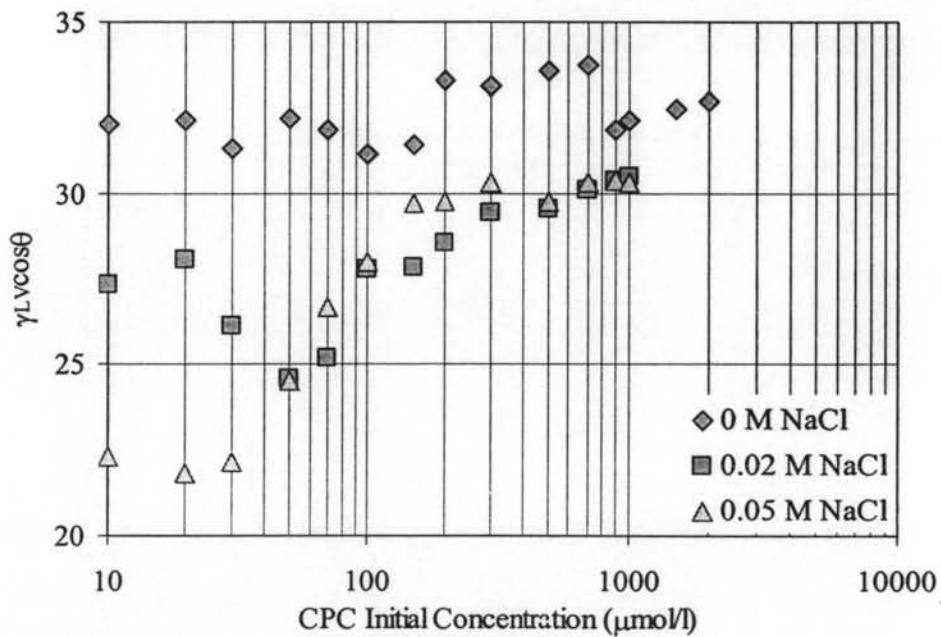


Figure 4.13 $\gamma_{LV} \cos \theta$ on Nylon6,6 related to equilibrium concentration of CPC solution.

Although, the γ_{SL} was not experimentally and directly measured, we could calculate the γ_{SL} relative to the γ_{SL} at a reference state, $\gamma_{SL}(w)$, which had no CPC presented or in a pure water, using the contact angle and the liquid/vapor surface tension data. Equation 2.1 may be written as

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

where (w) refers to the standard state when no CPC presents and (c) refers to the properties of the surfactant solution at concentration c.

Figures 4.14 - 4.16 show the correlation between the term $\gamma_{SL}(c) - \gamma_{SL}(w)$ and CPC concentration. If the term $\gamma_{SL}(w)$ was commonly assumed to be a constant, this plot would provide the relation between $\gamma_{SL}(c)$ and CPC concentration. From the figures, in case of pure CPC, the $\gamma_{SL}(c)$ was not a function of CPC concentration but the addition of NaCl could make this term related to CPC concentration as well as the results mentioned above.

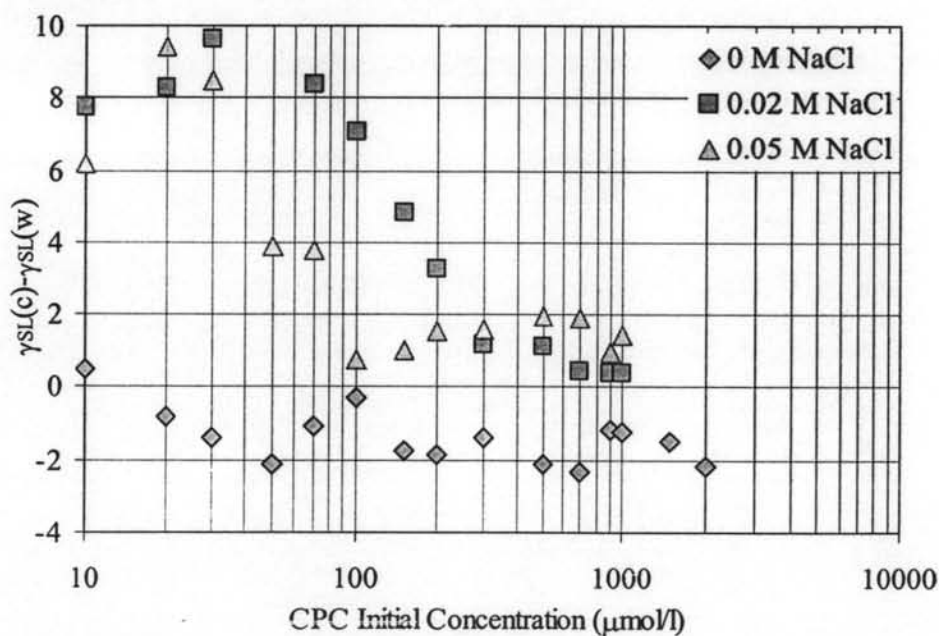


Figure 4.14 Relative solid/liquid interfacial tension of PMMA as a function of CPC concentration.

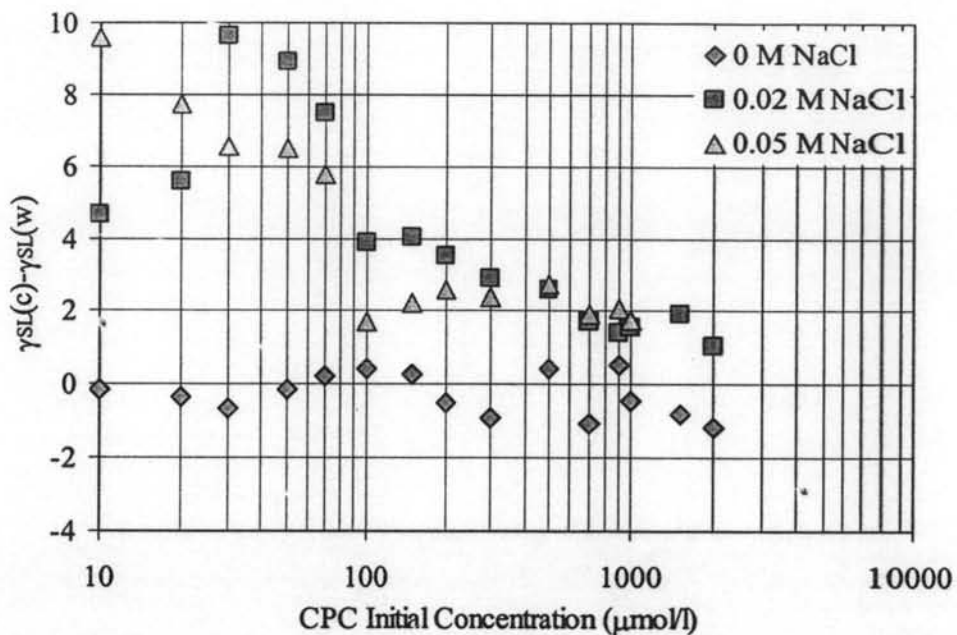


Figure 4.15 Relative solid/liquid interfacial tension of ABS as a function of CPC concentration.

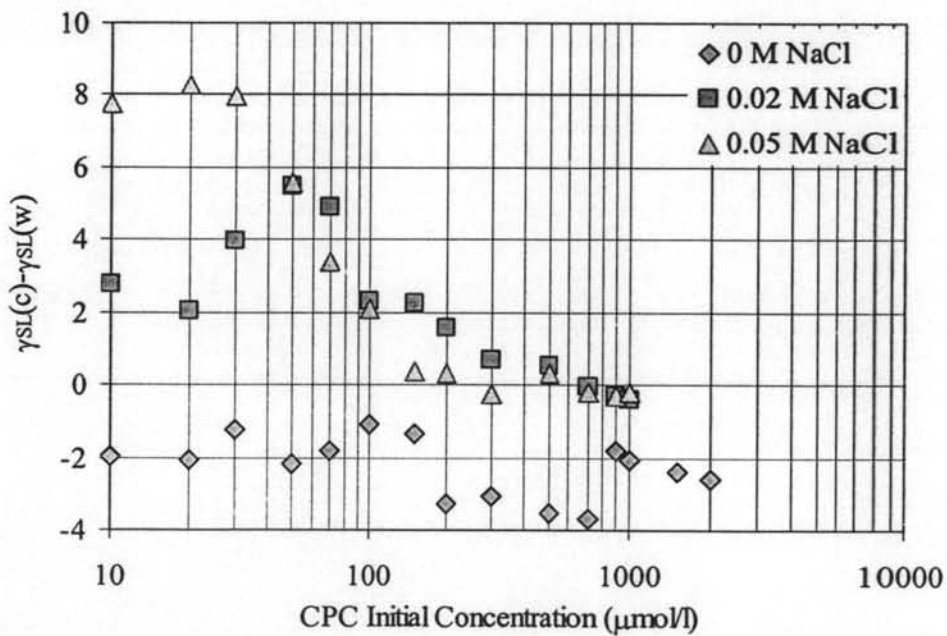


Figure 4.16 Relative solid/liquid interfacial tension of Nylon6,6 as a function of CPC concentration.

Figures 4.17 - 4.19 indicate that the increase in CPC adsorption had no effect on the γ_{SL} but the addition of NaCl was the cause of reduction in the γ_{SL} , which according to Equation 2.1, resulted in reduction of the contact angle. Therefore, for the polar plastic, the changes in contact angles induced by surfactant are attributed only to the changes in the γ_{LV} . Moreover, there were also attributed to the changes in the γ_{SL} in the addition of NaCl.

The possible reason was that for the non-NaCl condition, the γ_{SL} was small due to the natures of solid (polar) and water (polar) which were similar. According to the opposite charge between the solid surface and the hydrophilic group of CPC, the appearance of the adsorption would be in the horizontal form (CPC laid both hydrophobic and hydrophilic groups down) and led to the diminution of the adsorption area. Therefore, the increase in CPC concentration had no effect on the γ_{SL} .

In the presence of NaCl, Na^+ and Cl^- would neutralize the negative charge of CPC and positive charge of the surface, respectively. Then, the difference between the natures of two interfaces would be raised meaning that the γ_{SL} was enhanced. Furthermore, the addition of NaCl could make the adsorption appearance more inclined and allowed 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 had 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 is 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.

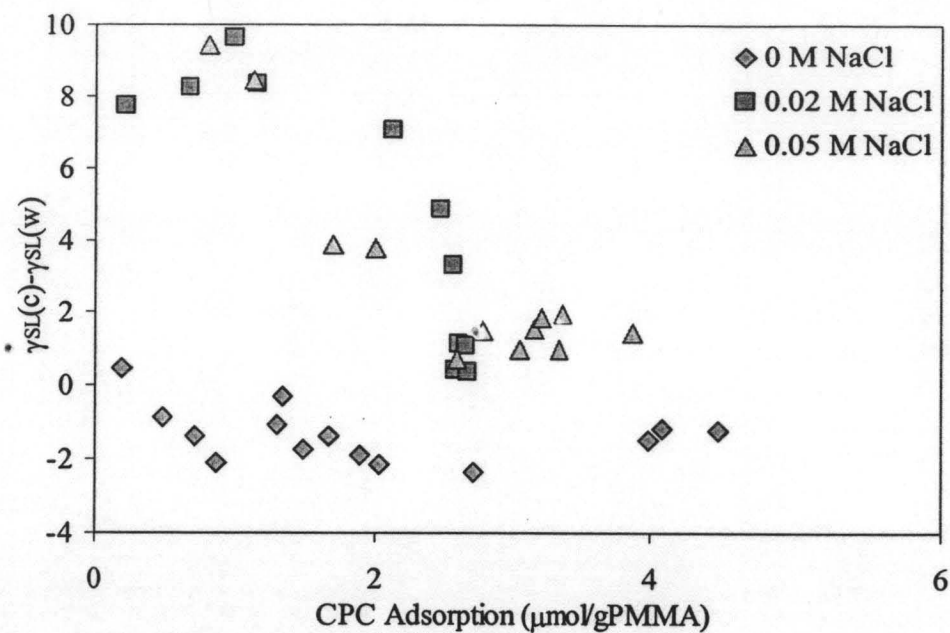


Figure 4.17 Relative solid/liquid interfacial tension of PMMA as a function of CPC adsorption.

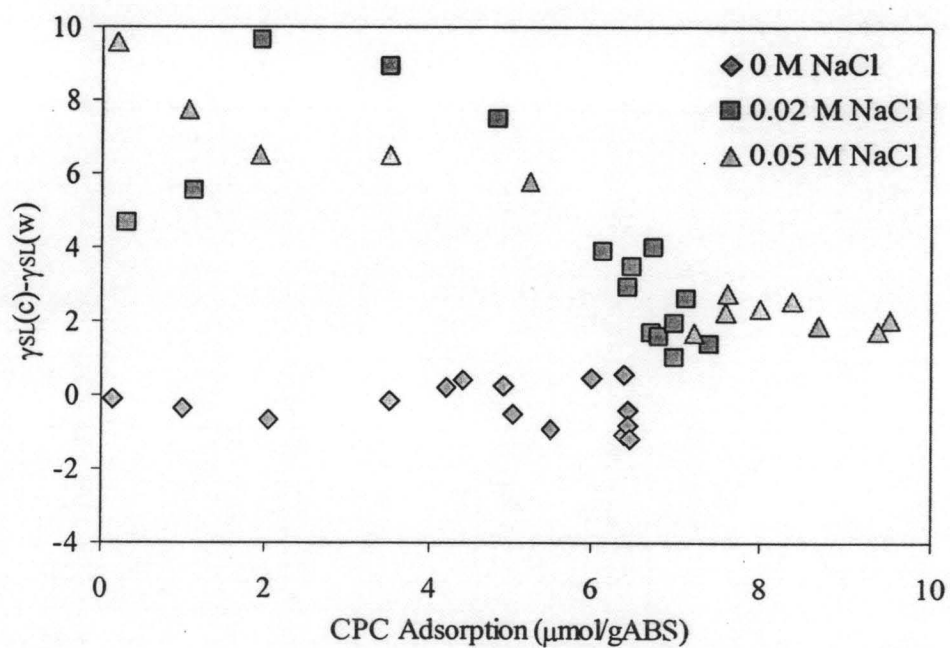


Figure 4.18 Relative solid/liquid interfacial tension of ABS as a function of CPC adsorption.

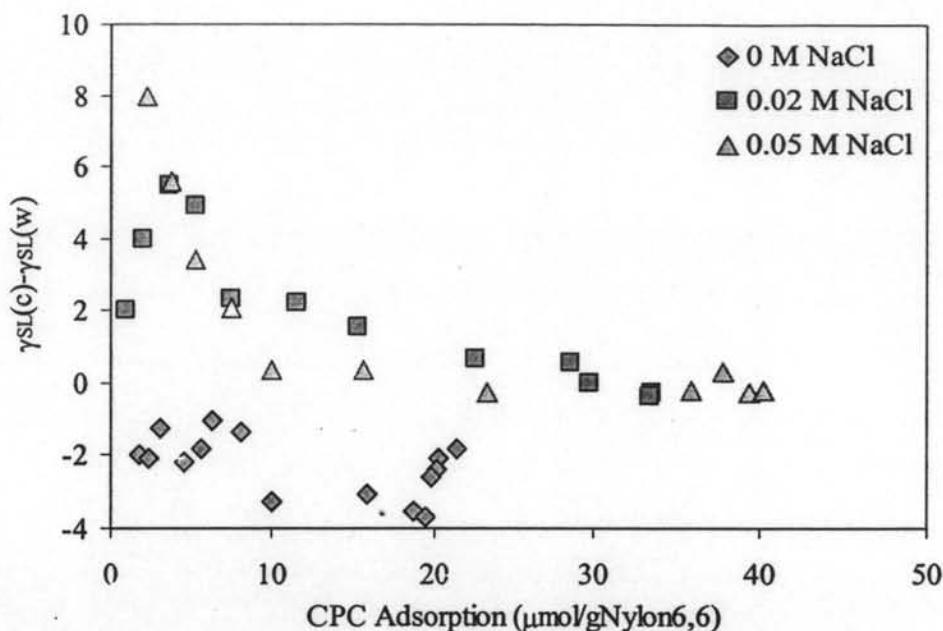


Figure 4.19 Relative solid/liquid interfacial tension of Nylon6,6 as a function of CPC adsorption.

Figures 4.20, 4.22 and 4.24 show the adhesion tension plot which illustrated the adhesion tension, $\gamma_{LV}\cos\theta$, related to the γ_{LV} of CPC solution. From Equation 2.2, if Γ_{SV} for a surfactant was assumed to be zero, this plot should have a slope of $-(\Gamma_{SL}/\Gamma_{LV})$ which was the ratio of surface excess concentration at solid/liquid to liquid/vapor interface.

For pure CPC solution, the plots show the straight line with slope of about zero which indicated that the Γ_{LV} was much higher than Γ_{SL} when the solid had polarity. Moreover, the presence of NaCl made the slope become more negative which indicated a raise of the Γ_{SL} .

The CPC solution varying with NaCl concentration did not produce the same contact angle at the same γ_{LV} . It produced a higher contact angle when the CPC solution had more ionic strength as predicted in Figures 4.21, 4.23 and 4.25. The possible reason was the difference between the nature of solid/liquid interface and liquid/vapor interface. This difference caused CPC to adsorb in a different way

at the interface. So, the addition of NaCl did not effectively reduce γ_{SL} as effectively as γ_{LV} .

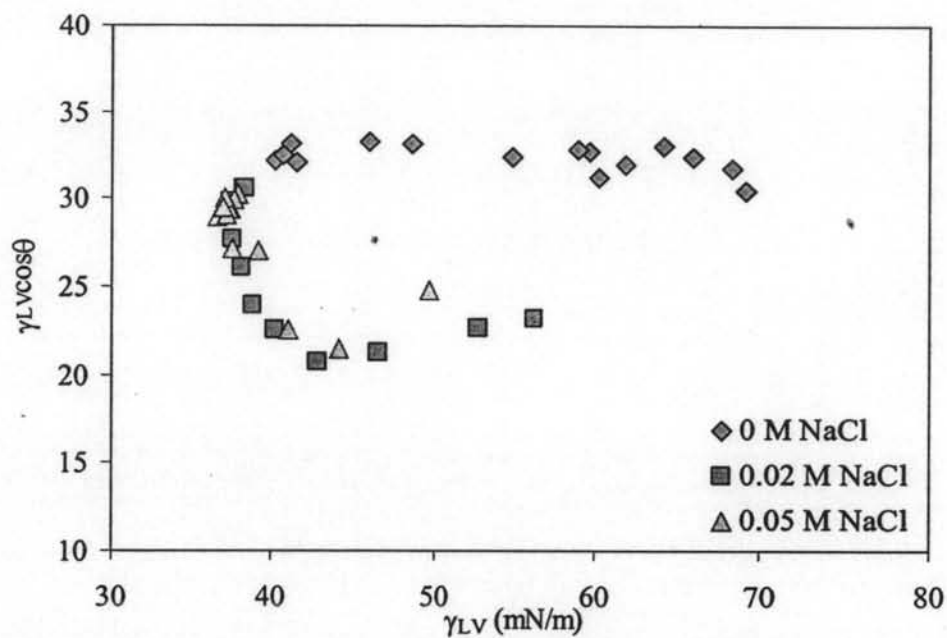


Figure 4.20 Adhesion tension plot of CPC solution on PMMA.

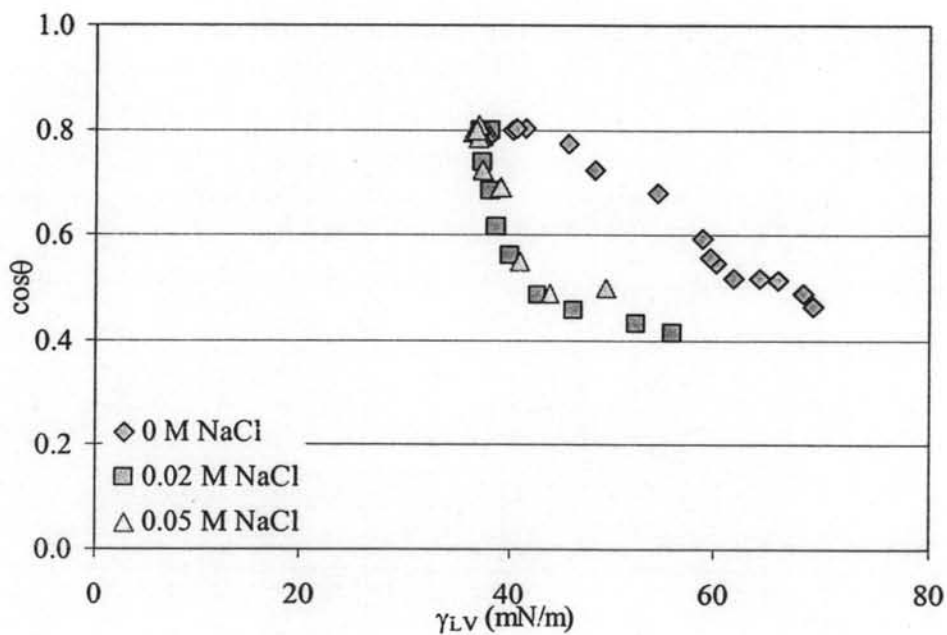


Figure 4.21 Contact angle of CPC on PMMA as a function of its γ_{LV} .

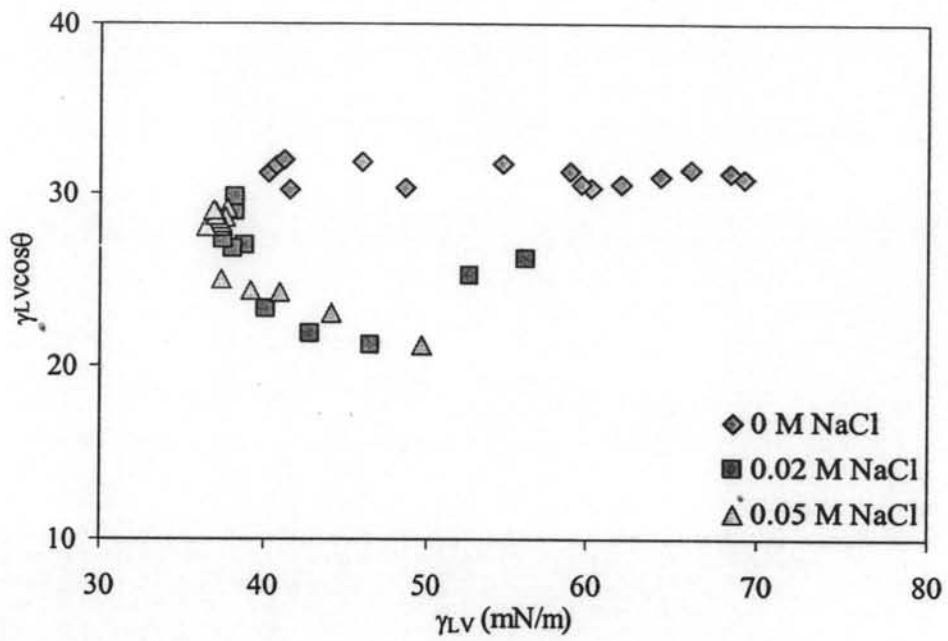


Figure 4.22 Adhesion tension plot of CPC solution on ABS

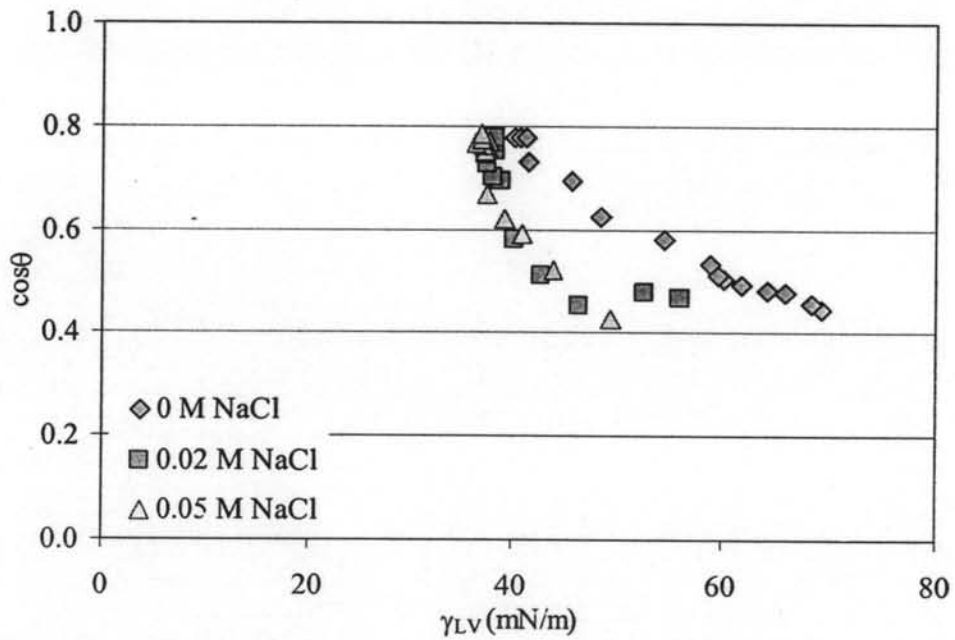


Figure 4.23 Contact angle of CPC on ABS as a function of its γ_{LV} .

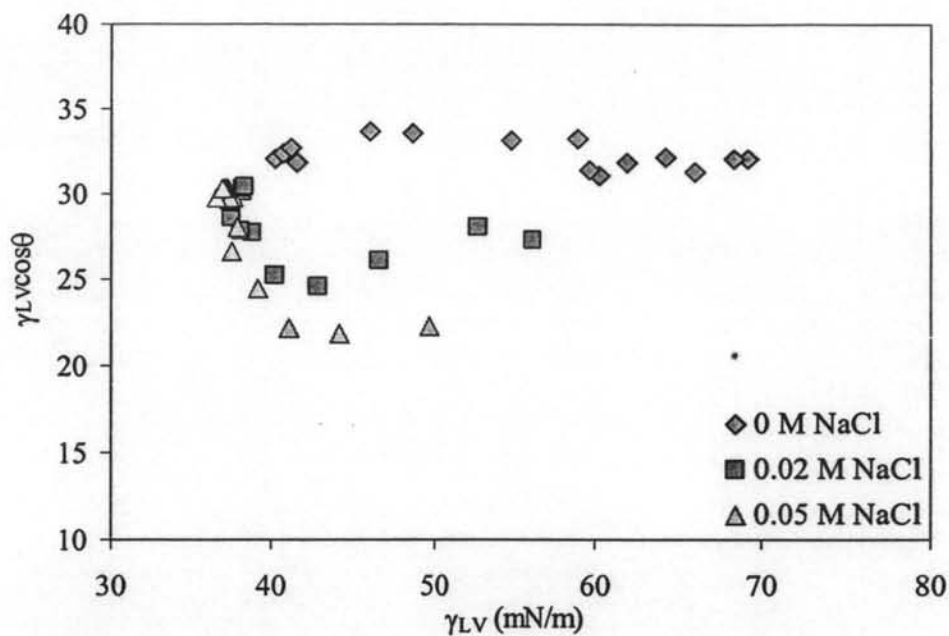


Figure 4.24 Adhesion tension plot of CPC solution on Nylon6,6.

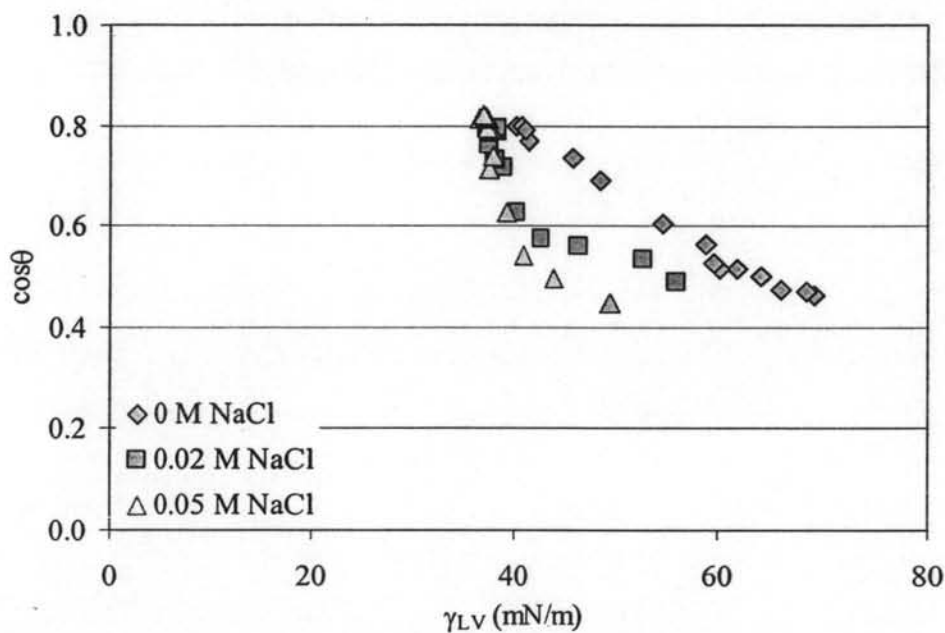


Figure 4.25 Contact angle of CPC on Nylon6,6 as a function of its γ_{LV} .

4.4 The Liquid/Vapor Surface Tension and CMC of NaOBS

Figure 4.26 shows the relation between the γ_{LV} and the equilibrium concentration of NaOBS solutions as a semi-logarithmic function. It performs that the γ_{LV} was decreased with increasing NaOBS concentration. At the same NaOBS concentration the presence of NaCl can cause the reduction of the γ_{LV} . The CMC of NaOBS solution is 10,000 μM . As expected, the CMC of CPC is respectively decreased to 7,000 and 5,000 μM in the present of NaCl at concentration 0.02 M and 0.05 M respectively.

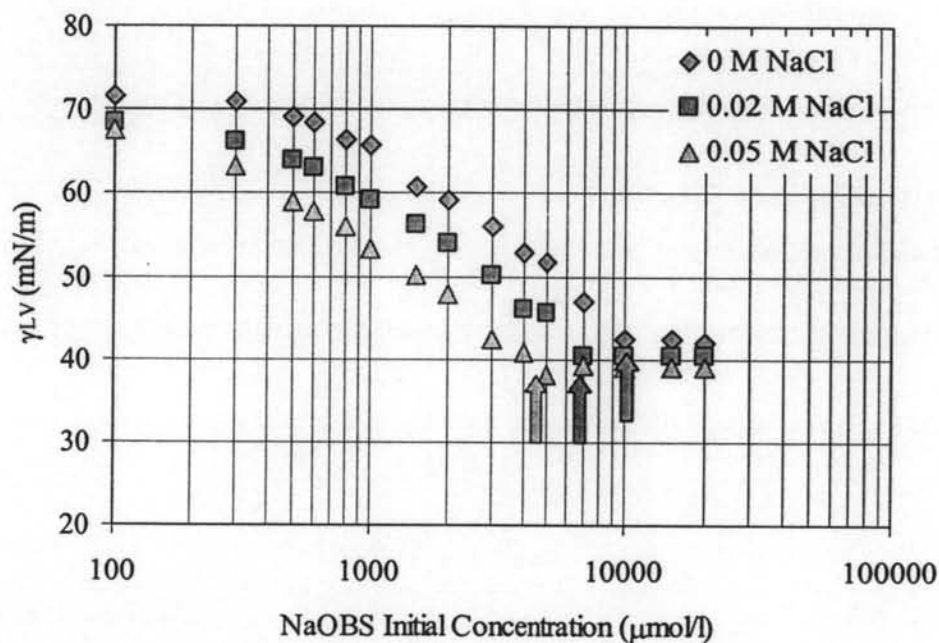


Figure 4.26 Liquid/vapor surface tension as a function of NaOBS concentration.

4.5 Adsorption of NaOBS and Its Wetting on Plastics

4.5.1 Adsorption Isotherm of NaOBS

The adsorption isotherm of NaOBS onto PMMA, ABS and Nylon6,6 with different salt concentrations are shown in Figures 4.27 - 4.29. As expected, the adsorbed amount of NaOBS increased with increasing its concentration until reach plateau at about CMC region. Moreover, the addition of NaCl had a little effect to increase the adsorption at below the CMC region.

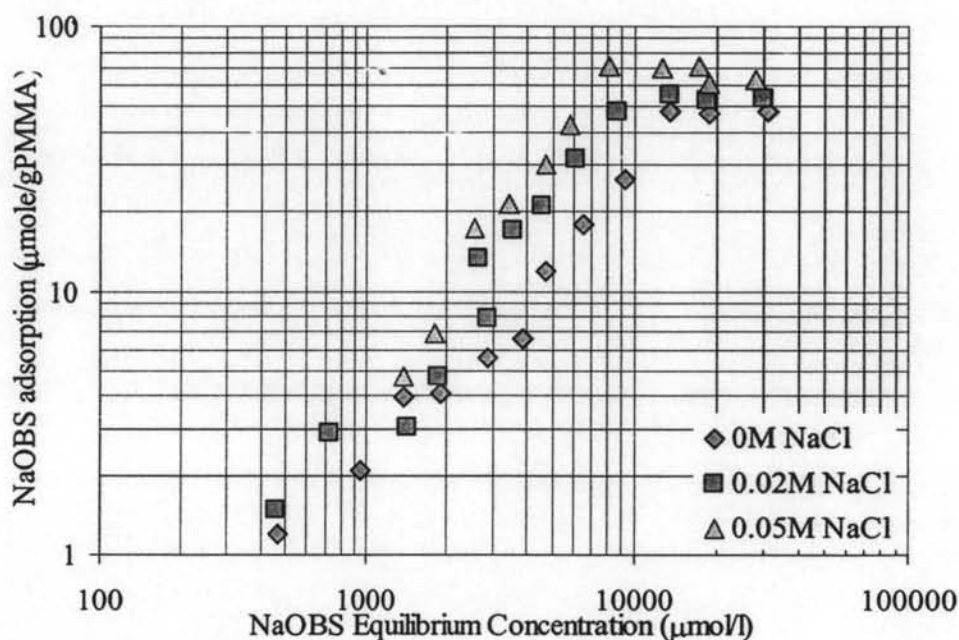


Figure 4.27 Adsorption isotherm of NaOBS on PMMA.

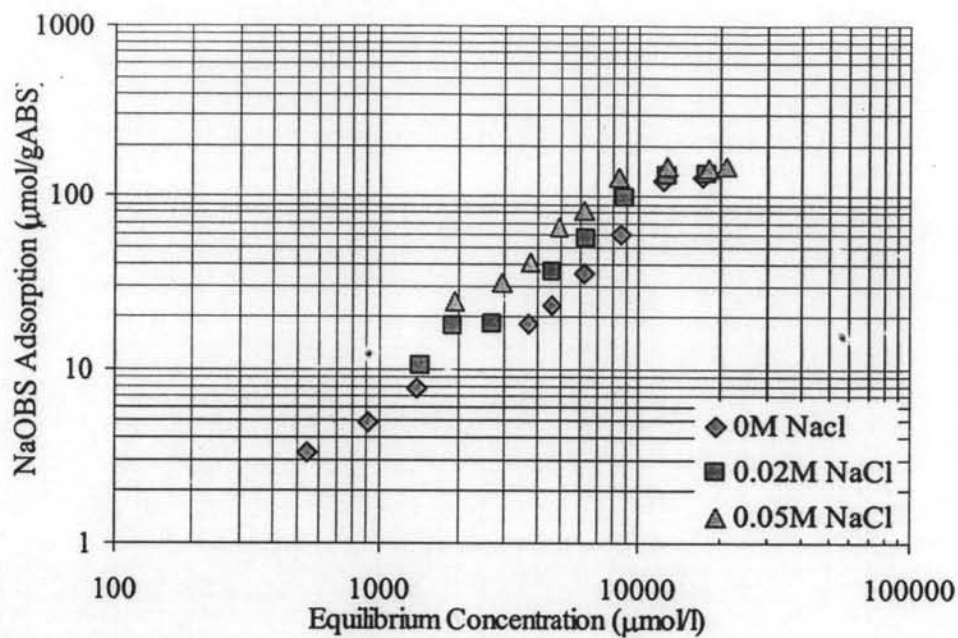


Figure 4.28 Adsorption isotherm of NaOBS on ABS.

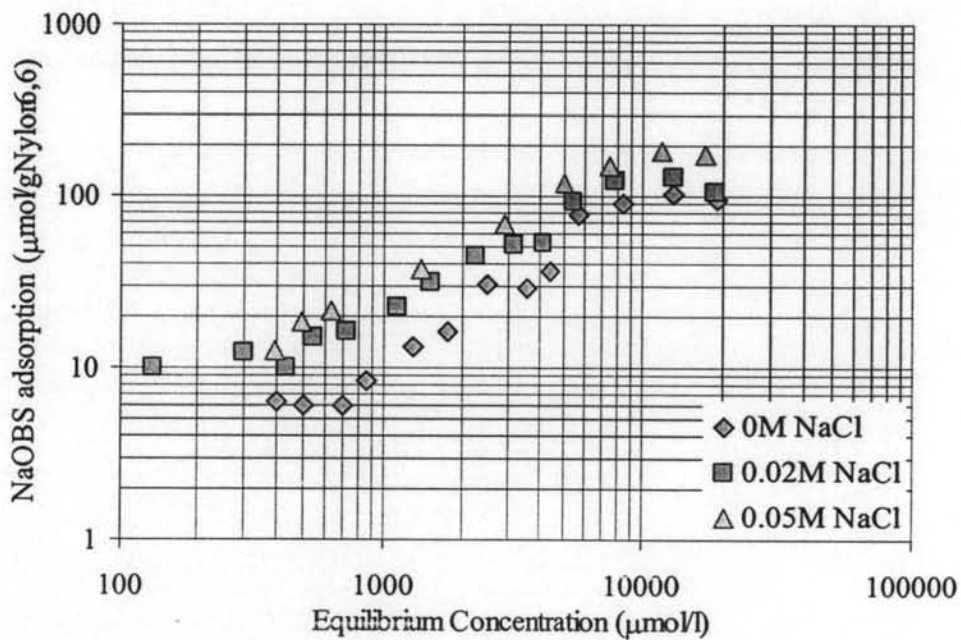


Figure 4.29 Adsorption isotherm of NaOBS on Nylon6,6.

4.5.2 Contact Angle of NaOBS Solution on Plastics

The static contact angles of NaOBS solutions on PMMA, ABS and Nylon6,6 are illustrated in Figures 4.30- 4.32 respectively. For all cases, the contact angles decrease significantly with increasing NaOBS concentration until becoming constant at above the CMC.

Furthermore, the NaOBS solution with the presence of NaCl yielded smaller contact angle as well as the results obtained from CPC.

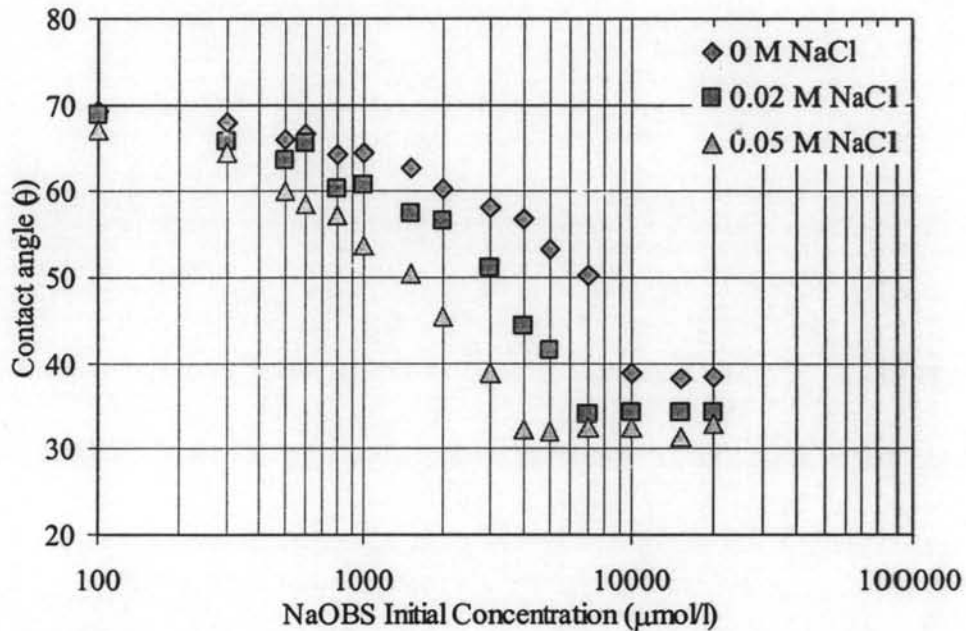


Figure 4.30 Contact angle of NaOBS solution on PMMA with varying NaOBS and NaCl concentration.

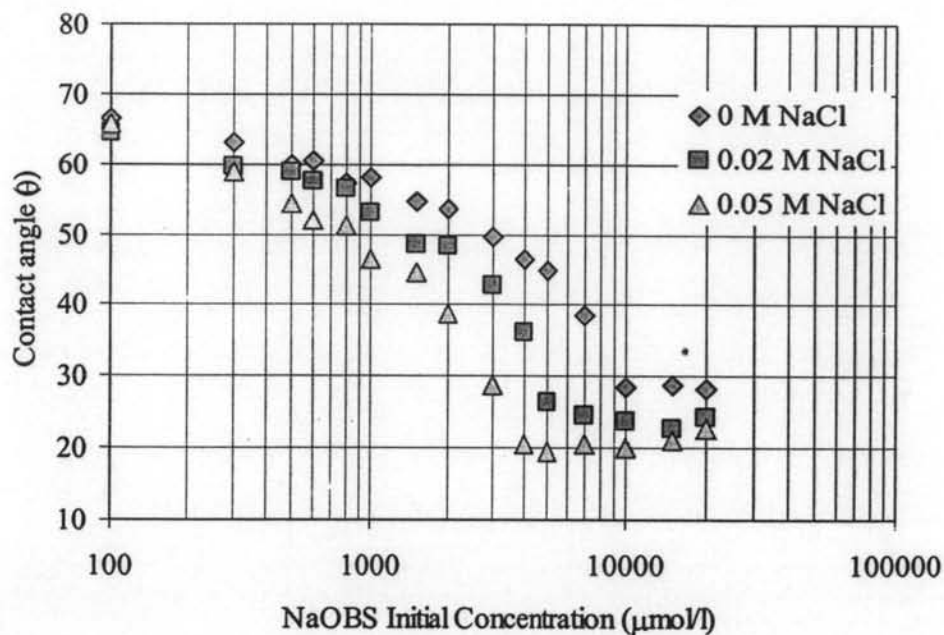


Figure 4.31 Contact angle of NaOBS solution on ABS with varying NaOBS and NaCl concentration.

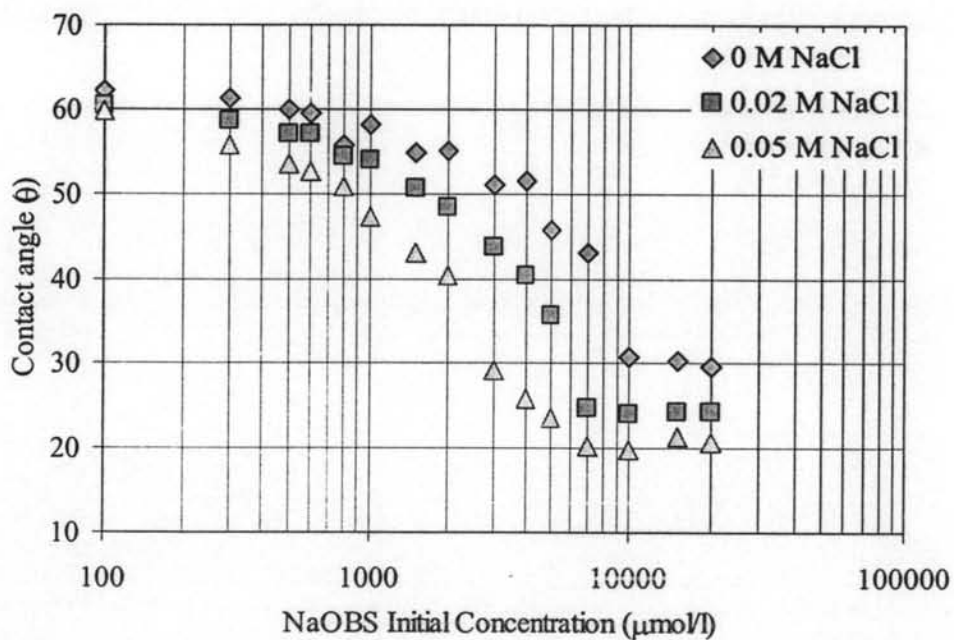


Figure 4.32 Contact angle of NaOBS solution on Nylon6,6 with varying NaOBS and NaCl concentration.

4.5.3 Wetting Enhancement by NaOBS

Figures 4.33 – 4.35 are the plot between $\cos \theta$ and $1/\gamma_{LV}$. Unlike CPC, the results did not show the linear relationship that intercepts at zero for all cases. This indicated that the value of $(\gamma_{SV} - \gamma_{SL})$ was not constant. Figure 4.36 – 4.38 also confirmed this. As mentioned early, the γ_{SL} should be a function of surfactant concentration for all cases.

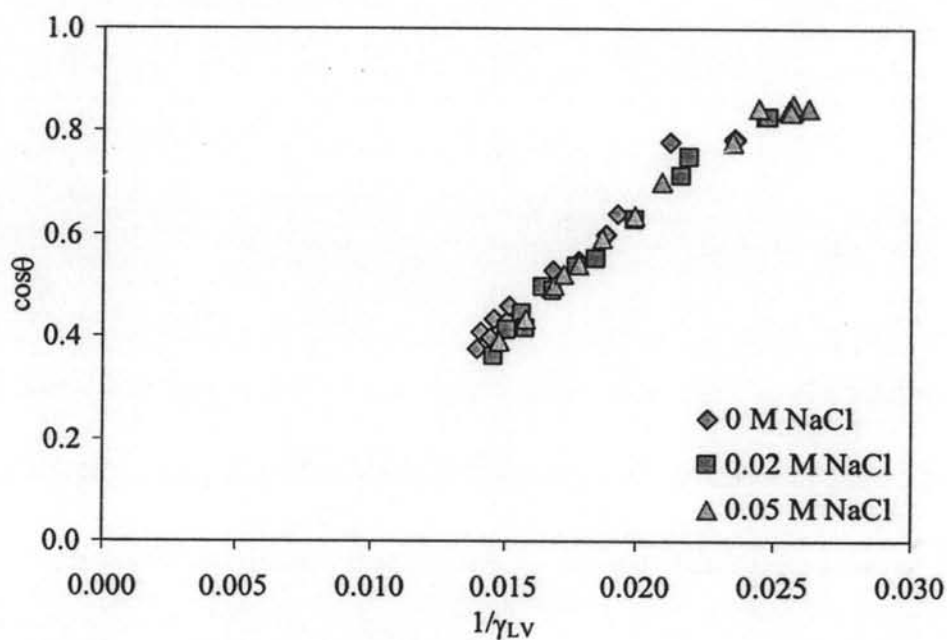


Figure 4.33 Contact angle on PMMA related to inversion of liquid/vapor surface tension of NaOBS solution.

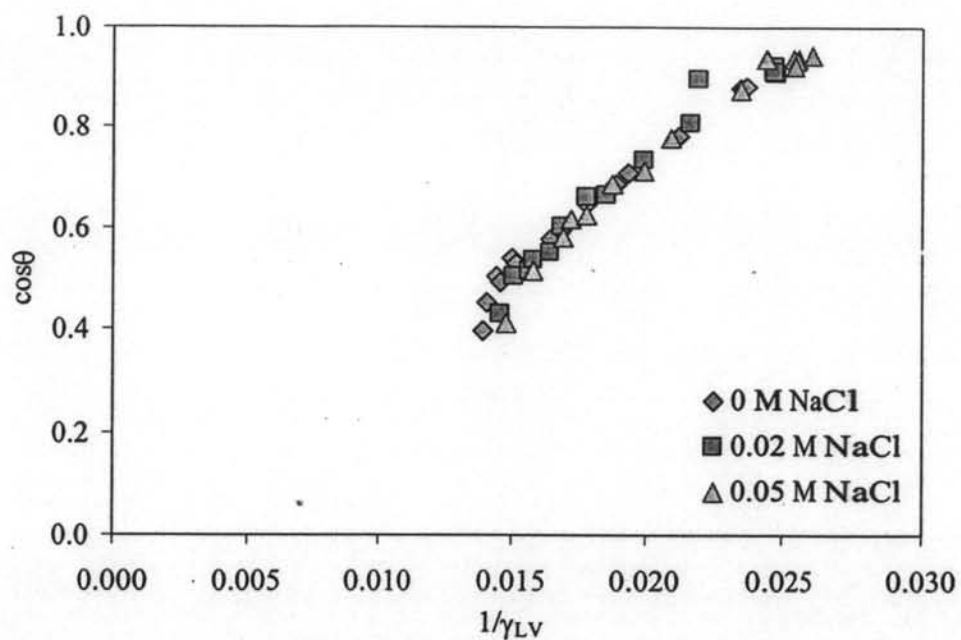


Figure 4.34 Contact angle on ABS related to inversion of liquid/vapor surface tension of NaOBS solution.

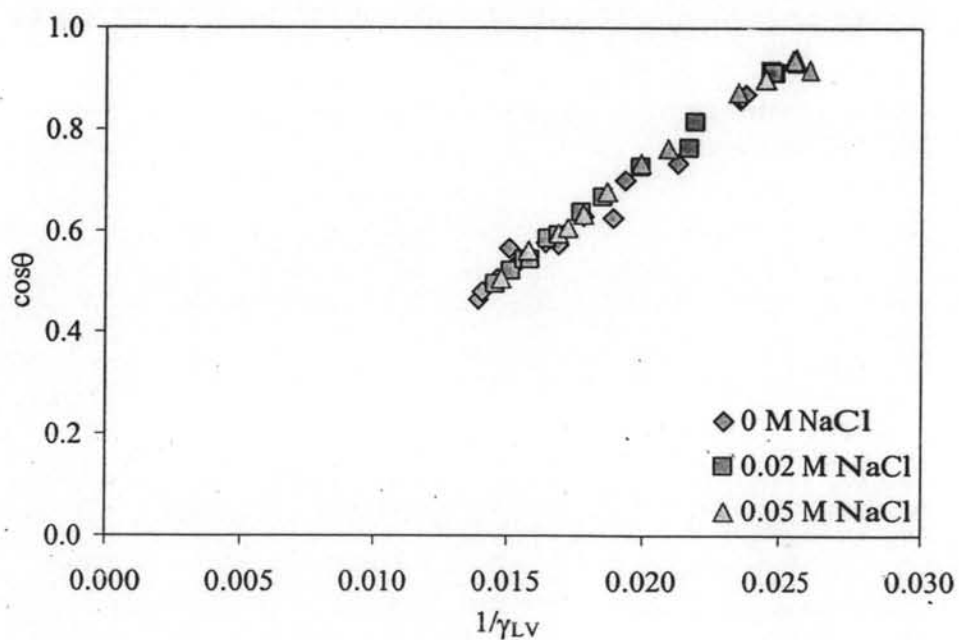


Figure 4.35 Contact angle on Nylon6,6 related to inversion of liquid/vapor surface tension of NaOBS solution.

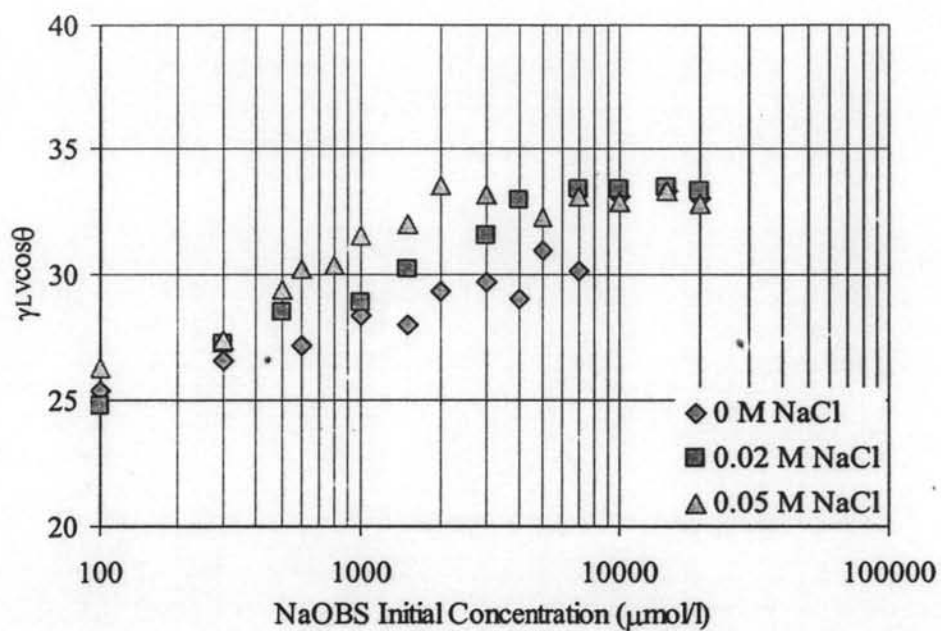


Figure 4.36 $\gamma_{LV} \cos \theta$ on PMMA related to equilibrium concentration of NaOBS solution.

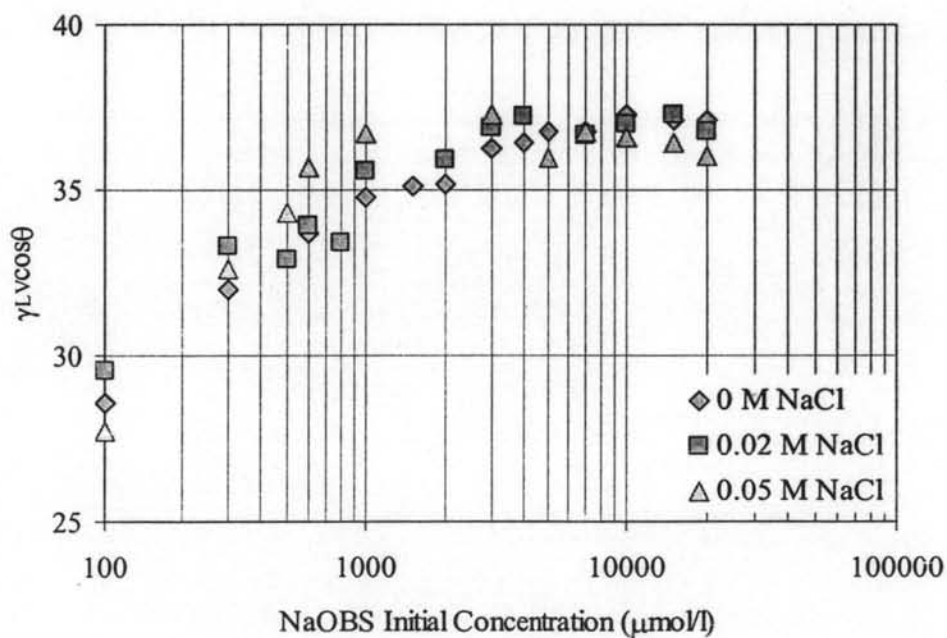


Figure 4.37 $\gamma_{LV} \cos \theta$ on ABS related to equilibrium concentration of NaOBS solution.

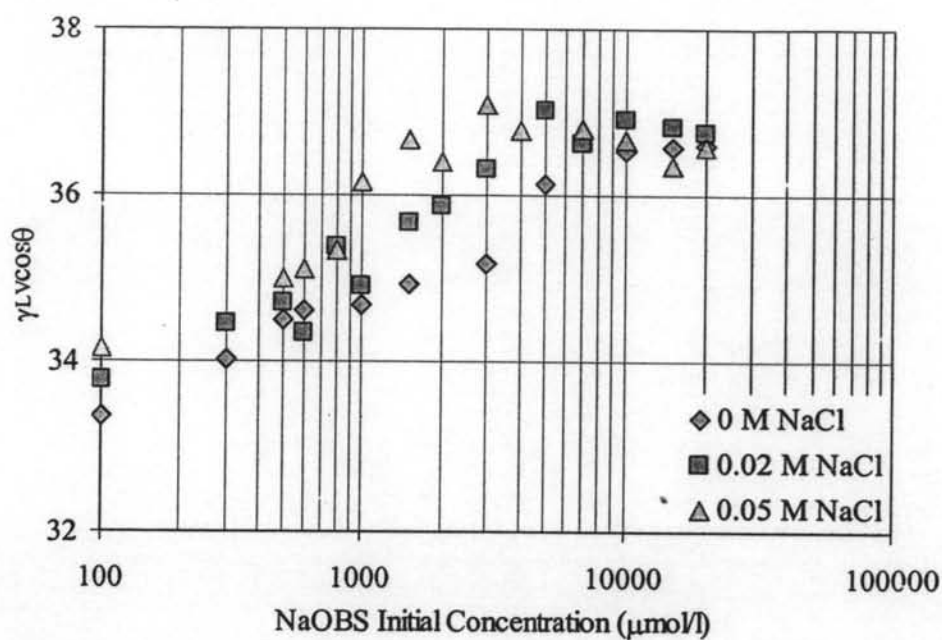


Figure 4.38 $\gamma_{LV} \cos \theta$ on Nylon6,6 related to equilibrium concentration of NaOBS solution.

Figures 4.39 – 4.41 show that the γ_{SL} decreased with increasing NaOBS concentration. This performed that the γ_{SL} was a function of NaOBS concentration. Nevertheless, at the same NaOBS concentration, the solution that had a higher ionic strength would have a lower γ_{SL} because the addition of NaCl allowed more NaOBS to adsorb at the solid/liquid interface.

Figures 4.42 – 4.44 display the relation between the γ_{SL} and NaOBS adsorption amount. As well as the latter relation, the γ_{SL} decreased with increasing NaOBS adsorption which could confirm the same conclusion.

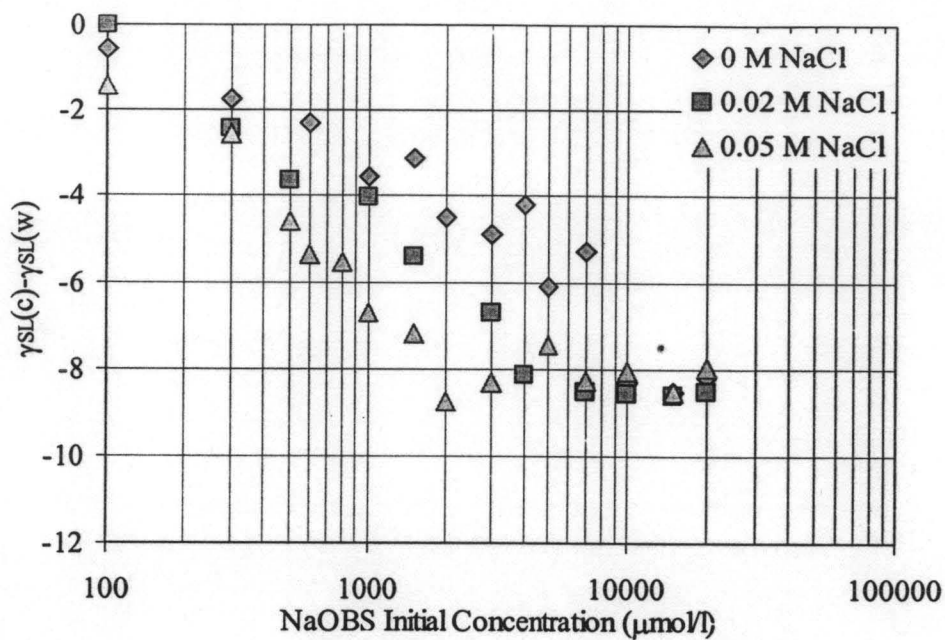


Figure 4.39 Relative solid/liquid interfacial tension of PMMA as a function of NaOBS concentration.

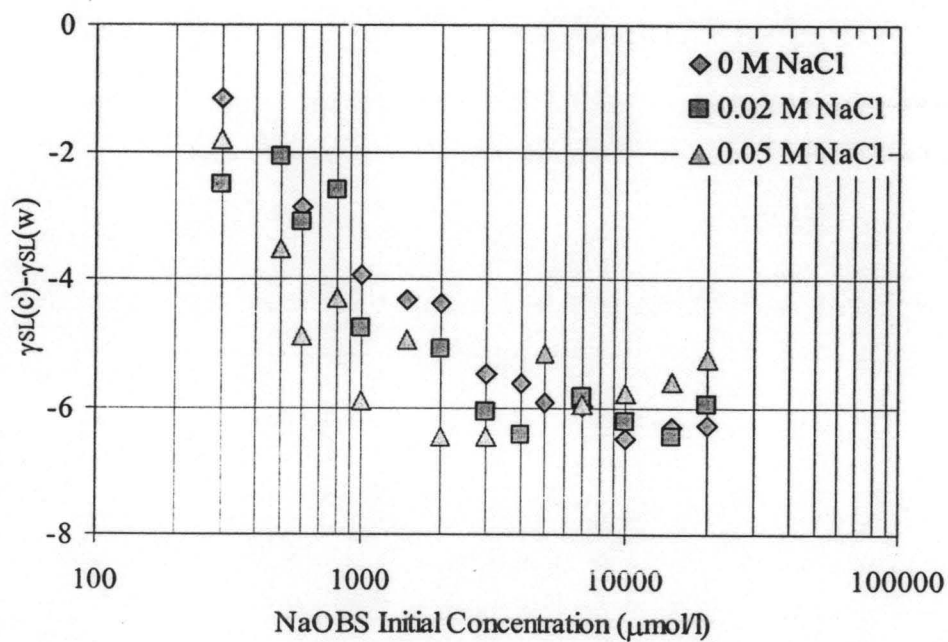


Figure 4.40 Relative solid/liquid interfacial tension of ABS as a function of NaOBS concentration.

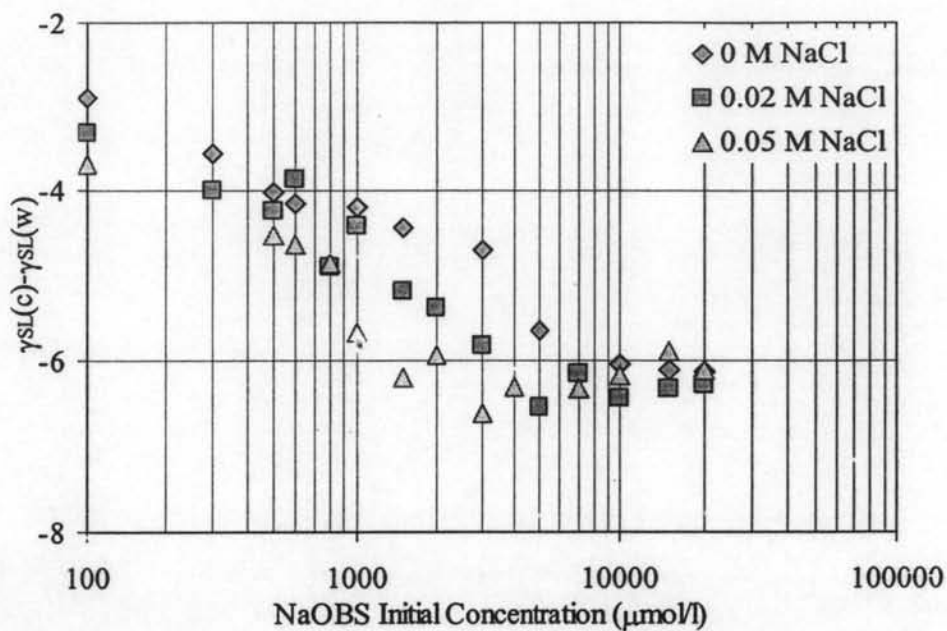


Figure 4.41 Relative solid/liquid interfacial tension of Nylon6,6 as a function of NaOBS concentration.

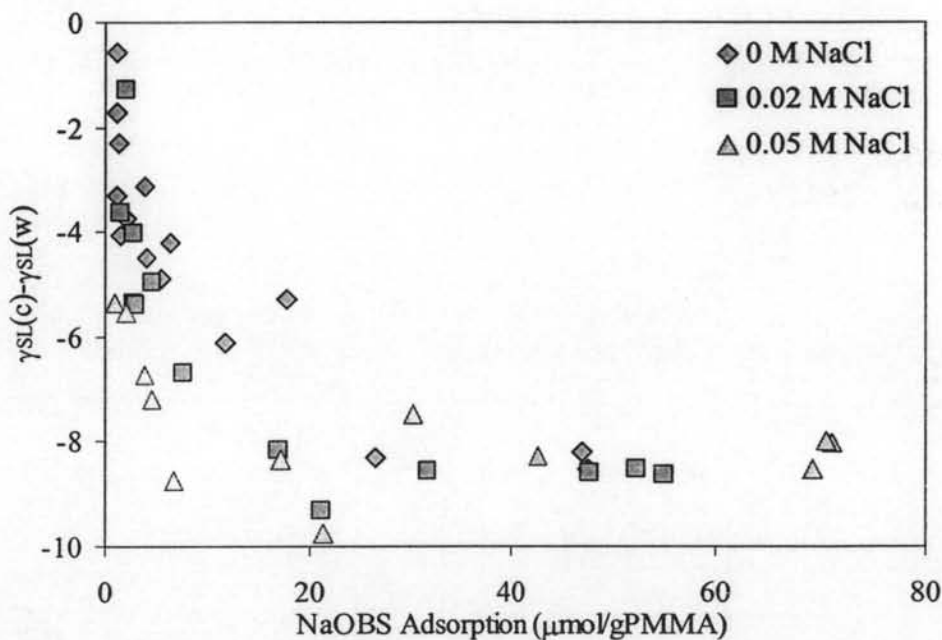


Figure 4.42 Relative solid/liquid interfacial tension of PMMA as a function of NaOBS adsorption.

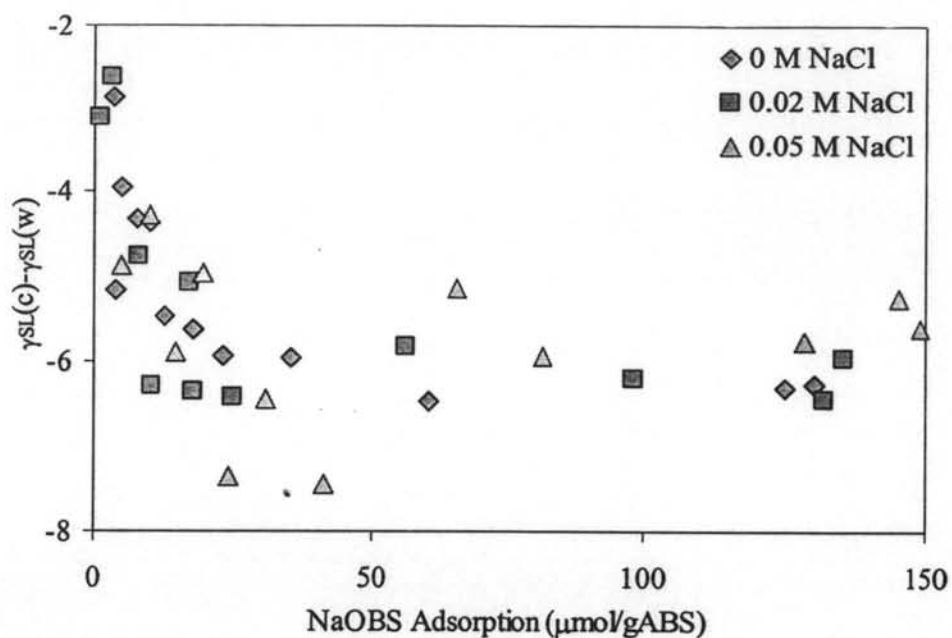


Figure 4.43 Relative solid/liquid interfacial tension of ABS as a function of NaOBS adsorption.

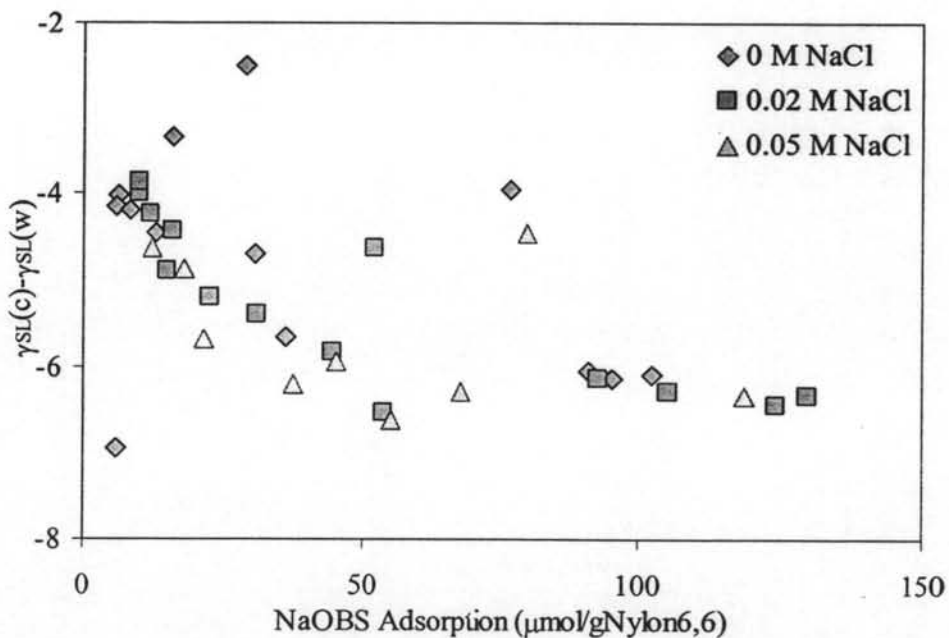


Figure 4.44 Relative solid/liquid interfacial tension of Nylon6,6 as a function of NaOBS adsorption.

From Figures 4.45 – 4.47, the adhesion tension plots exhibit the straight line with slope between 0 and -1. It could be suggested that NaOBS adsorbed on both liquid/vapor and solid/liquid interface and it preferred adsorb on liquid/vapor interface.

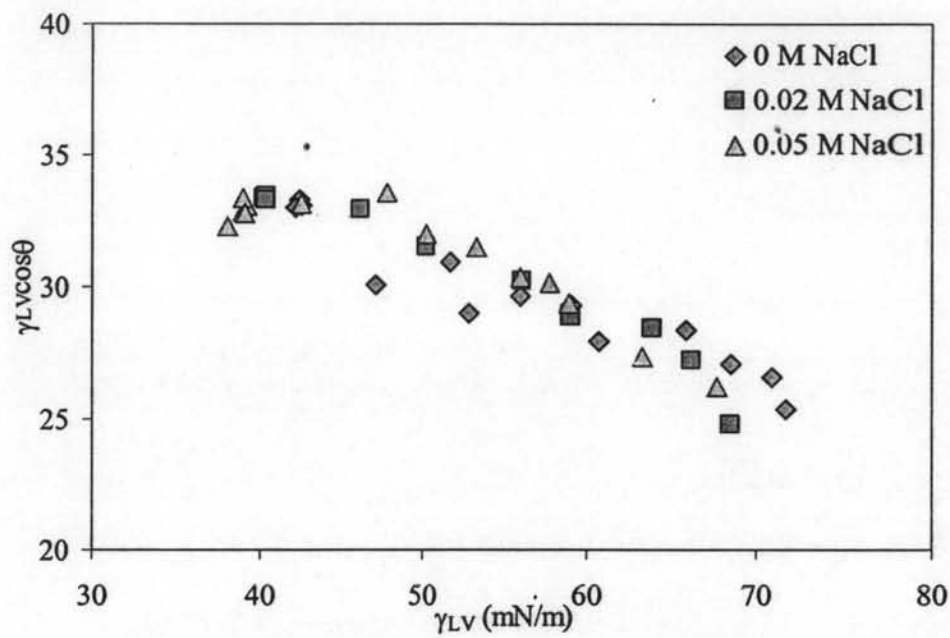


Figure 4.45 Adhesion tension plot of NaOBS solution on PMMA.

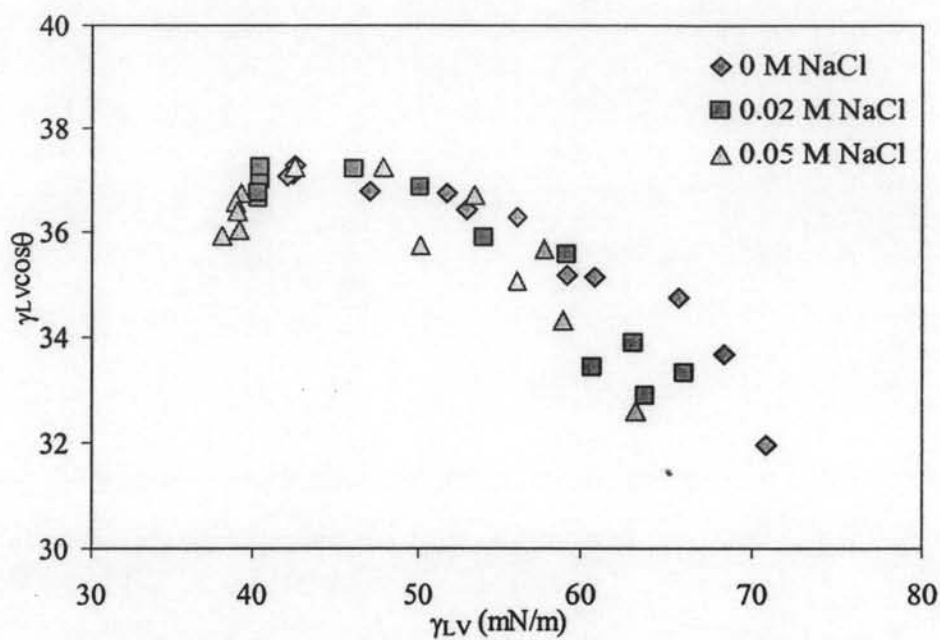


Figure 4.46 Adhesion tension plot of NaOBS solution on ABS.

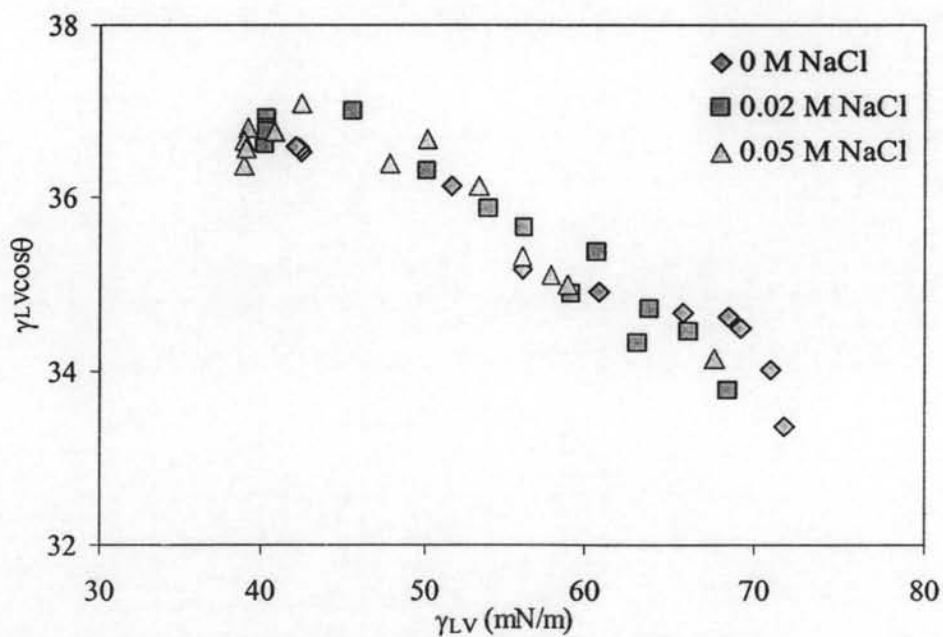


Figure 4.47 Adhesion tension plot of NaOBS solution on Nylon6,6.

On the same type of plastic, all NaOBS solutions that have the same γ_{LV} produced almost the same contact angle. Contrary to CPC, the presence of NaCl seemed to have no effect on the contact angle of solution with the same γ_{LV} , as shown in Figures 4.48 – 4.50. These Zisman's plots were not deviated due to both the structure (Supalassate, 2004) and the charge of NaOBS.

For the structure: The difference in the structure of CPC which has 16 carbon atoms and NaOBS which has 8 carbon atoms, CPC with a longer tail adsorbed on the surface like an anchor structure which limited the movement of CPC molecules. Hence, the addition of NaCl might not be able to allow more CPC to adsorb. On the other hand, NaOBS with a shorter tail could adsorb more freely on the surface. Consequently, the addition of NaCl would be able to allow more NaOBS to adsorb on the surface. The γ_{SL} would be reduced almost as effectively as γ_{SL} (Supalassate, 2004).

For the charge: CPC, which has the opposite charge to the surfaces, adsorbed on the surface in horizontal appearance and lowered the adsorption area. Therefore, the addition of NaCl could not allow more CPC to adsorb or could allow just a small amount. NaOBS, which has the same charge as the surfaces, adsorbed on the surface in vertical line and remained more adsorption area. So, the presence of NaCl could allow more NaOBS to adsorb and led to reduction in the γ_{SL} as well as the γ_{LV} .

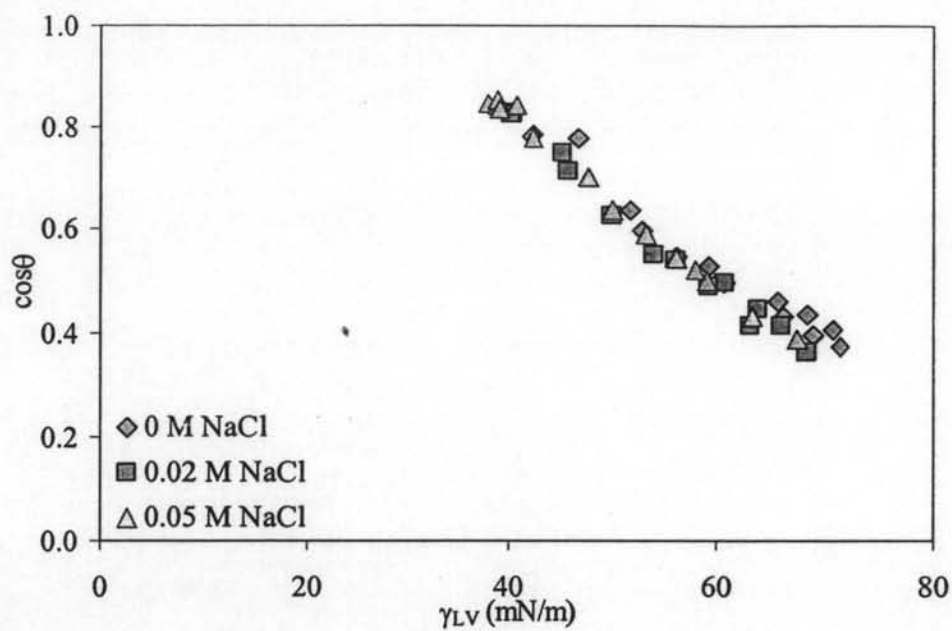


Figure 4.48 Contact angle of NaOBS on PMMA as a function of its liquid/vapor surface tension.

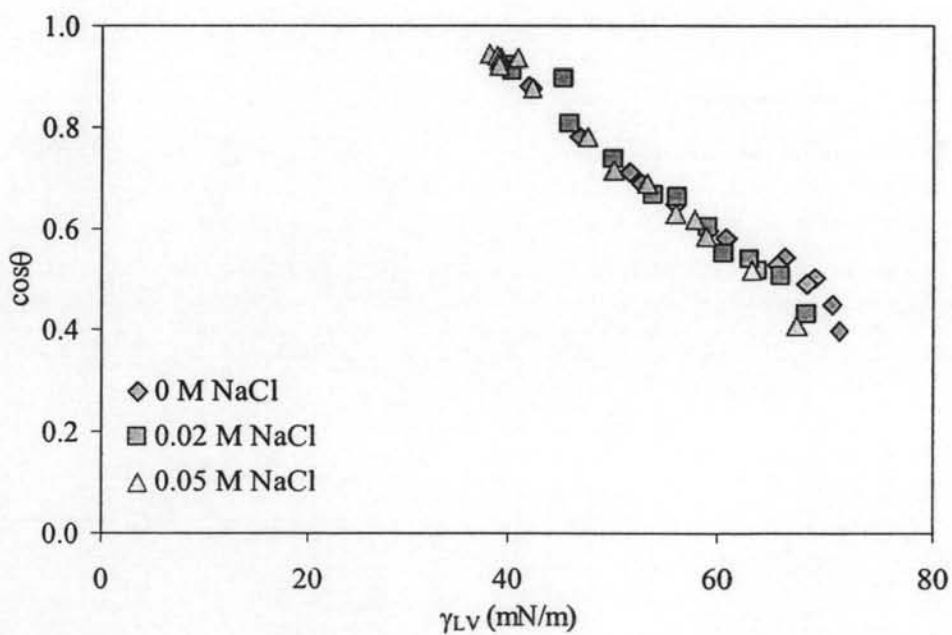


Figure 4.49 Contact angle of NaOBS on ABS as a function of its liquid/vapor surface tension.

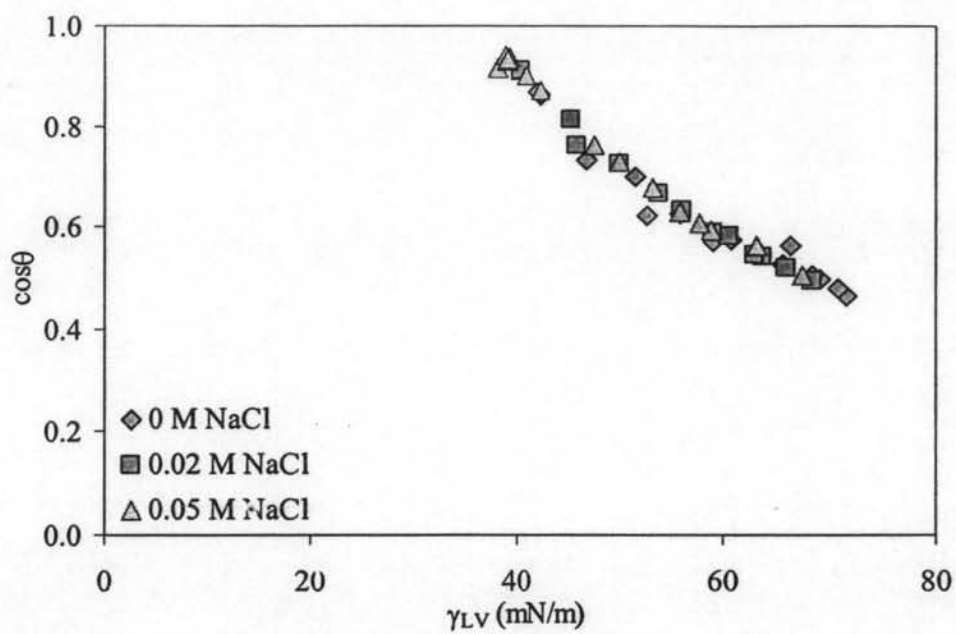


Figure 4.50 Contact angle of NaOBS on Nylon6,6 as a function of its liquid/vapor surface tension.

4.6 The Liquid/Vapor Surface Tension and CMC of OPEO₁₀

The liquid/vapor surface tension (γ_{LV}) of OPEO₁₀ solutions were plotted as a semi-logarithmic function of its concentration as shown in Figure 4.51. The liquid/vapor surface tension (γ_{LV}) decreases with OPEO₁₀ concentration until reaching CMC at about 200 μM .

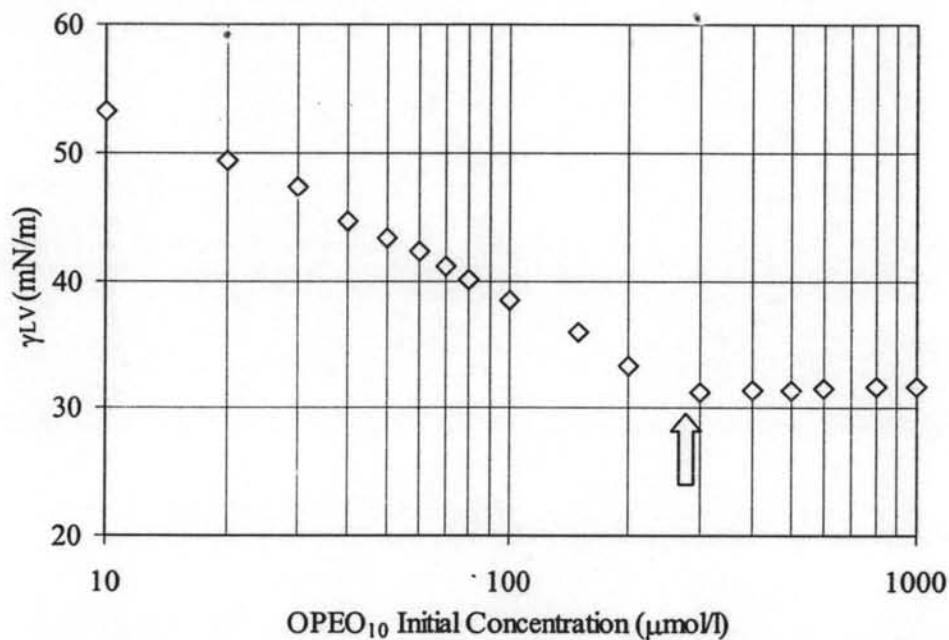


Figure 4.51 Liquid/vapor surface tension as a function of OPEO₁₀ concentration.

4.7 Adsorption of OPEO₁₀ and Its Wetting on Plastics

4.7.1 Adsorption Isotherm of OPEO₁₀

The adsorption isotherms of OPEO₁₀ on PMMA, ABS and Nylon6,6 are shown in Figure 4.52. The adsorption increased with surfactant concentration until reach plateau at about CMC.

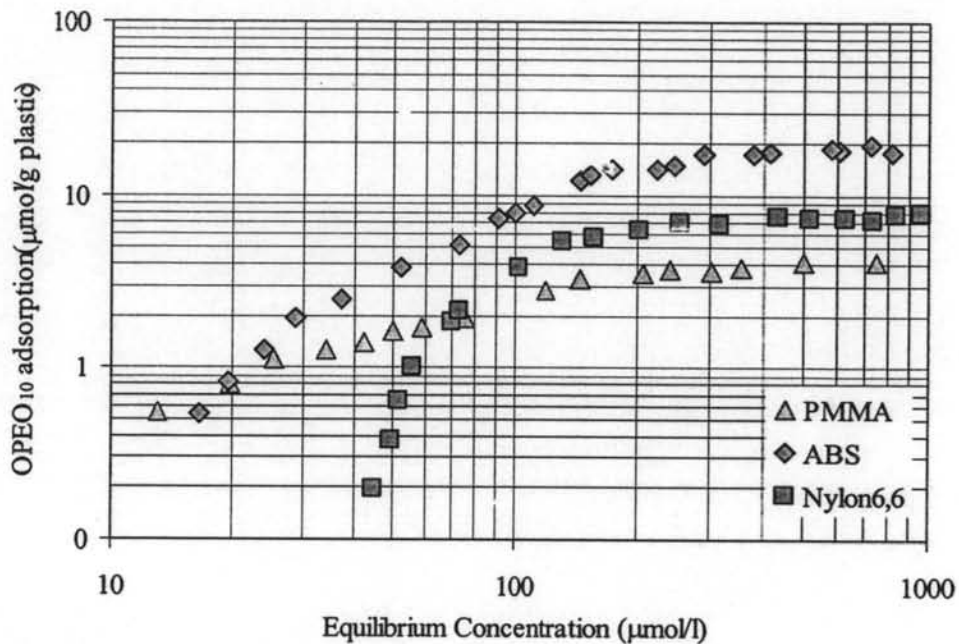


Figure 4.52 Adsorption isotherm of OPEO₁₀ on plastics.

4.7.2 Contact Angle of OPEO₁₀ Solution on Plastics

The contact angle of OPEO₁₀ solutions on PMMA, ABS and Nylon6,6 illustrated in Figure 4.53. As observed in the case of CPC and NaOBS, the contact angle decreased with increasing concentration and become nearly constant at the CMC region.

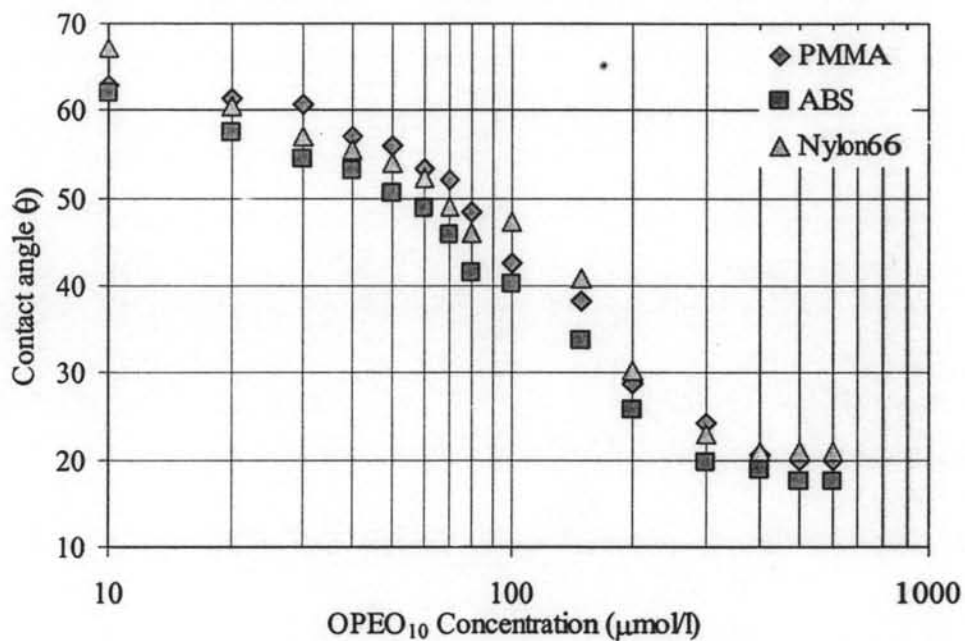


Figure 4.53 Contact angle of OPEO₁₀ solution on PMMA, ABS and Nylon6,6.

4.7.3 Wetting Enhancement by OPEO₁₀

As well as CPC and NaOBS, the relation in Figure 4.54 expresses the relationship between contact angle on plastics and the inversion of γ_{LV} which was not a linear relation that intercept at zero. Moreover, Figure 4.55–4.56 also depict that the relative interfacial tension decreased with increasing OPEO₁₀ concentration and adsorption.

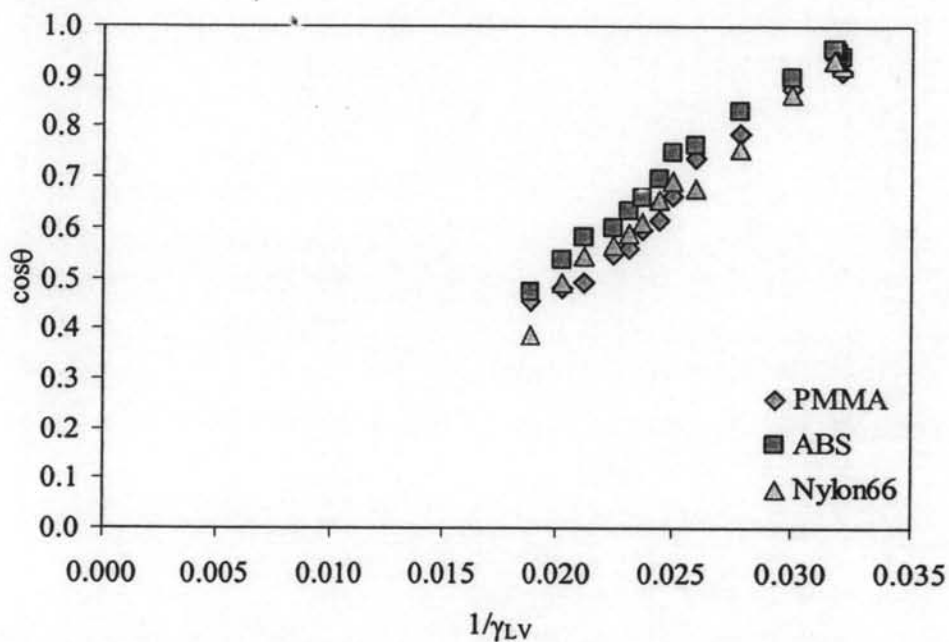


Figure 4.54 Contact angle on plastics related to inversion of liquid/vapor surface tension of OPEO₁₀ solution.

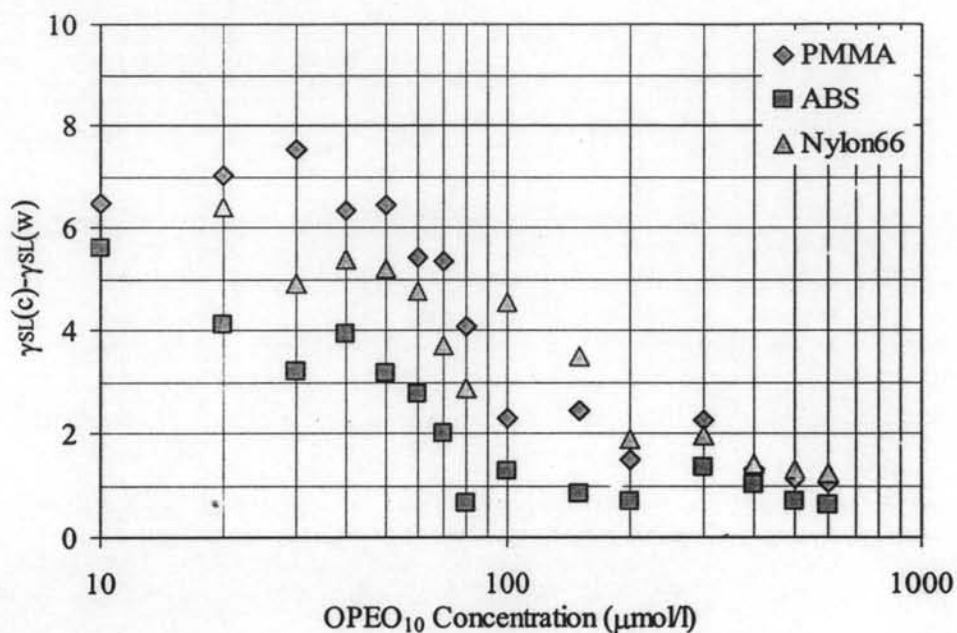


Figure 4.55 Relative solid/liquid interfacial tension of plastic as a function of OPEO₁₀ concentration.

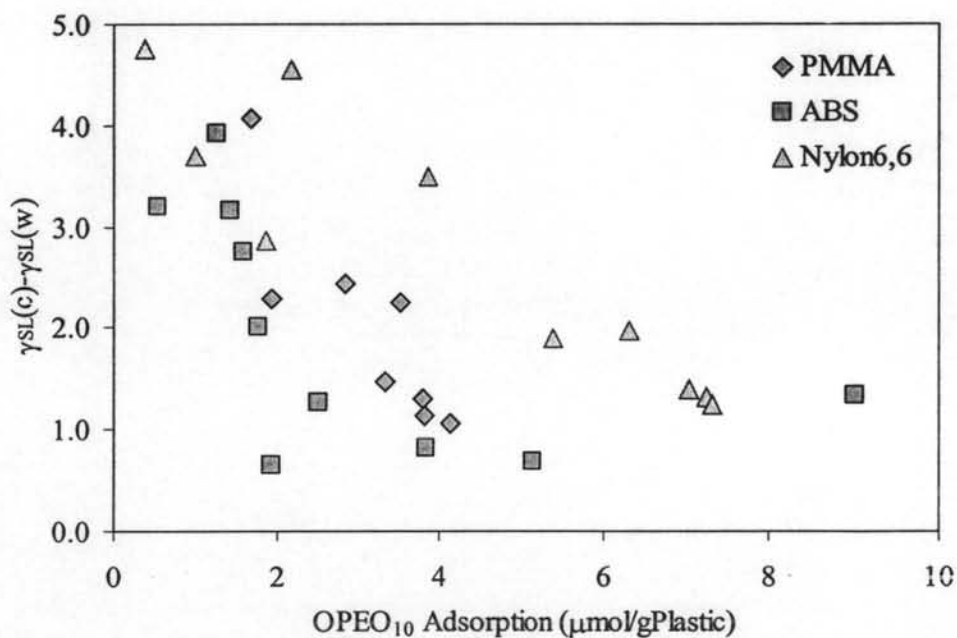


Figure 4.56 Relative solid/liquid interfacial tension of plastic as a function of OPEO₁₀ adsorption.

As obtained from NaOBS, the slopes of the adhesion tension plots were between 0 and -1. It could be suggested that OPEO₁₀ adsorbed on both liquid/vapor and solid/liquid interface and it preferred adsorb on liquid/vapor interface.

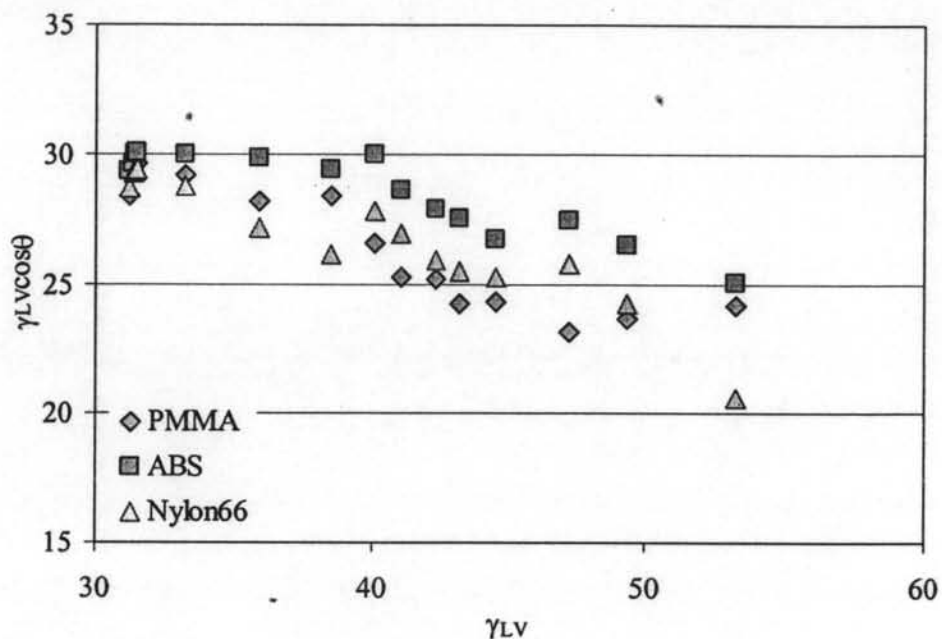


Figure 4.57 Adhesion tension plot of OPEO₁₀ solution on plastic.