

## CHAPTER IV

### RESULT AND DISCUSSION

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

The adsorption isotherms and contact angle measurements of AEs, NPE-9, and MES were done on three plastic surface; PTFE, PVC, and PMMA.

##### 4.1.1 Properties of Plastics

The contact angle of water on plastics, the specific surface area of plastics, and conditions for preparing polymer surfaces are shown in Table 4.1.

**Table 4.1** Properties of plastics

Materials	Contact angle (degree)	Specific surface area <sup>†</sup> (m <sup>2</sup> /g)	Compression molding condition <sup>‡</sup>
PTFE	100	4.152	preheat 20 min; compress 5 min (T: 200 °C; P: 15 tons)
PVC	84	3.025	preheat 20 min; compress 5 min (T: 200 °C; P: 15 tons)
PMMA	80	1.939	preheat 2 min; compress 2 min (T: 180 °C; P: 15 tons)

<sup>†</sup> The plastic powder was dried and outgassed in the sample cell at 60 °C for 18 h before the adsorption. The specific surface area of each plastic was evaluated from the seven BET adsorption isotherm.

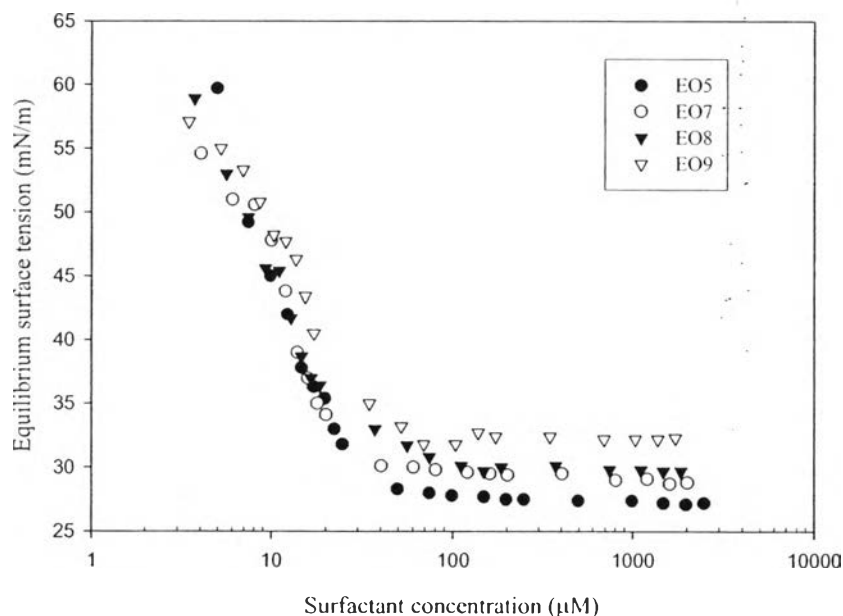
<sup>‡</sup> Polymer plates were prepared by compressing. Only some parts of prepared plates could be used in contact angle measurement due to nonhomogeneous heat transfer from heating plate.

From Table 4.1, the contact angle of pure water on PTFE is the highest followed by PVC, and PMMA, respectively. This result indicates that the degree of hydrophobicity of plastics increases in the order of: PTFE > PVC > PMMA. The values are near with the previous study (Szymczyk *et al.*, 2005). For the specific surface

area, the specific surface areas of plastics are quite low due to limited performance of grinding machine.

#### 4.2 The Liquid/Vapor Surface Tension and CMC of AEs

The liquid/vapor interfacial tensions of AEs were done by using tensiometer with Wilhelmy plate method at 1 h and 30 °C. CMC,  $\gamma_{CMC}$ ,  $\pi_{CMC}$ , and  $a^s$  were determined.



**Figure 4.1** Surface tension isotherms of alcohol ethoxylate LS5 (EO5), alcohol ethoxylate LS7 (EO7), alcohol ethoxylate LS8 (EO8), and alcohol ethoxylate LS9 (EO9).

Figure 4.1 shows the relations between the liquid/vapor interfacial tension ( $\gamma_{LV}$ ) and the initial concentration of AE solutions as a semi-logarithmic function. It demonstrates that the  $\gamma_{LV}$  of solution decreases with increasing surfactant concentration. It indicates that surfactant in the aqueous solution can adsorb at the liquid/vapor interface and changes the amount of work required to expand that interface.

The  $\gamma_{LV}$  decreases continuously until levels off at certain concentration. At that concentration, no more area which surfactant molecules can adsorb but they aggregate themselves as micelle and that concentration is known as critical micelle concentration or CMC. According to the results, the CMC increases with increasing the number of polyethylene oxide (POE) group in their surfactant structures. The reasonable for CMC change is that increasing EO chain length increase water solubility by increasing hydration and then increase the amount of energy required dehydrating the molecule during its incorporation into the micelle. Increasing EO content therefore increases the CMC. Another reason comes from molecular structure of surfactants. The reason is that increasing EO chain length also increases molecular size, which makes it more difficult for the ethoxylate to pack at the air–water interface. The ability to lower surface tension (surfactant effectiveness,  $\pi_{CMC}$ ) is therefore reduced as the EO content is increased (Cox, 1989). This reason is supported by the minimum area occupied by a surfactant molecule ( $a^s$ ) calculated from Equation 2.3 which show that surfactant with high EO number occupies larger area. This trend was also found in other POE nonionics (Hama *et al.*, 1997a, 1997b). The CMC of the studied AEs are summarized in Table 4.2 also including  $\gamma_{CMC}$ ,  $\pi_{CMC}$ , and  $a^s$ . In addition, the shapes of  $\gamma_{LV}$ –concentration curves seem to be affected by the EO content. This may be related to the capacity of the EO chain to interact (via hydrogen bonding) with other molecules (Cox, 1989).

**Table 4.2** CMC,  $\gamma_{CMC}$ ,  $\pi_{CMC}$ , and  $a^s$  of AEs

Surfactants	CMC ( $\mu\text{M}$ )	$\gamma_{CMC}$ (mN/m)	$\pi_{CMC}^\dagger$ (mN/m)	$a^{s\dagger}$ ( $\text{\AA}^2$ )
Alcohol ethoxylate LS5 (EO5)	25	27.2	45.6	23.70
Alcohol ethoxylate LS7 (EO5)	30	28.8	44.0	26.72
Alcohol ethoxylate LS8 (EO8)	45	29.7	43.1	29.59
Alcohol ethoxylate LS9 (EO9)	70	32.3	40.5	34.41

<sup>†</sup> The effectiveness in surface tension reduction (mN/m);  $\pi_{CMC} = \gamma_i - \gamma_f$

<sup>‡</sup> Minimum area occupied by a molecule of surfactant ( $\text{\AA}^2$ ); Equation 2.3

The given CMC values are close to other studies but slightly below (Cox, 1989; Hama, 1997b; Rosen, 2004). The reason may be due to the dispersity of the studied surfactants. The alkyl chain distribution of each studied AE was C12 to C14 due to heterogeneity of raw material used. It may behave kind of mixture of surfactants that normally provide lower CMC and  $\gamma_{\text{CMC}}$  than single surfactant.

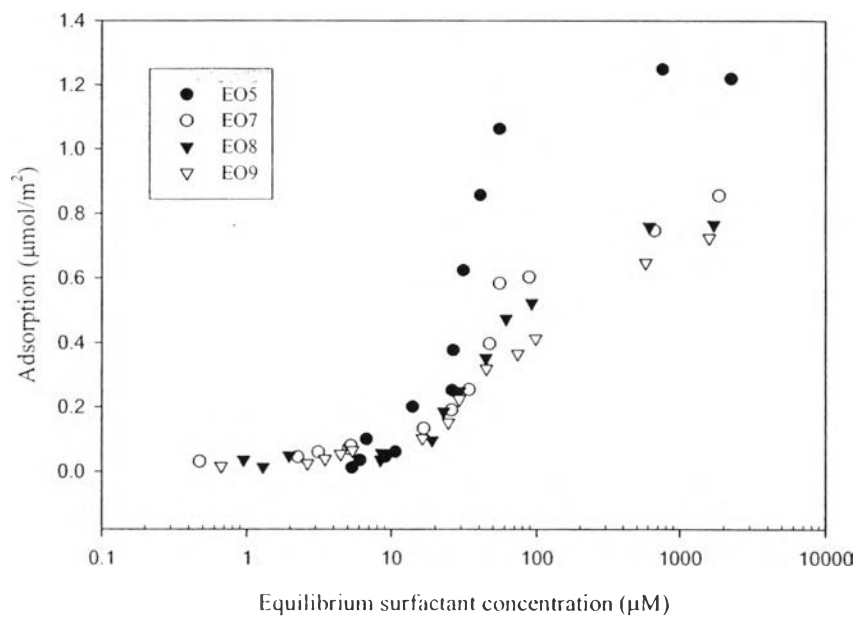
### 4.3 Adsorption of AEs and their Wettings on Plastics

The adsorptions of AEs were done on three plastic surface; PTFE, PVC, and PMMA at equilibration time of 5 days and temperature of 30 °C. Contact angle measurements were done at temperature of 30 °C. The given data came from the equilibrium time of 1 min.

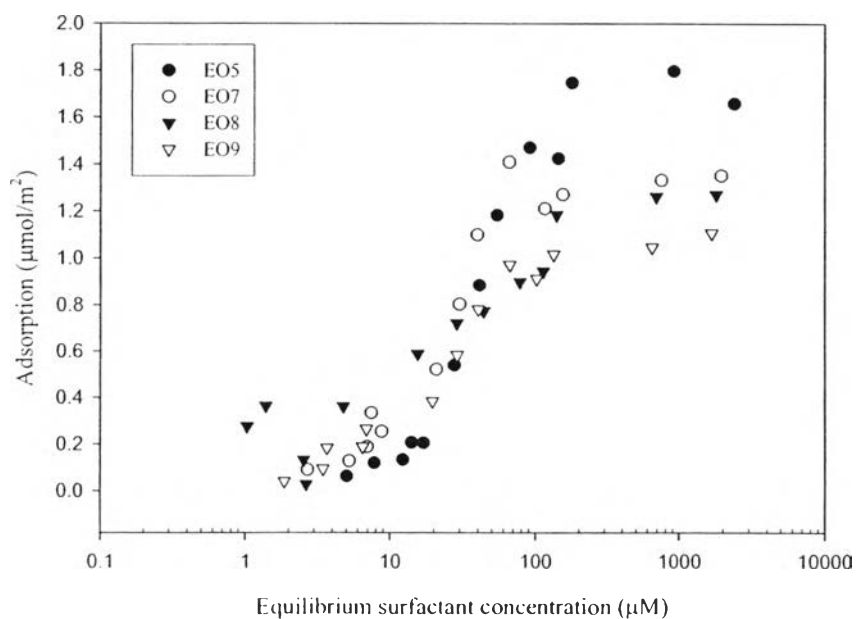
#### 4.3.1 Adsorption Isotherms of AEs

The adsorbed amount of surfactant on polymer surface was plotted versus the logarithm of the equilibrium concentration of surfactant solution; or so called “the adsorption isotherm”. The adsorption isotherms of AEs on PTFE, PVC, and PMMA are shown in Figures 4.2 to 4.4, respectively.

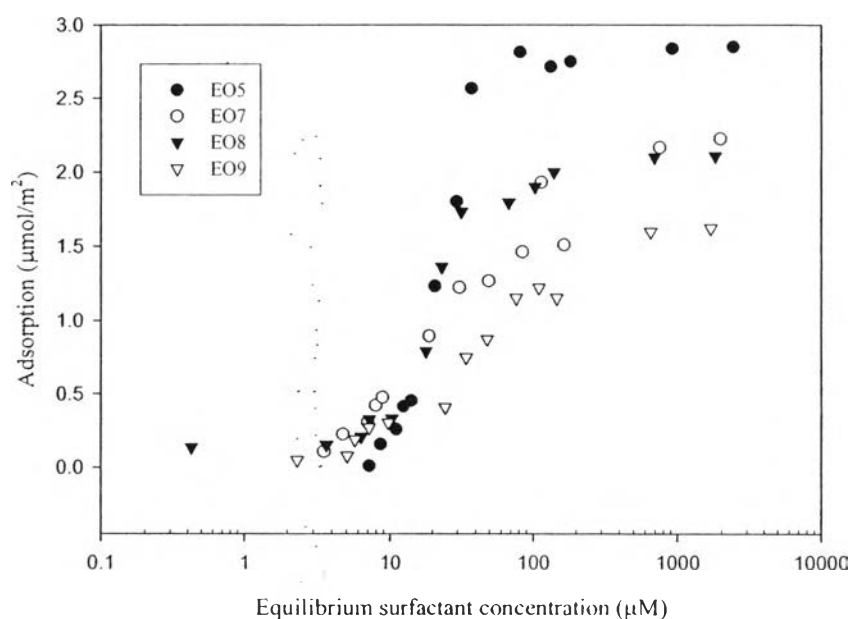
The result shows that the adsorption of each AE slightly increases with increasing equilibrium concentration of corresponding surfactant and levels off to the plateau at around the CMC region. In addition, the amount of AE adsorbed decreases as the number of ethylene oxide units in the AE molecule increases. The result was in line with other POE nonionics studies (Scales *et al.*, 1986; Romero-Cano *et al.*, 1998). The reasonable explanation is that the longer polyoxyethylene chain creates more excluded area, and then limits the amount adsorbed. In addition, the configuration of the POE chain affects on the amount of surfactant adsorbed. However, the amount of AEs adsorbed decreases with increasing the length of the oxyethylene chain, it does especially when the change goes from 5 to 7 oxyethylene groups, but decreases slightly when the number of the EO group increases more. It may indicate that the longer POE chain shows a random coil configuration which projects a similar excluded area for the incoming molecules (González-García *et al.*, 2004).



**Figure 4.2** Adsorption isotherms of alcohol ethoxylate LS5 (EO5), alcohol ethoxylate LS7 (EO7), alcohol ethoxylate LS8 (EO8), and alcohol ethoxylate LS9 (EO9) on PTFE.

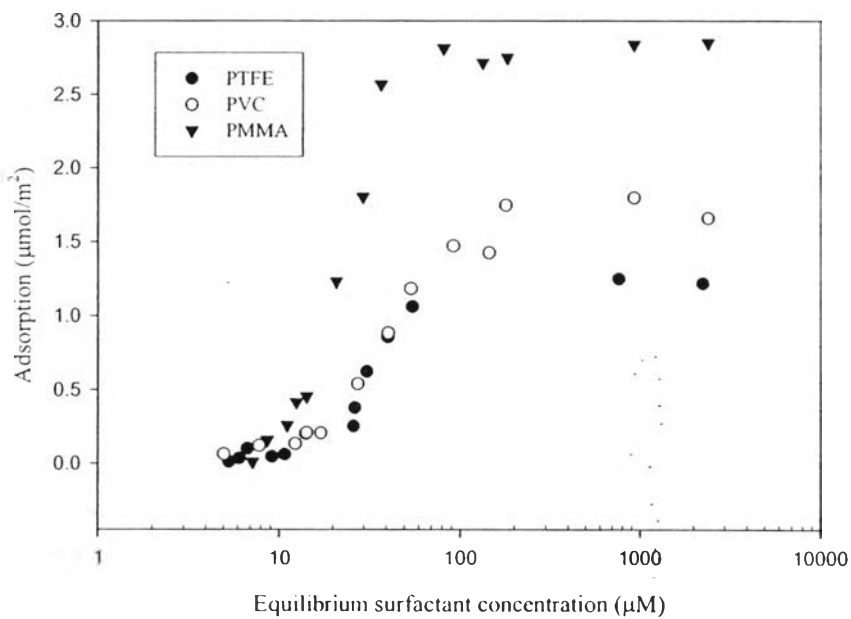


**Figure 4.3** Adsorption isotherms of alcohol ethoxylate LS5 (EO5), alcohol ethoxylate LS7 (EO7), alcohol ethoxylate LS8 (EO8), and alcohol ethoxylate LS9 (EO9) on PVC.

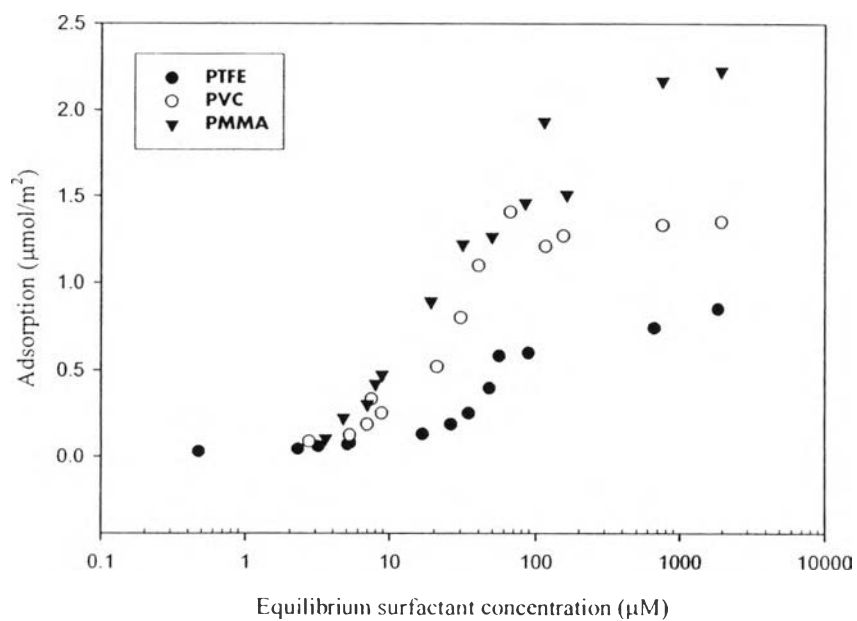


**Figure 4.4** Adsorption isotherms of alcohol ethoxylate LS5 (EO5), alcohol ethoxylate LS7 (EO7), alcohol ethoxylate LS8 (EO8), and alcohol ethoxylate LS9 (EO9) on PMMA.

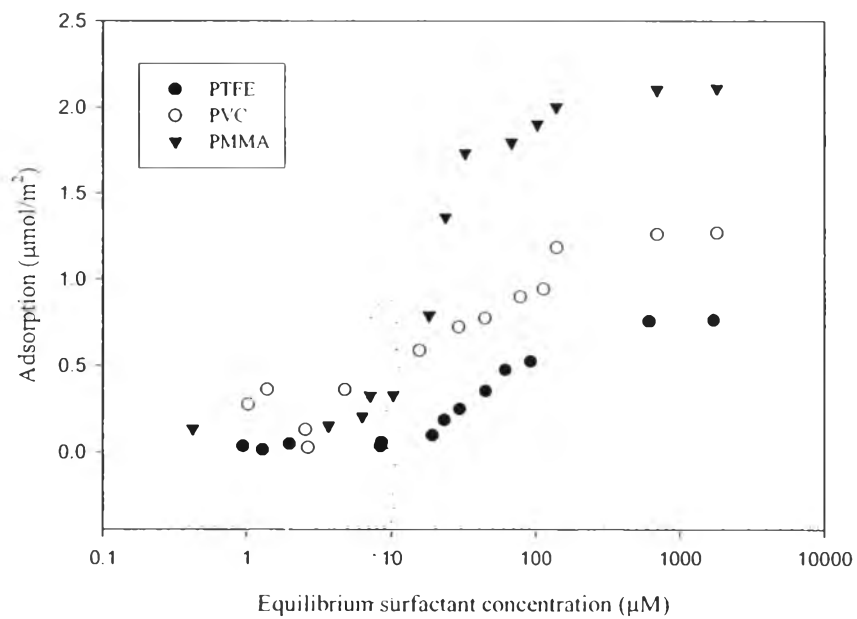
Figures 4.5 to 4.8 show the effect of hydrophobicity of the surface on the adsorption of AEs. The result indicates that the amount of AE adsorbed increases with decreasing hydrophobicity of the surface. It may be due to the similarity of polarity between the surfactants and the surfaces facilitate the surfactant to adsorb more easily, thus the amount of surfactant adsorbed is enhanced. The given result is in agreement with previous studies (Meerit, 2005; Puttharak, 2006; Thongpae, 2007).



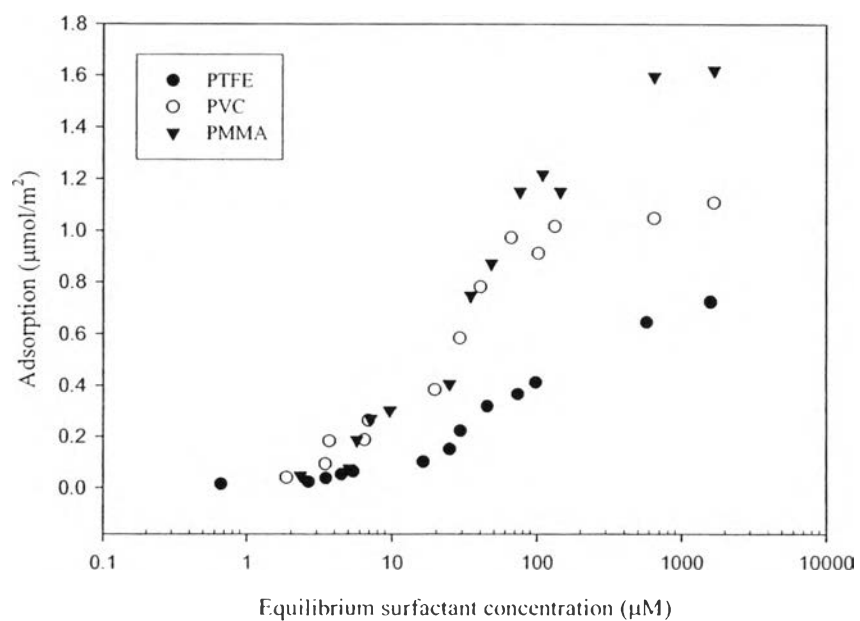
**Figure 4.5** Adsorption isotherms of alcohol ethoxylate LS5 (EO5) on PTFE, PVC, and PMMA.



**Figure 4.6** Adsorption isotherms of alcohol ethoxylate LS7 (EO7) on PTFE, PVC, and PMMA.



**Figure 4.7** Adsorption isotherms of alcohol ethoxylate LS8 (EO8) on PTFE, PVC, and PMMA.



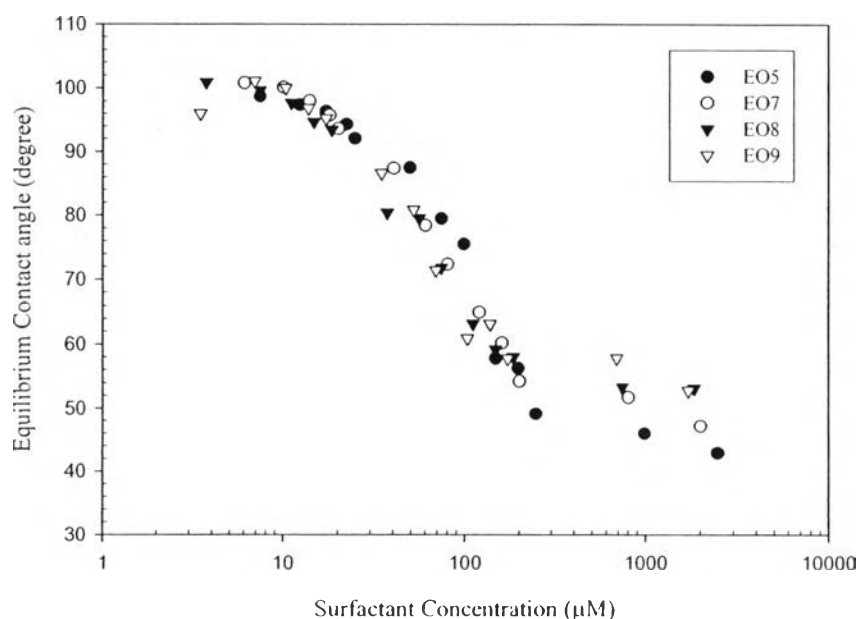


**Figure 4.8** Adsorption isotherms of alcohol ethoxylate LS9 (EO9) on PTFE, PVC, and PMMA.

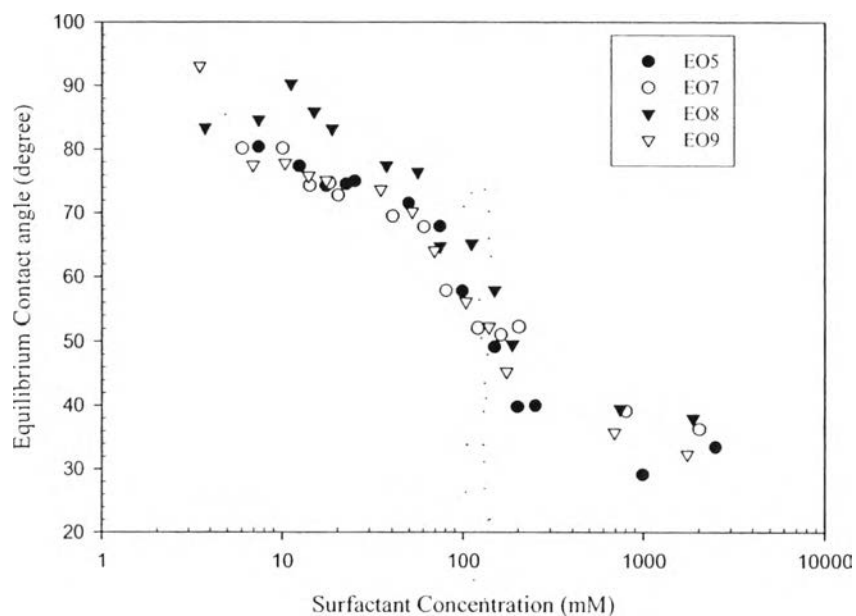
#### 4.3.2 Contact Angle of AE Solutions on Plastics

The relation between the static contact angle on PTFE, PVC, and PMMA and concentration of AE solutions are shown in Figures 4.9 to 4.11.

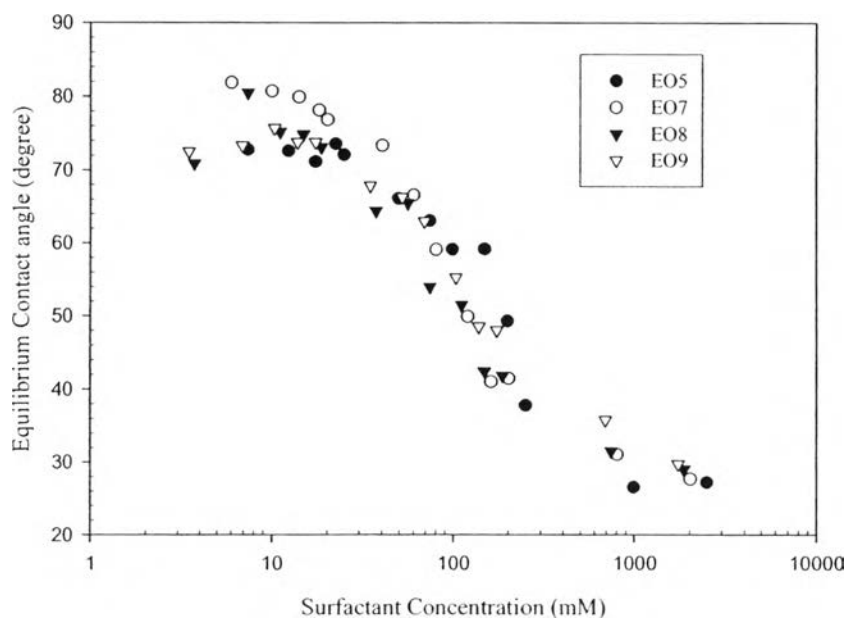
From the plot, the contact angle decreases significantly with increasing AE concentration and become nearly constant above the CMC. In addition, the contact angle of AEs on each surface decreases as the number of ethylene oxide unit in the AEs molecules decreases. In other word, the wettability of AEs on each surface increases with decreasing the number of POE group. The reason is kind of same as the reason for adsorption. The result is definitely in the same trend with other POE nonionics study (Scales *et al.*, 1986). However, the trend becomes reverses for the wettability study of surfactant with alkyl chain longer than C16 (Hama *et al.*, 1997a) that may be because the too much hydrophobicity of alkyl chain of surfactant suppresses the wettability.



**Figure 4.9** Contact angle of alcohol ethoxylate LS5 (EO5), alcohol ethoxylate LS7 (EO7), alcohol ethoxylate LS8 (EO8), and alcohol ethoxylate LS9 (EO9) on PTFE.

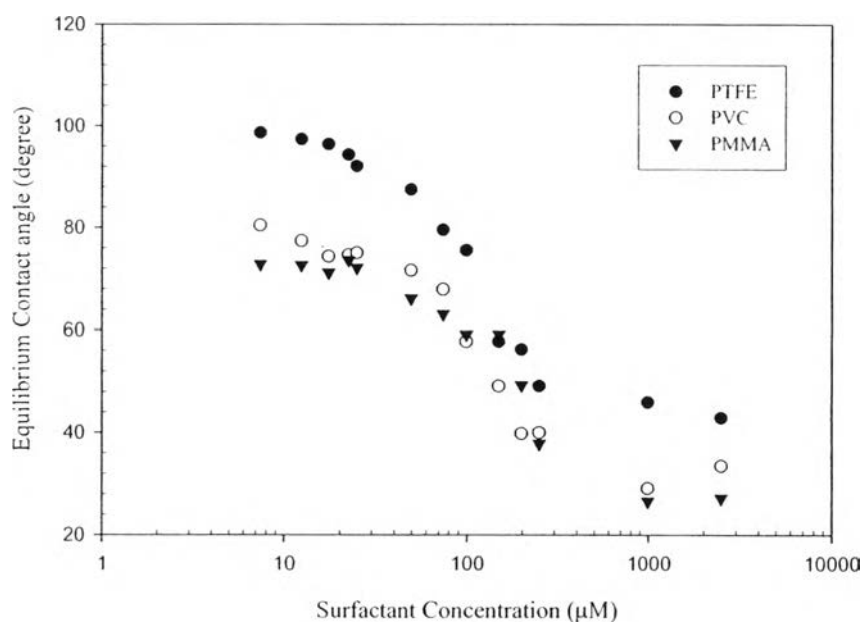


**Figure 4.10** Contact angle of alcohol ethoxylate LS5 (EO5), alcohol ethoxylate LS7 (EO7), alcohol ethoxylate LS8 (EO8), and alcohol ethoxylate LS9 (EO9) on PVC.

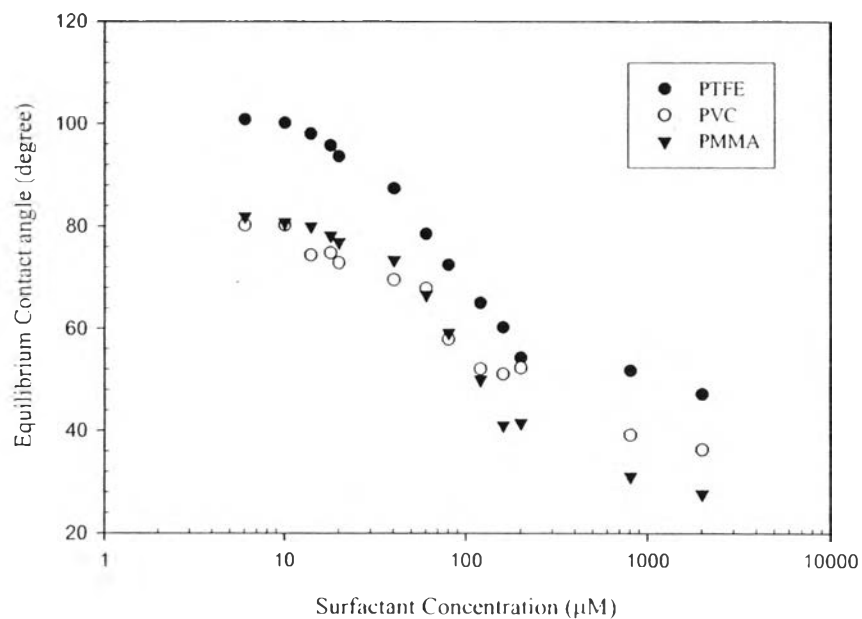


**Figure 4.11** Contact angle of alcohol ethoxylate LS5 (EO5), alcohol ethoxylate LS7 (EO7), alcohol ethoxylate LS8 (EO8), and alcohol ethoxylate LS9 (EO9) on PMMA.

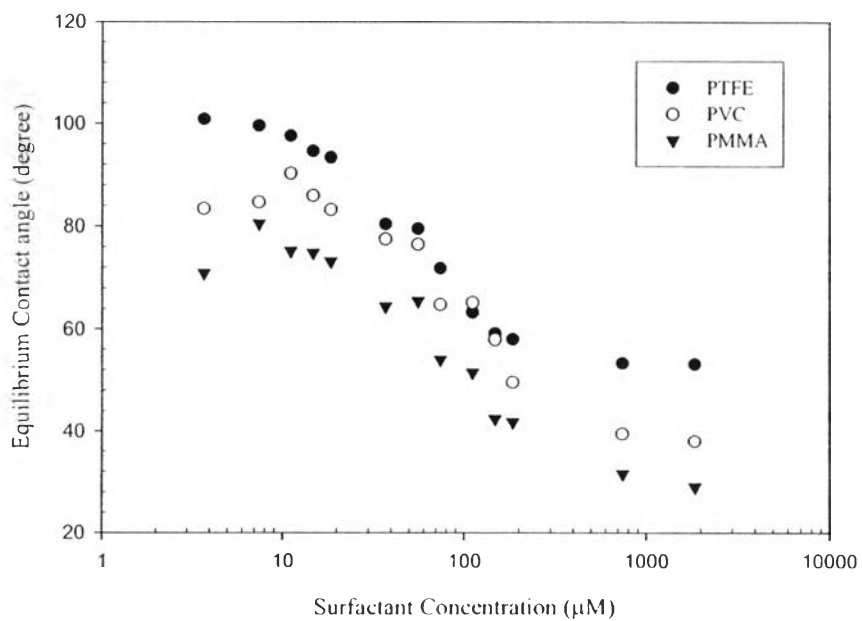
The contact angles of AEs on different plastics shown in Figures 4.12 to 4.15 are in the vicinity values corresponding to the polarity and hydrophobicity, of plastics as shown in Table 4.1. The result indicates that the wettability of AEs increases with increasing hydrophilicity of the surface. It may be due to the similarity of polarity between the surfactants and the surfaces facilitate the surfactant to adsorb more easily, thus the wettability is enhanced. The given result is in the same trend with previous studies (Meerit, 2005; Puttharak, 2006; Thongpae, 2007).



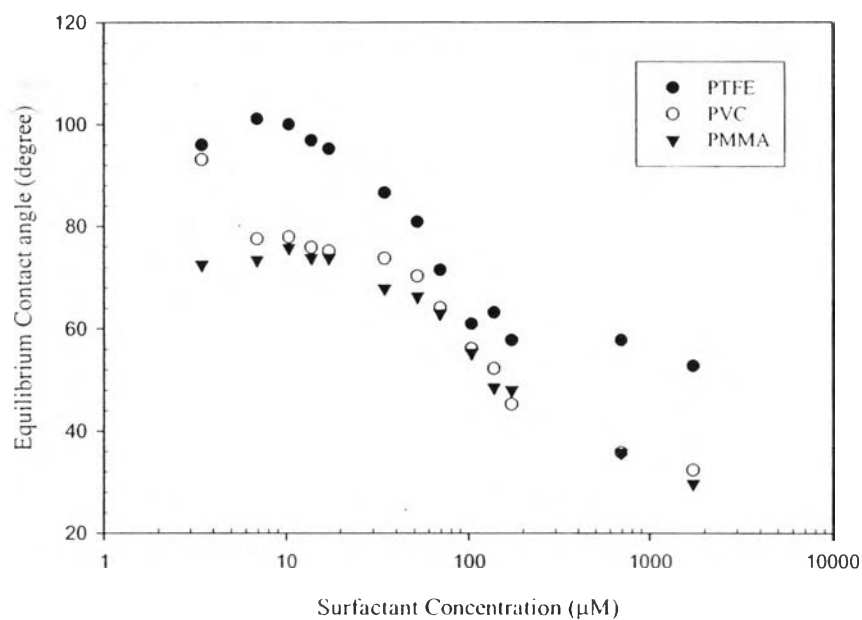
**Figure 4.12** Contact angle of alcohol ethoxylate LS5 (EO5) on PTFE, PVC, and PMMA.



**Figure 4.13** Contact angle of alcohol ethoxylate LS7 (EO9) on PTFE, PVC, and PMMA.



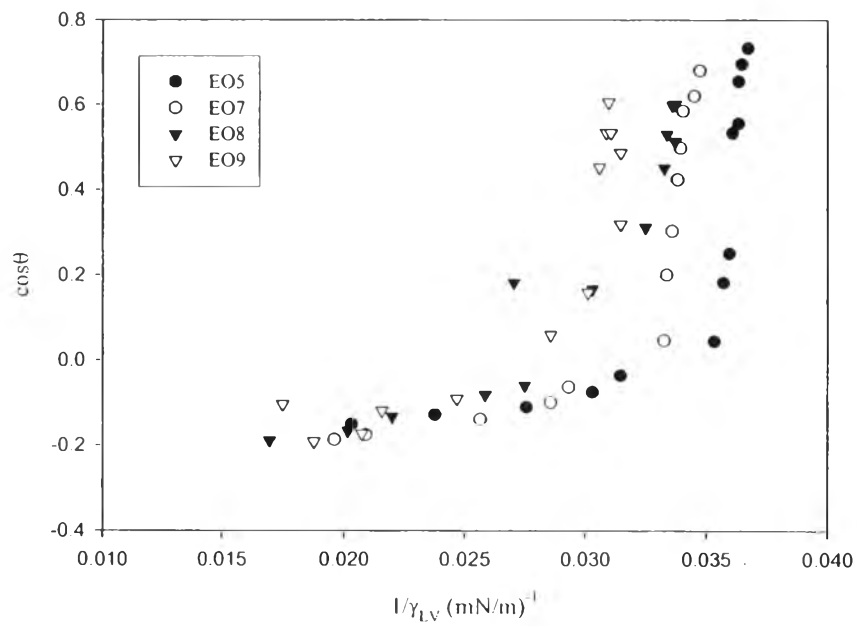
**Figure 4.14** Contact angle of alcohol ethoxylate LS8 (EO9) on PTFE, PVC, and PMMA.



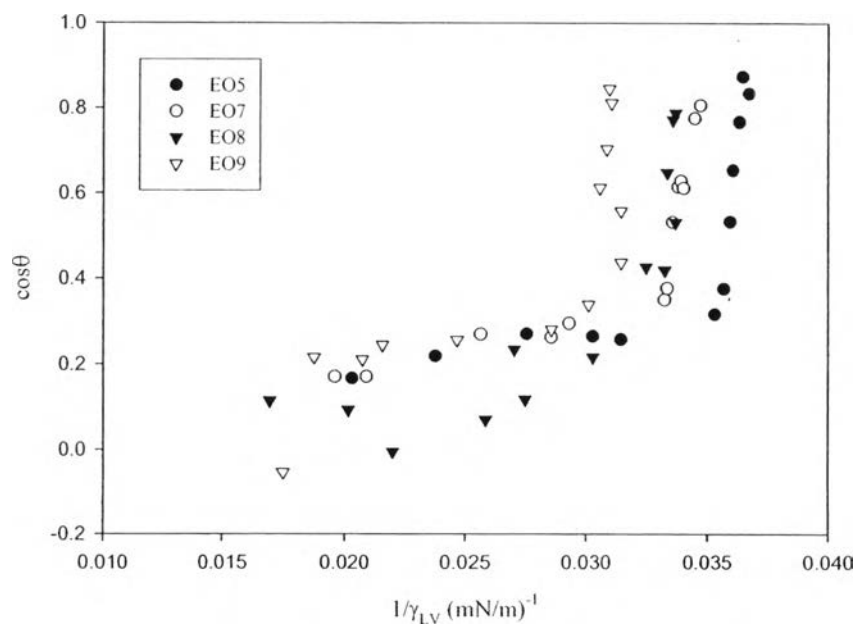
**Figure 4.15** Contact angle of alcohol ethoxylate LS9 (EO9) on PTFE, PVC, and PMMA.

#### 4.3.3 Wetting Enhancement by AEs

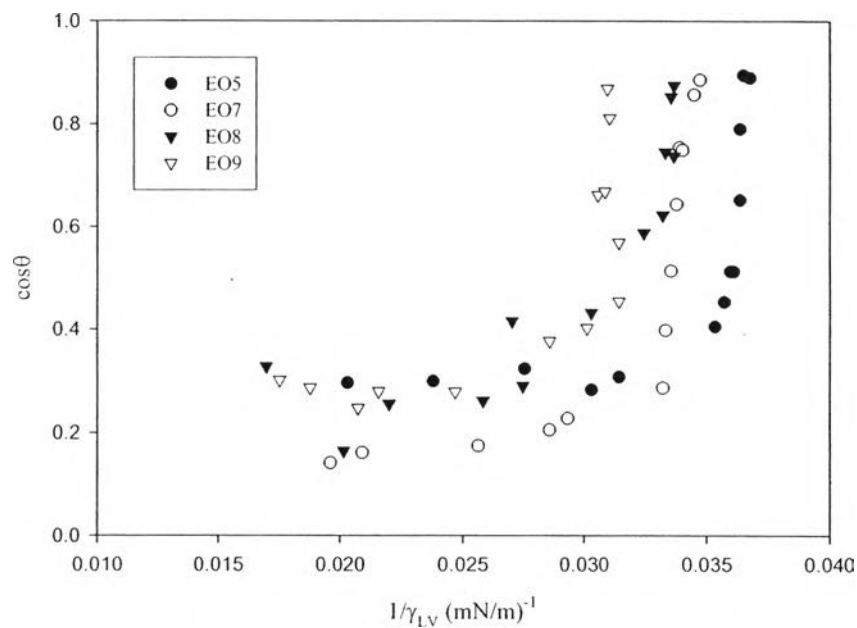
From Young's equation (Equation 2.10), if the relation between  $\cos\theta$  and  $1/\gamma_{LV}$  was plotted, the plot should be a straight line with the slope of  $(\gamma_{SV}-\gamma_{SL})$  and intercepted at the origin. Figures 4.16 to 4.18 show that for pure AE solutions the interceptions, though, are near but not at the origin for all plastics and the slope increases with increasing  $1/\gamma_{LV}$  meaning that  $(\gamma_{SV}-\gamma_{SL})$  term increases.



**Figure 4.16**  $\cos\theta$  on PTFE surface related to  $1/\gamma_{LV}$  of surfactant solutions.

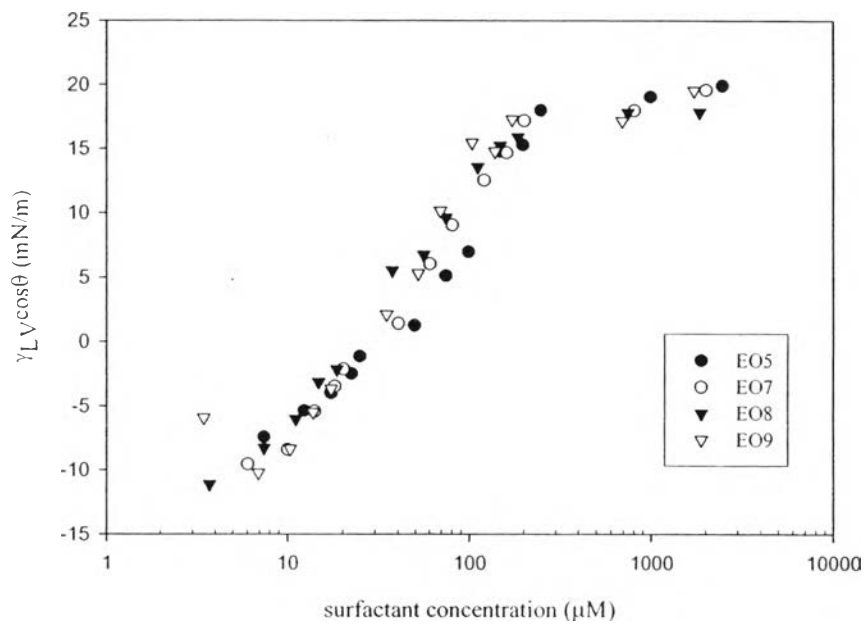


**Figure 4.17**  $\cos\theta$  on PVC surface related to  $1/\gamma_{LV}$  of surfactant solutions.

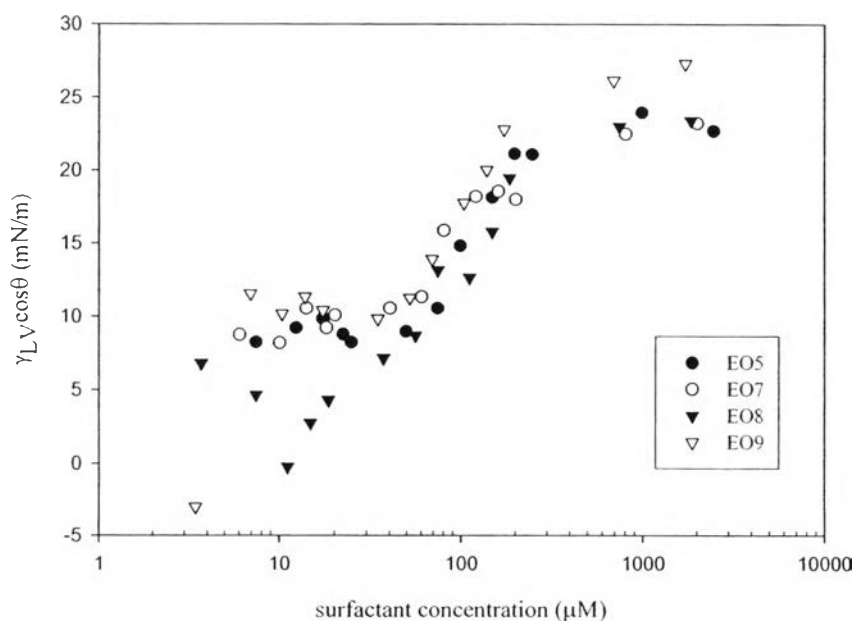


**Figure 4.18**  $\cos\theta$  on PMMA surface related to  $1/\gamma_{LV}$  of surfactant solutions.

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  $\gamma_{LV}$  or  $\gamma_{LV}\cos\theta$ . From Equation 2.10, if  $(\gamma_{LV}\cos\theta)$  was constant, the value of  $(\gamma_{SV}-\gamma_{SL})$  would be constant. Figures 4.19 to 4.21 show that  $\gamma_{LV}\cos\theta$  increases with increasing surfactant concentration meaning that  $(\gamma_{SV}-\gamma_{SL})$  term increases.

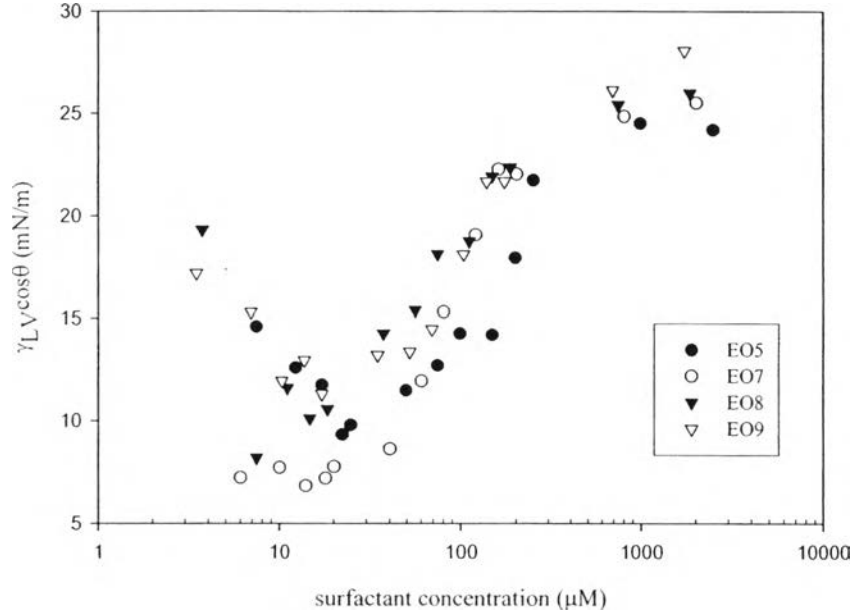


**Figure 4.19**  $\gamma_{LV}\cos\theta$  on PTFE surface related to concentration of surfactant solutions.



**Figure 4.20**  $\gamma_{LV}\cos\theta$  on PVC surface related to concentration of surfactant solutions.





**Figure 4.21**  $\gamma_{LV}\cos\theta$  on PMMA surface related to concentration of surfactant solutions.

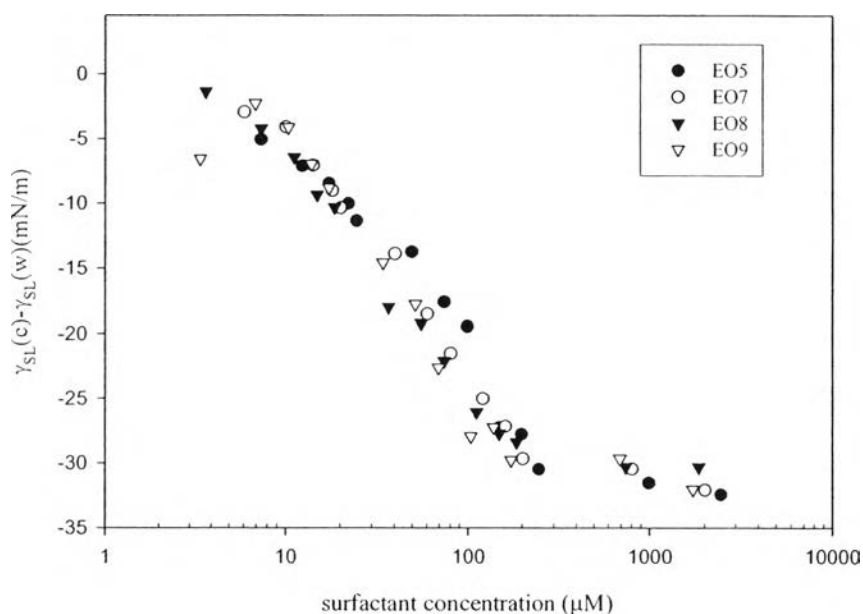
In practical, the value of the  $\gamma_{SV}$  could be assumed to be independent of the surfactant concentration because the dry solid had not been contacted by the solution yet and the transfer of the non-volatile surfactants to the solid/vapor interface during measurement of contact angles via vapor phase seemed unlikely (Gau and Zografí, 1990). This indicates that  $\gamma_{SL}$  is constant in case of pure AEs.

Although, the  $\gamma_{SL}$  was not experimentally and directly measured, we could calculate the  $\gamma_{SL}$  relative to the  $\gamma_{SL}$  at a reference state,  $\gamma_{SL}(w)$ , which had no AEs presented or in a pure water, using the contact angle and the liquid/vapor surface tension data. Equation 2.10 may be written as

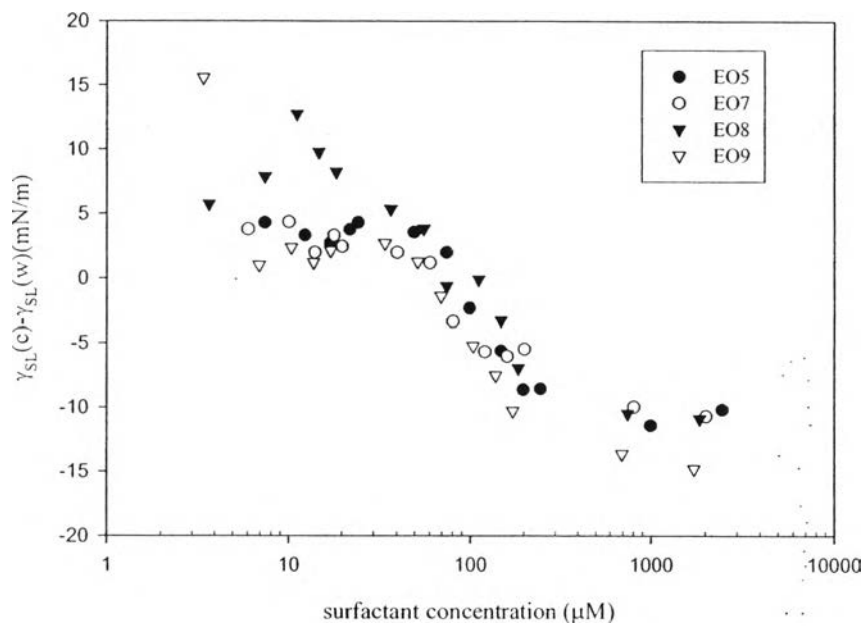
$$\begin{aligned} \gamma_{LV}(w) \cos\theta(w) - \gamma_{LV}(c) \cos\theta(c) &= [\gamma_{SV}(w) - \gamma_{SV}(c)] - [\gamma_{SV}(c) - \gamma_{SV}(c)] \\ &= \gamma_{SL}(c) - \gamma_{SL}(w) \end{aligned} \quad (4.1)$$

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

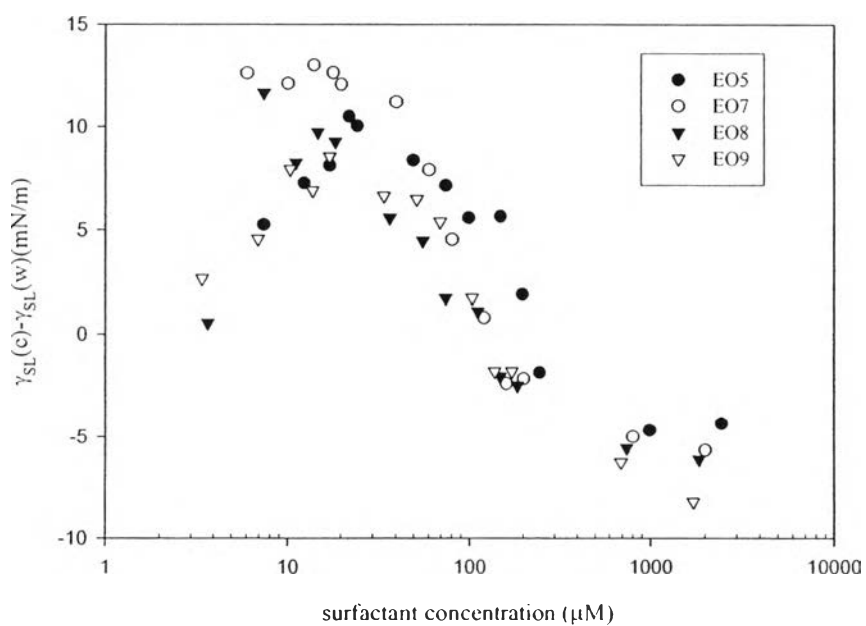
Figures 4.22 to 4.24 show the correlation between the term  $\gamma_{SL}(c) - \gamma_{SL}(w)$  and AEs concentration. If the term  $\gamma_{SL}(w)$  was commonly assumed to be a constant, this plot would provide the relation between  $\gamma_{SL}(c)$  and AEs concentration. From the Figures, in case of pure AEs, the  $\gamma_{SL}(c)$  decreases with increasing surfactant concentration. It indicates that increase in surfactant concentration not only decreases  $\gamma_{LV}$  but also decreases  $\gamma_{SL}$ .



**Figure 4.22** Relative interfacial tension at solid/liquid interface of PTFE surface related to concentration of surfactant solutions.

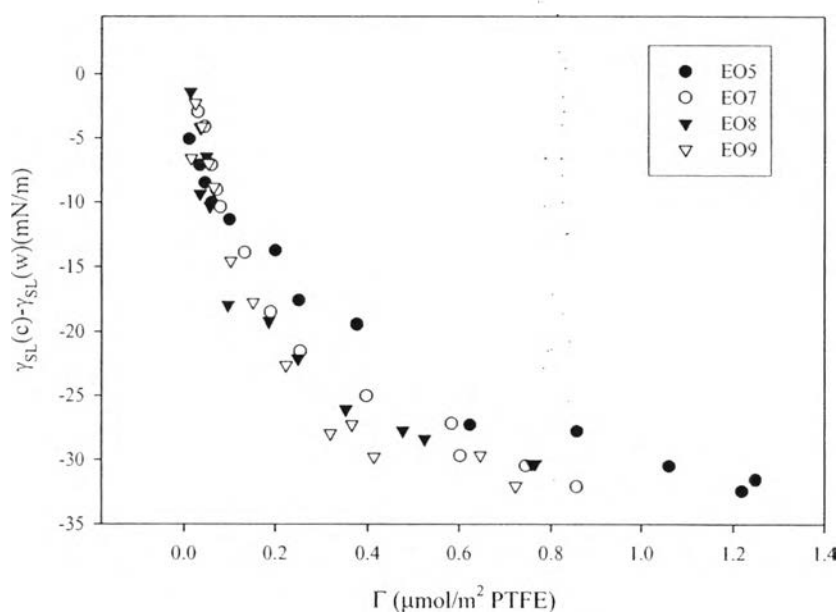


**Figure 4.23** Relative interfacial tension at solid/liquid interface of PVC surface related to concentration of surfactant solutions.

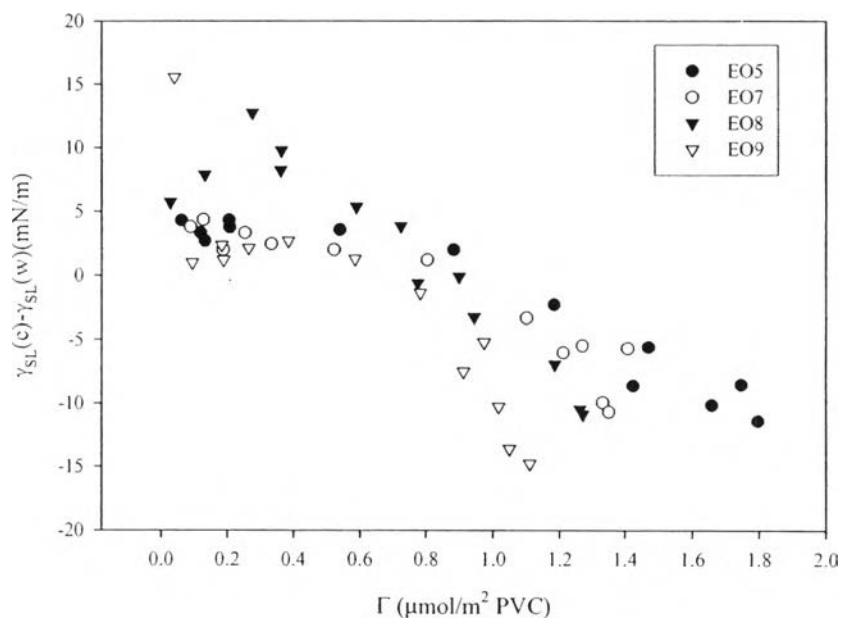


**Figure 4.24** Relative interfacial tension at solid/liquid interface of PMMA surface related to concentration of surfactant solutions.

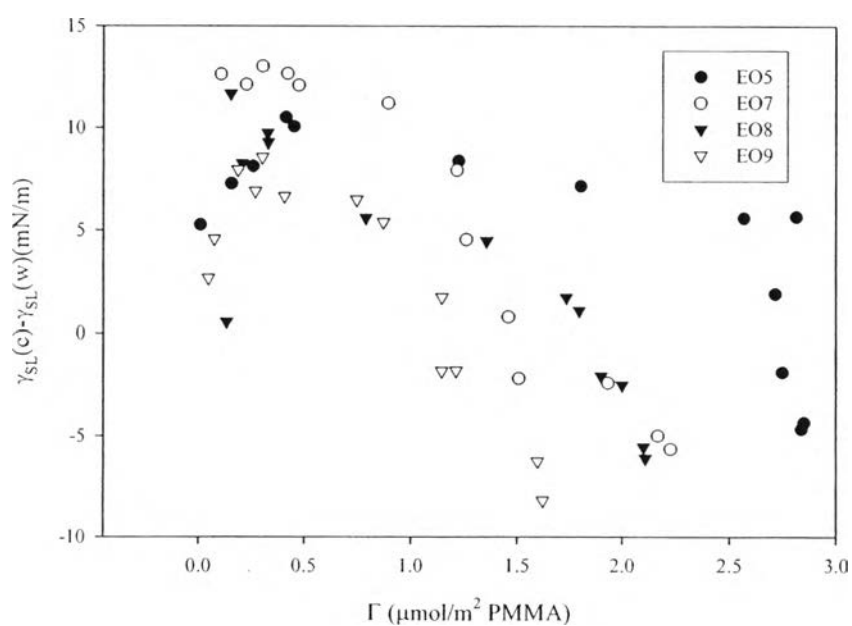
Figures 4.25 to 4.27 indicate that the increase in AE adsorption effects on the  $\gamma_{SL}$ . It might be concluded that reduction of  $\gamma_{SL}$  is derived from adsorption of surfactant at solid/liquid interface. Therefore, the changes in contact angles induced by surfactant attributes to the changes in the  $\gamma_{LV}$  and  $\gamma_{SL}$ .



**Figure 4.25** Relative interfacial tension at solid/liquid interface of PTFE surface related to adsorption of surfactant solutions.



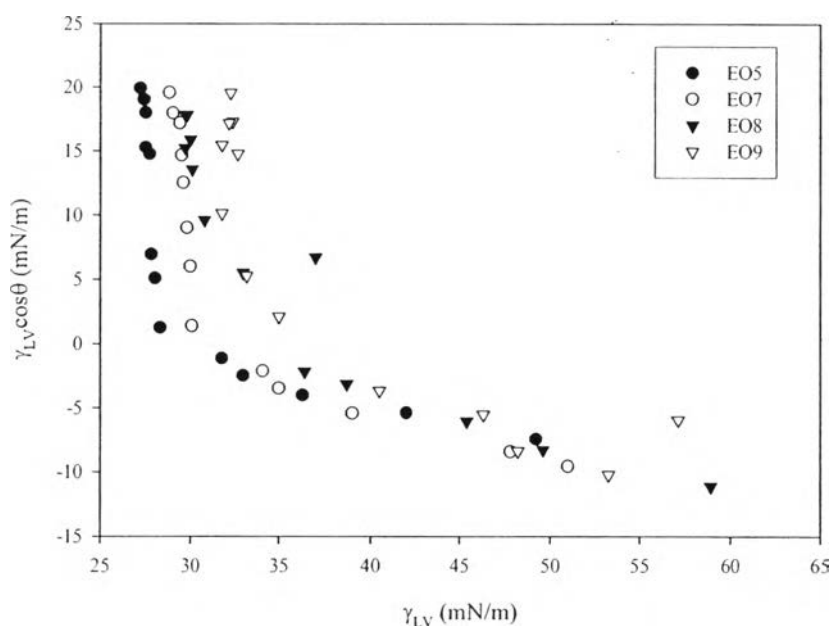
**Figure 4.26** Relative interfacial tension at solid/liquid interface of PVC surface related to adsorption of surfactant solutions.



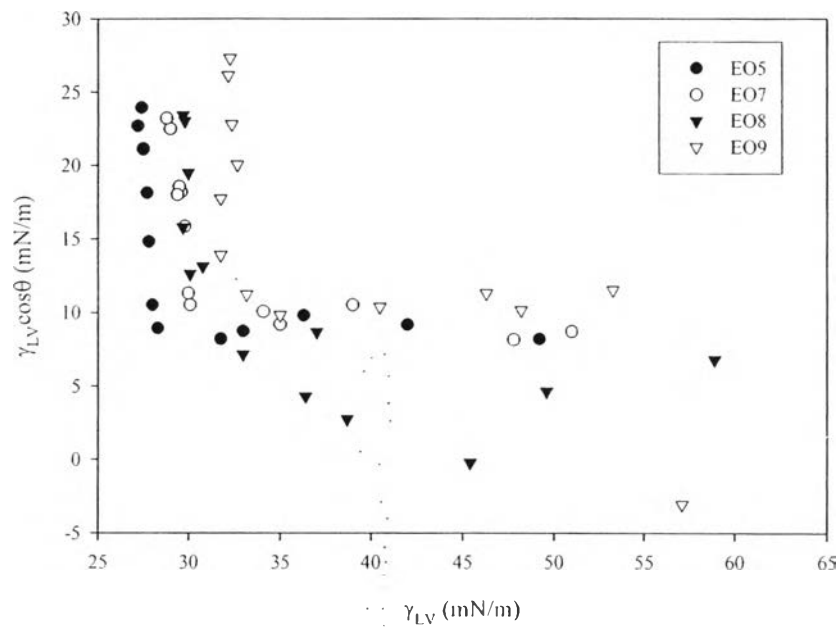
**Figure 4.27** Relative interfacial tension at solid/liquid interface of PMMA surface related to adsorption of surfactant solutions.

Figures 4.28 to 4.30 show the adhesion tension plots which illustrate the adhesion tension,  $\gamma_{LV}\cos\theta$ , related to the  $\gamma_{LV}$  of AE solutions. From Equation 2.11, if  $\Gamma_{SV}$  for a surfactant was assumed to be zero, this plot should have slope of  $-(\Gamma_{SL}/\Gamma_{LV})$  which was the ratio of surface excess concentration at solid/liquid to liquid/vapor interface.

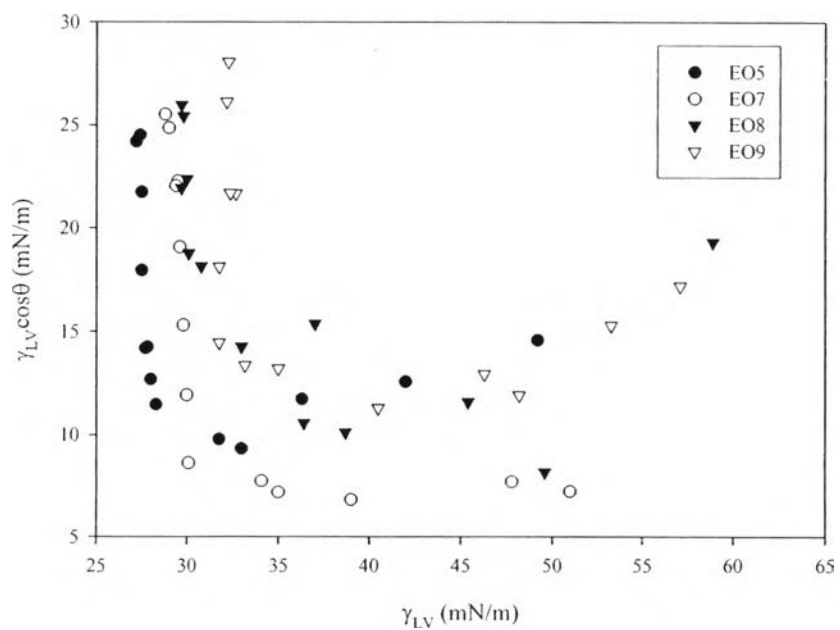
For pure AEs solution, the plots show the straight line with slope in the range of  $-1/2$  and  $0$  which indicates that the  $\Gamma_{LV}$  is higher than  $\Gamma_{SL}$ . For the effect of hydrophobicity of surface, the slope approaches to zero as the hydrophobicity decreases meaning that  $\Gamma_{SL}$  increases compared with  $\Gamma_{LV}$ . It is concluded that surfactant can adsorb at solid/liquid interface at lower hydrophobic surface better than at higher hydrophobic surface. The result is in line with the result from the adsorption isotherm (Figures 4.2 to 4.4).



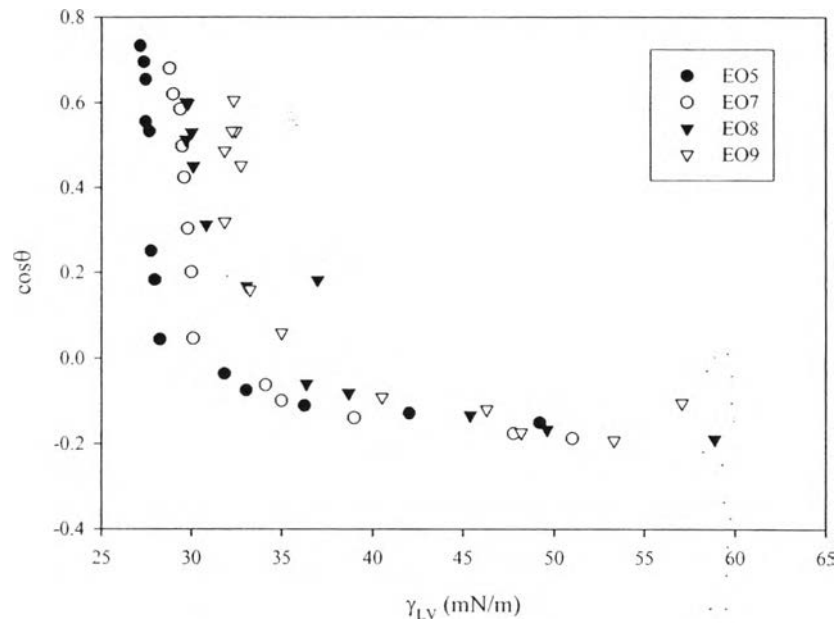
**Figure 4.28** Adhesion tension plot for AE solutions on PTFE.



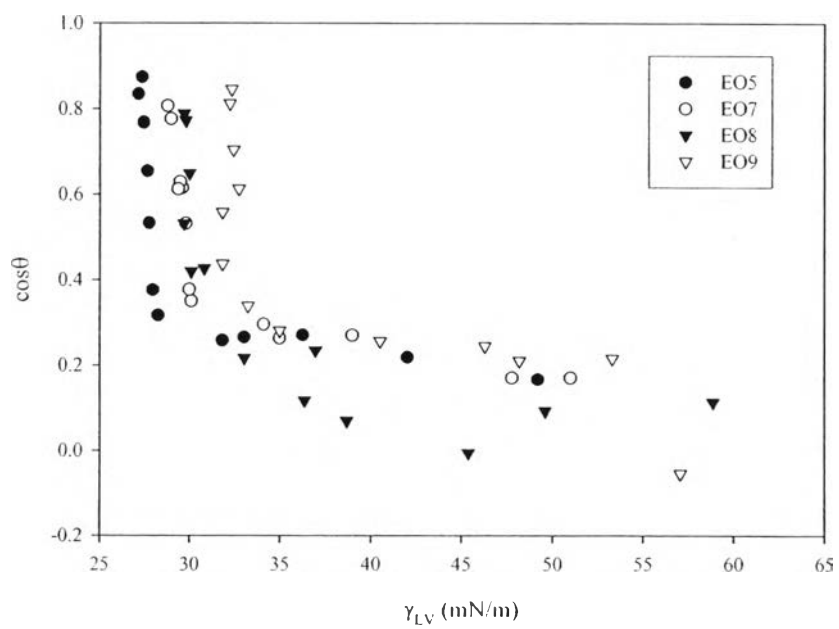
**Figure 4.29** Adhesion tension plot for AE solutions on PVC.



**Figure 4.30** Adhesion tension plot for AE solutions on PMMA.

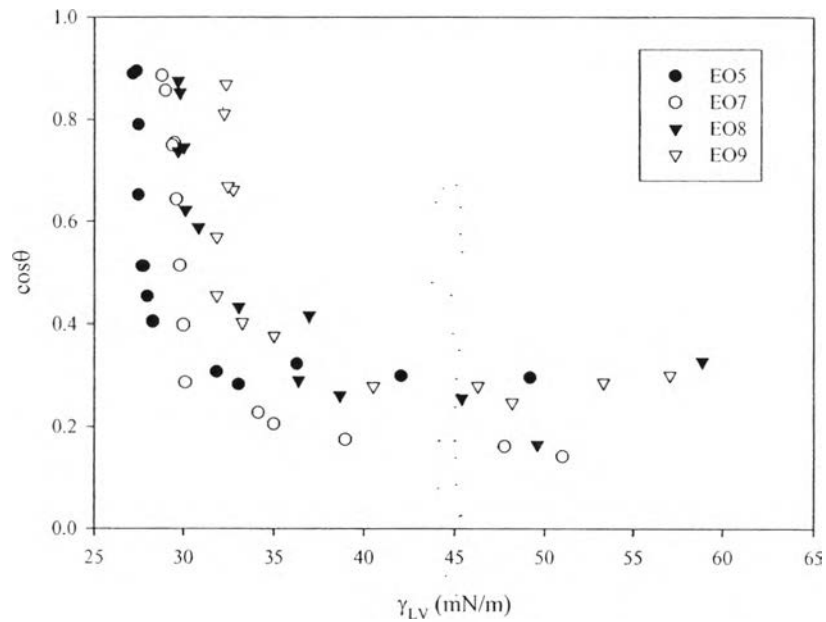


**Figure 4.31** Cosine of contact angle for AE solutions on PTFE surface related to its  $\gamma_{LV}$ .



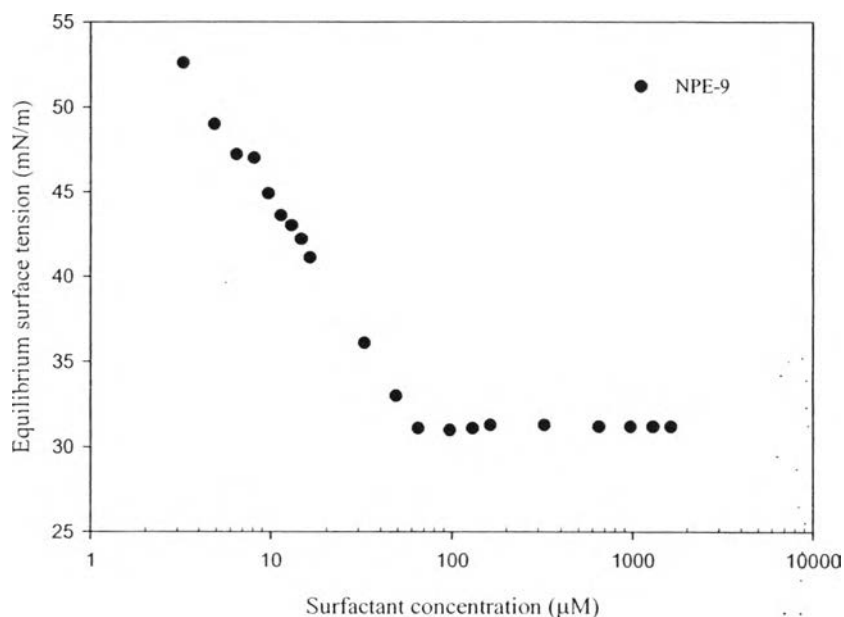


**Figure 4.32** Cosine of contact angle for AE solutions on PVC surface related to its  $\gamma_{LV}$ .



**Figure 4.33** Cosine of contact angle for AE solutions on PMMA surface related to its  $\gamma_{LV}$ .

#### 4.4 The Liquid/Vapor Surface Tension and CMC of NPE-9



**Figure 4.34** Surface tension isotherm of nonylphenol ethoxylate 9 (NPE-9).

Figure 4.34 shows the relation between the liquid/vapor interfacial tension ( $\gamma_{LV}$ ) and the initial concentration of NPE-9 solution as a semi-logarithmic function. It demonstrates that the  $\gamma_{LV}$  of solution decreases with increasing surfactant concentration until level off at their CMC. The CMC of NPE-9 is summarized in Table 4.3 also including  $\gamma_{CMC}$ ,  $\pi_{CMC}$ , and  $a^s$ . The results are in agreement with other studies (xxx).

**Table 4.3** CMC,  $\gamma_{CMC}$ ,  $\pi_{CMC}$ , and  $a^s$  of NPE-9

Parameter	Value
CMC ( $\mu\text{M}$ )	60
$\gamma_{CMC}$ (mN/m)	31.2
$\pi_{CMC}$ (mN/m)	41.6
$a^s$ ( $\text{\AA}^2$ )	51.48

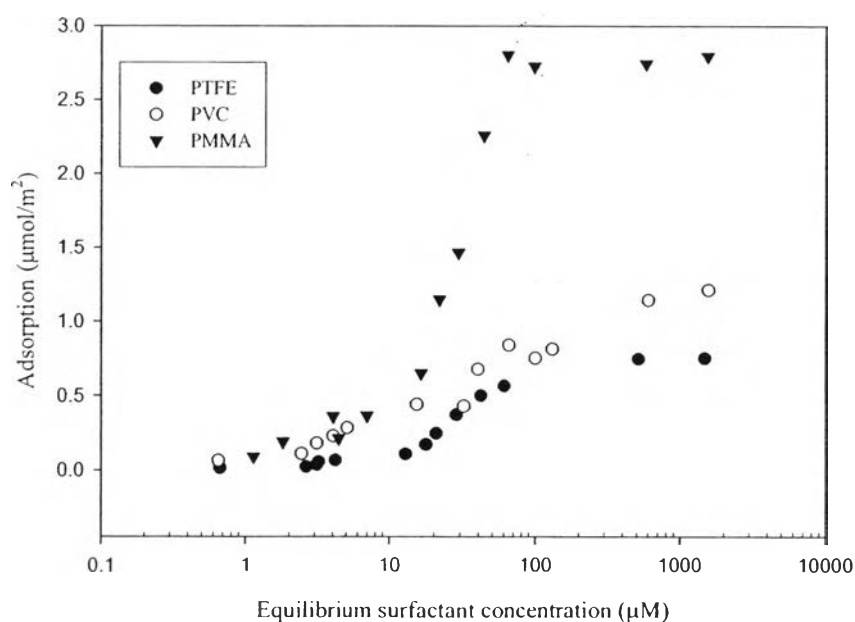
#### 4.5 Adsorption of NPE-9 and its Wetting on Plastics

The adsorption of NPE-9 was done on three plastic surface; PTFE, PVC, and PMMA at equilibration time of 5 days and temperature of 30 °C. Contact angle measurement was done at temperature of 30 °C. The given data came from the equilibrium time of 1 min.

#### 4.5.1 Adsorption Isotherm of NPE-9

The adsorbed amount of surfactant on polymer surface was plotted versus the logarithm of the equilibrium concentration of surfactant solution. The adsorption isotherms of NPE-9 on PTFE, PVC, and PMMA are shown in Figure 4.35.

The result shows that the adsorption of each NPE-9 slightly increases with increasing equilibrium concentration of corresponding surfactant and levels off to the plateau at around the CMC region. The results were in agreement with other studies (xxx).



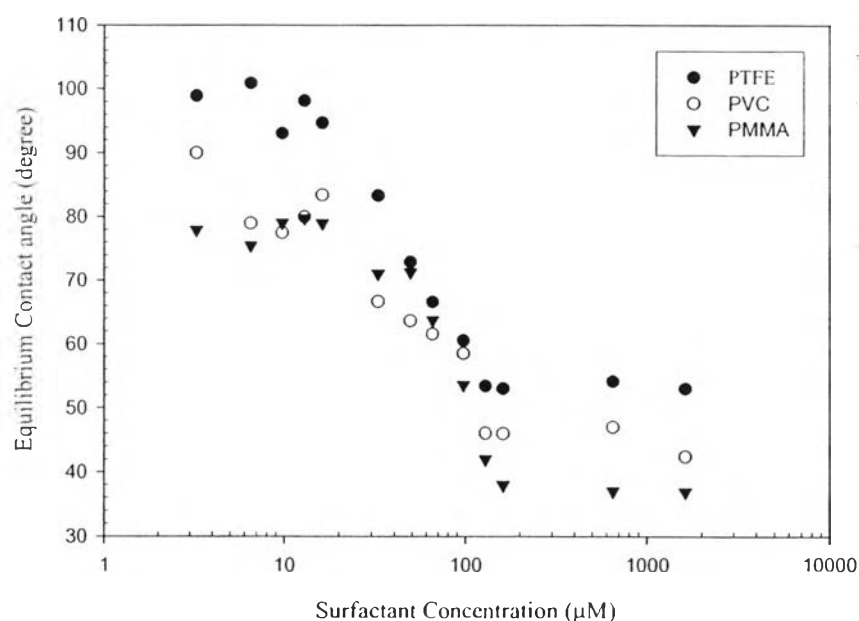
**Figure 4.35** Adsorption isotherm of nonylphenol ethoxylate 9 (NPE-9) on polymer surfaces.

#### 4.5.2 Contact Angle of NPE-9 Solution on Plastics

The relations between the static contact angle on PTFE, PVC, and PMMA and concentration of NPE-9 solution are shown in Figure 4.36.

From the plot, the contact angles decrease significantly with increasing NPE-9 concentration and become nearly constant above the CMC.

The contact angles of NPE-9 on different plastics are also shown and are in the vicinity values corresponding to the polarity and hydrophobicity, of plastics as shown in Table 4.1. The result indicates that the wettability of NPE-9 increases with increasing hydrophilicity of the surface. The given result is in the same trend with previous studies (Meerit, 2005; Puttharak, 2006; Thongpae, 2007).

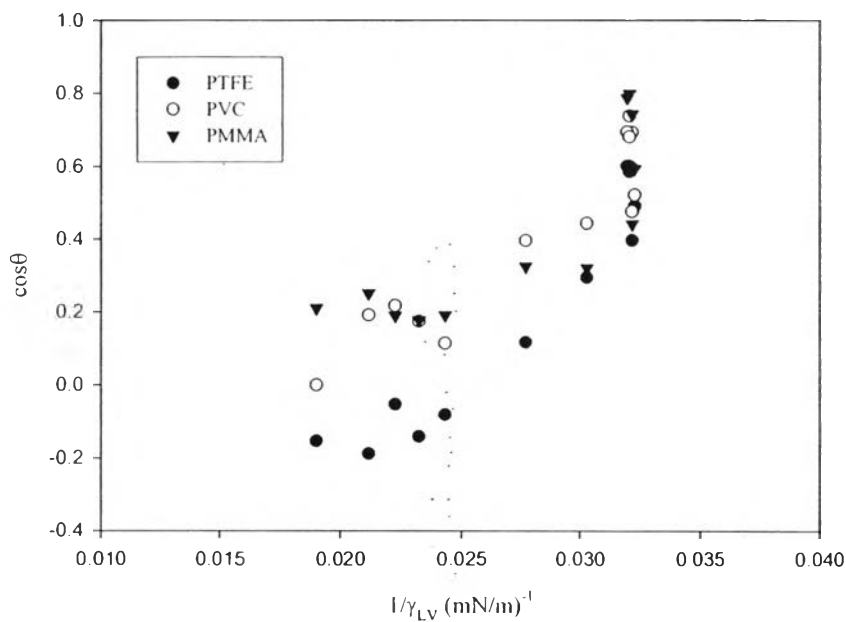


**Figure 4.36** Contact angle of nonylphenol ethoxylate 9 (NPE-9) on polymer surfaces.

#### 4.5.3 Wetting Enhancement by NPE-9

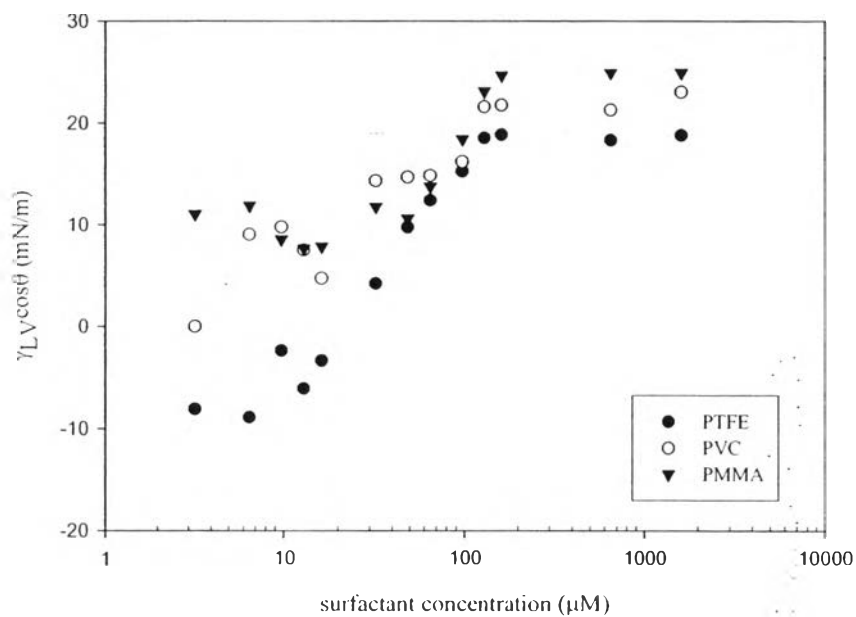
From Young's equation (Equation 2.10), if the relation between  $\cos\theta$  and  $1/\gamma_{LV}$  was plotted, the plot should be a straight line with the slope of  $(\gamma_{LV}-\gamma_{SL})$  and intercepted at the origin. Figure 4.37 shows that for pure NPE-9 solution the in-

terceptions, though, are near but not at the origin for all plastics and the slope increases with increasing  $1/\gamma_{LV}$  meaning that  $(\gamma_{SV}-\gamma_{SL})$  term increases.



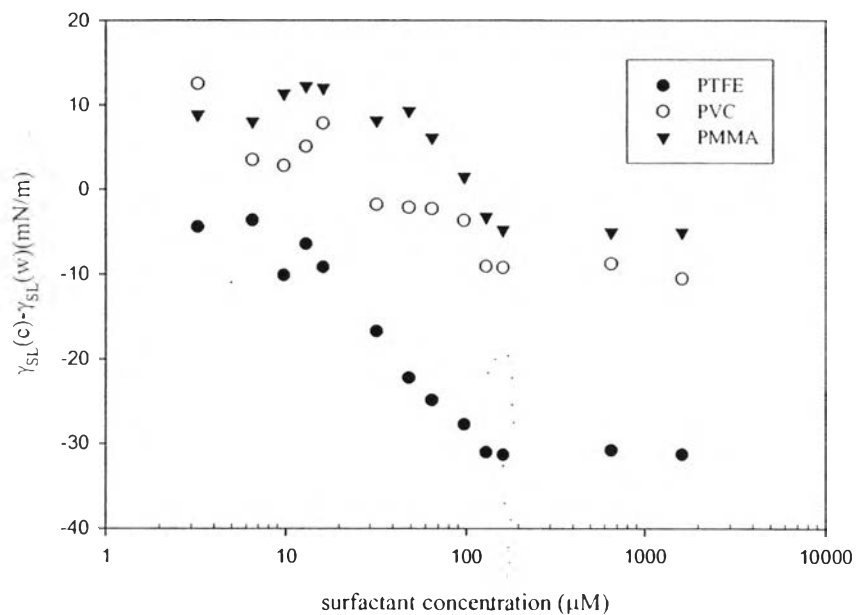
**Figure 4.37**  $\cos\theta$  on polymer surfaces related to  $1/\gamma_{LV}$  of nonylphenol ethoxylate 9 (NPE-9).

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  $\gamma_{LV}$  or  $\gamma_{LV}\cos\theta$ . From Equation 2.10, if  $(\gamma_{LV}\cos\theta)$  was constant, the value of  $(\gamma_{SV}-\gamma_{SL})$  would be constant. Figure 4.38 shows that  $\gamma_{LV}\cos\theta$  increases with increasing surfactant concentration meaning that  $(\gamma_{SV}-\gamma_{SL})$  term increases.



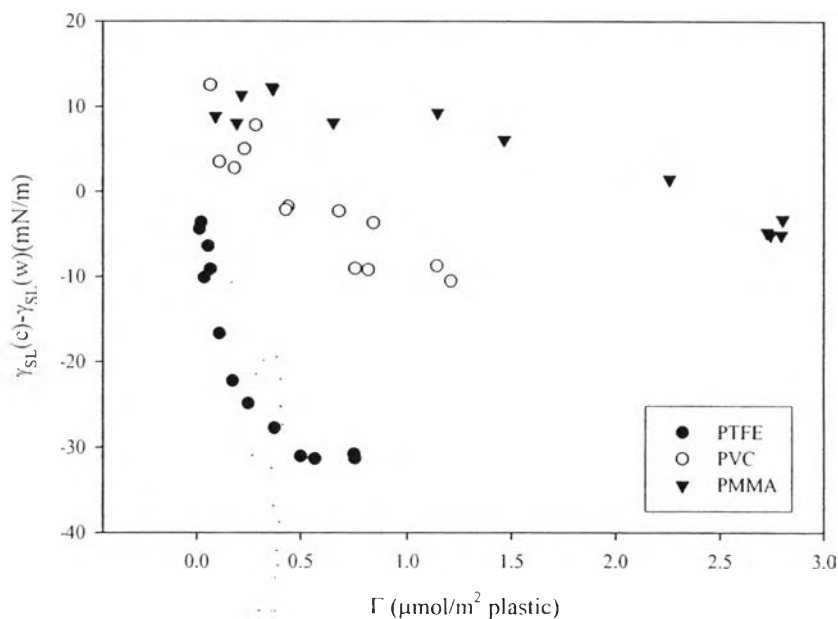
**Figure 4.38**  $\gamma_{LV}\cos\theta$  on polymer surfaces related to concentration of nonylphenol ethoxylate 9 (NPE-9).

Figure 4.39 shows the correlation between the term  $\gamma_{SL}(c) - \gamma_{SL}(w)$  and NPE-9 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 NPE-9 concentration. From the Figures, in case of pure NPE-9, the  $\gamma_{SL}(c)$  decreases with increasing surfactant concentration. It indicates that increase in surfactant concentration not only decreases  $\gamma_{LV}$  but also decreases  $\gamma_{SL}$ .



**Figure 4.39** Relative interfacial tension at solid/liquid interface of polymers related to concentration of nonylphenol ethoxylate 9 (NPE-9).

Figure 4.40 indicate that the increase in NPE-9 adsorption effects on the  $\gamma_{SL}$ . It might be concluded that reduction of  $\gamma_{SL}$  is derived from adsorption of surfactant at solid/liquid interface. Therefore, the changes in contact angles induced by surfactant attributes to the changes in the  $\gamma_{LV}$  and  $\gamma_{SL}$ .

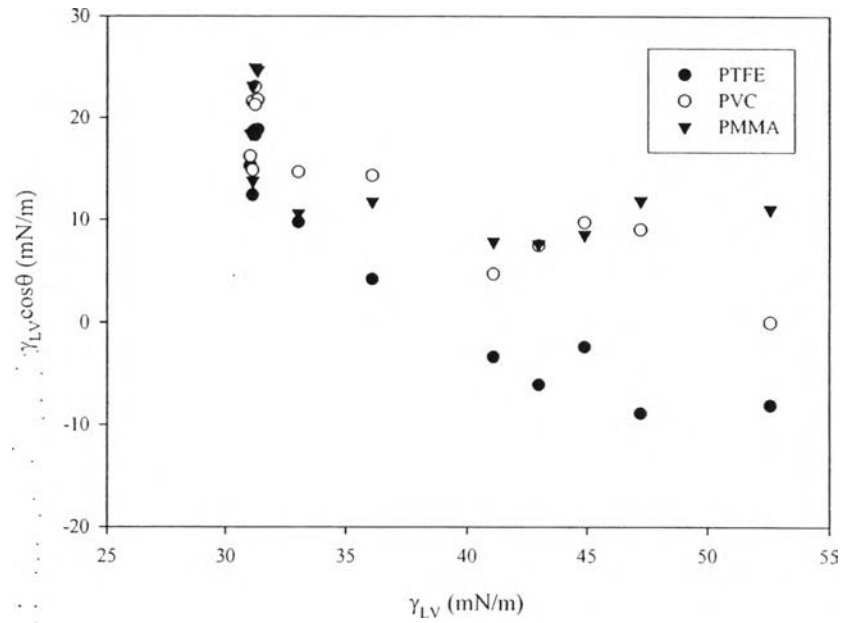


**Figure 4.40** Relative interfacial tension at solid/liquid interface of polymer related to adsorption of nonylphenol ethoxylate 9 (NPE-9).

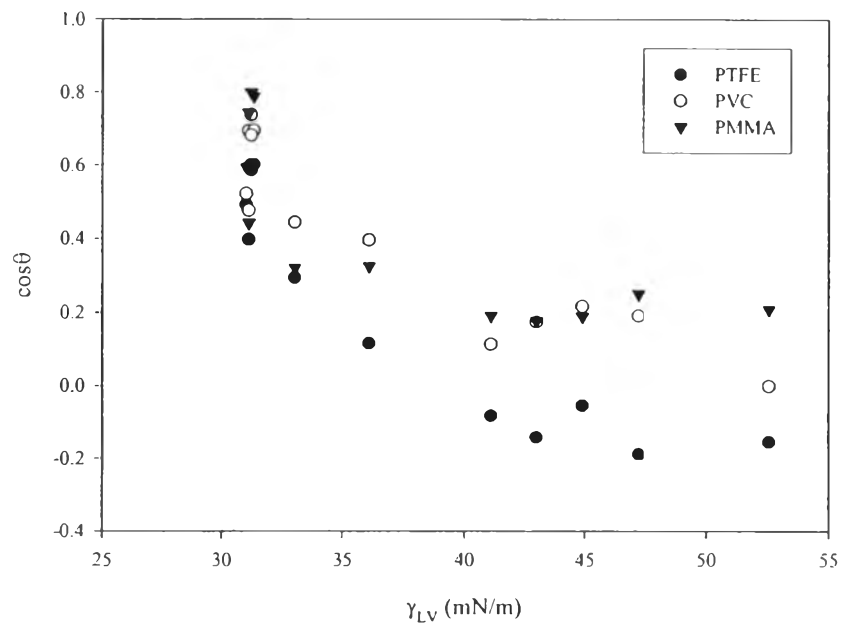
Figure 4.41 show the adhesion tension plot which illustrates the adhesion tension,  $\gamma_{LV}\cos\theta$ , related to the  $\gamma_{LV}$  of NPE-9 solutions. From Equation 2.11, if  $\Gamma_{SV}$  for a surfactant was assumed to be zero, this plot should have slope of  $-(\Gamma_{SL}/\Gamma_{LV})$  which was the ratio of surface excess concentration at solid/liquid to liquid/vapor interface.

For pure NPE-9 solution, the plots show the straight line with slope in the range of  $-1/2$  and  $0$  which indicates that the  $\Gamma_{LV}$  is higher than  $\Gamma_{SL}$ . For the effect of hydrophobicity of surface, the slope approaches to zero as the hydrophobicity decreases meaning that  $\Gamma_{SL}$  increases compared with  $\Gamma_{LV}$ . It is concluded that surfactant can adsorb at solid/liquid interface at lower hydrophobic surface better than at higher hydrophobic surface. The result is in line with the result from the adsorption isotherm (Figures 4.35).



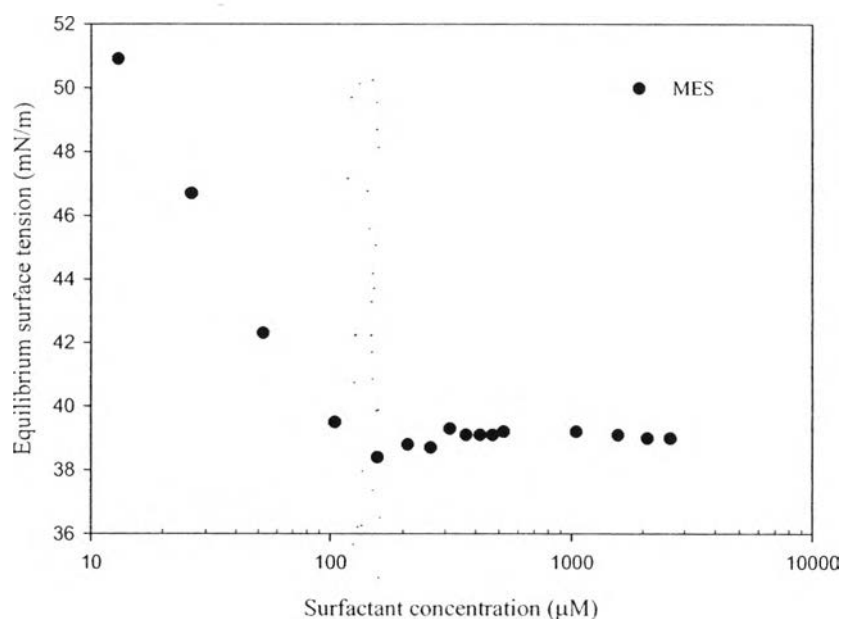


**Figure 4.41** Adhesion tension plot for nonylphenol ethoxylate 9 (NPE-9) on polymers.



**Figure 4.42** Cosine of contact angle for nonylphenol ethoxylate 9 (NPE-9) on polymer surfaces related to its  $\gamma_{LV}$ .

#### 4.6 The Liquid/Vapor Surface Tension and CMC of MES



**Figure 4.43** Surface tension isotherm of methyl ester sulfonate (MES).

Figure 4.43 shows the relation between the liquid/vapor interfacial tension ( $\gamma_{LV}$ ) and the initial concentration of MES solution as a semi-logarithmic function. It demonstrates that the  $\gamma_{LV}$  of solution decreases with increasing surfactant concentration until level off at their CMC. The CMC of MES is summarized in Table 4.4 also including  $\gamma_{CMC}$ ,  $\pi_{CMC}$ , and  $a^s$ .

**Table 4.4** CMC,  $\gamma_{CMC}$ ,  $\pi_{CMC}$ , and  $a^s$  of MES

Parameter	Value
CMC ( $\mu\text{M}$ )	130
$\gamma_{CMC}$ (mN/m)	39
$\pi_{CMC}$ (mN/m)	33.8

$a^s (\text{\AA}^2)$	66.35
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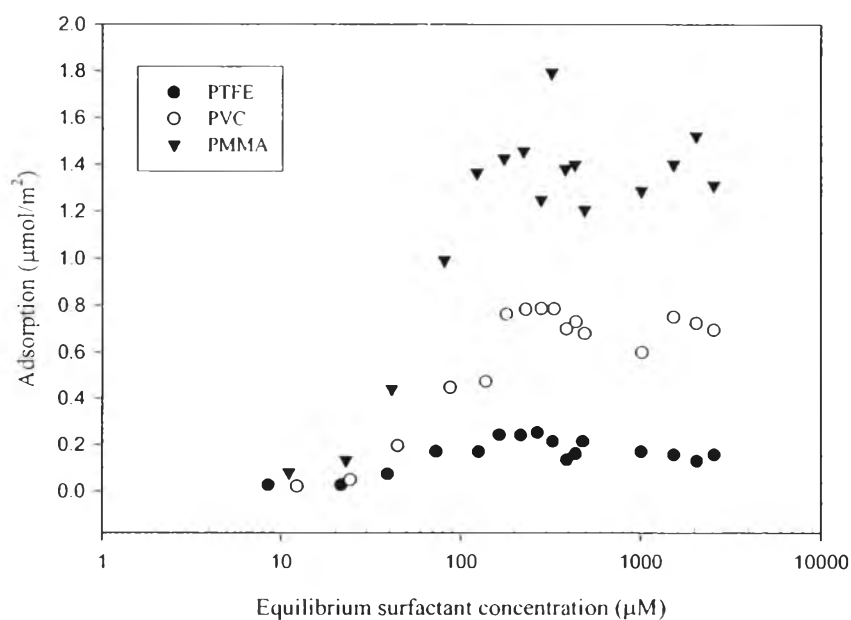
#### 4.7 Adsorption of MES and its Wetting on Plastics

The adsorption of MES was done on three plastic surface; PTFE, PVC, and PMMA at equilibration time of 5 days and temperature of 30 °C. Contact angle measurement was done at temperature of 30 °C. The given data came from the equilibrium time of 1 min.

##### 4.7.1 Adsorption Isotherm of MES

The adsorbed amount of surfactant on polymer surface was plotted versus the logarithm of the equilibrium concentration of surfactant solution. The adsorption isotherms of MES on PTFE, PVC, and PMMA are shown in Figure 4.44.

The result shows that the adsorption of each MES slightly increases with increasing equilibrium concentration of corresponding surfactant and levels off to the plateau at around the CMC region. The result is in agreement with other studies (xxx).



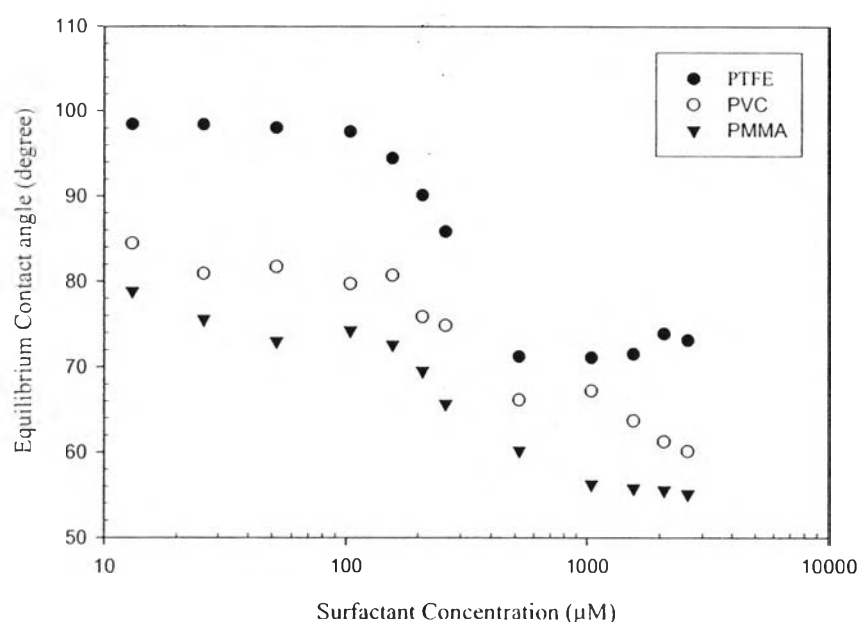
**Figure 4.44** Adsorption isotherm of methyl ester sulfonate (MES) on polymer surfaces.

#### 4.7.2 Contact Angle of MES Solution on Plastics

The relations between the static contact angle on PTFE, PVC, and PMMA and concentration of MES solution is shown in Figure 4.45.

From the plot, the contact angle decreases significantly with increasing MES concentration and becomes nearly constant above the CMC.

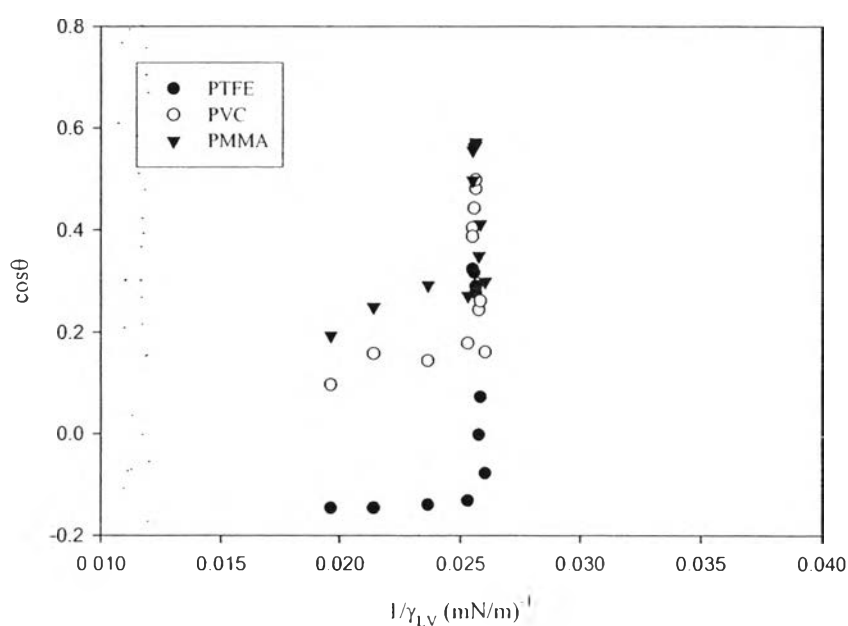
The contact angles of MES on different plastics are also shown and are in the vicinity values corresponding to the polarity and hydrophobicity, of plastics as shown in Table 4.1. The result indicated that the wettability of MES increase with increasing hydrophilicity of the surface. The given result was in the same trend with previous studies (Meerit, 2005; Puttharak, 2006; Thongpae, 2007).



**Figure 4.45** Contact angle of methyl ester sulfonate (MES) on polymer surfaces.

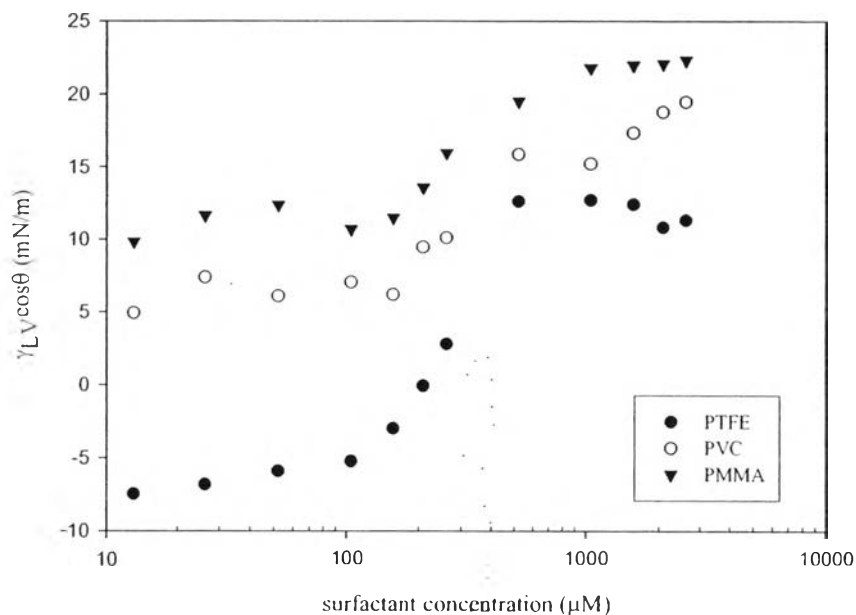
#### 4.7.3 Wetting Enhancement by MES

From Young's equation (Equation 2.10), if the relation between  $\cos\theta$  and  $1/\gamma_{LV}$  was plotted, the plot should be a straight line with the slope of  $(\gamma_{LV}-\gamma_{SL})$  and intercepted at the origin. Figure 4.46 shows that for pure MES solution the intercepts, though, are near but not at the origin for all plastics and the slope increases with increasing  $1/\gamma_{LV}$  meaning that  $(\gamma_{SV}-\gamma_{SL})$  term increases.



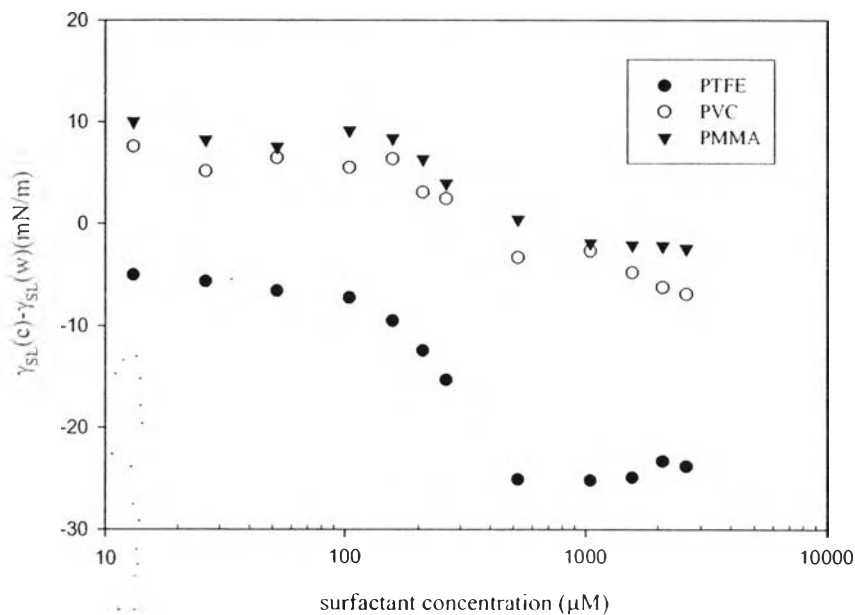
**Figure 4.46**  $\cos\theta$  on polymer surfaces related to  $1/\gamma_{LV}$  of methyl ester sulfonate (MES).

Another possible way to examine the variation of the  $(\gamma_{LV}-\gamma_{SL})$  term is to look at the product of  $\cos\theta$  multiply with  $\gamma_{LV}$  or  $\gamma_{LV}\cos\theta$ . From Equation 2.10, if  $(\gamma_{LV}\cos\theta)$  was constant, the value of  $(\gamma_{LV}-\gamma_{SL})$  would be constant. Figure 4.47 shows that  $\gamma_{LV}\cos\theta$  increases with increasing surfactant concentration meaning that  $(\gamma_{SV}-\gamma_{SL})$  term increases.



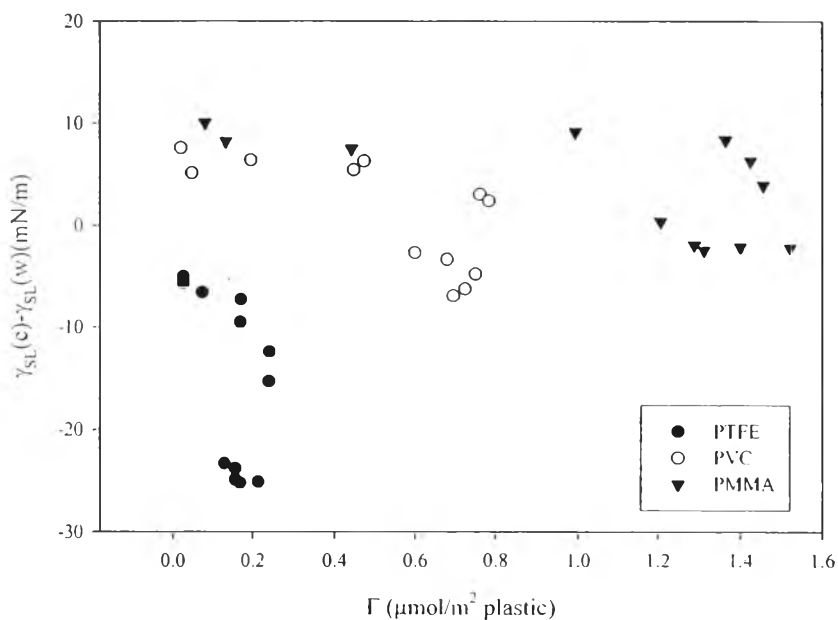
**Figure 4.47**  $\gamma_{LV}\cos\theta$  on polymer surfaces related to concentration of methyl ester sulfonate (MES).

Figure 4.48 shows the correlation between the term  $\gamma_{SL}(c)-\gamma_{SL}(w)$  and MES 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 MES concentration. From the Figures, in case of pure MES, the  $\gamma_{SL}(c)$  decreases with increasing surfactant concentration. It indicates that increase in surfactant concentration not only decreases  $\gamma_{LV}$  but also decreases  $\gamma_{SL}$ .



**Figure 4.48** Relative interfacial tension at solid/liquid interface of polymers related to concentration of methyl ester sulfonate (MES).

Figure 4.49 indicates that the increase in MES adsorption effects on the  $\gamma_{SL}$ . It might be concluded that reduction of  $\gamma_{SL}$  is derived from adsorption of surfactant at solid/liquid interface. Therefore, the changes in contact angles induced by surfactant attributes to the changes in the  $\gamma_{LV}$  and  $\gamma_{SL}$ .

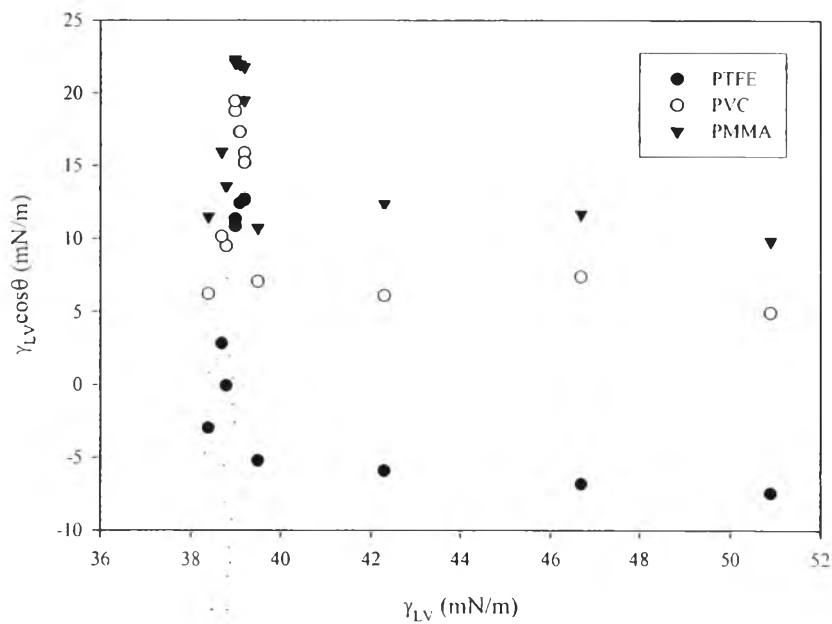


**Figure 4.49** Relative interfacial tension at solid/liquid interface of polymer related to adsorption of methyl ester sulfonate (MES).

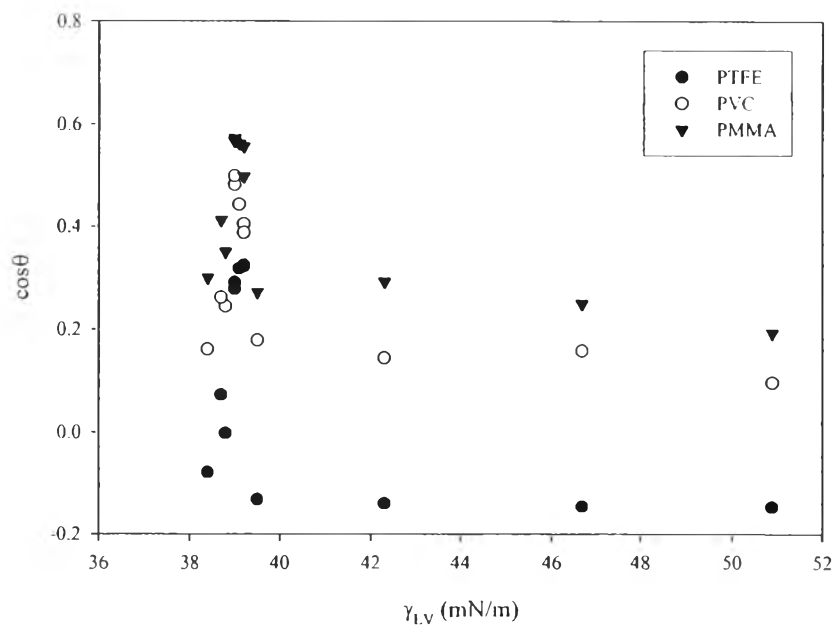
Figure 4.50 shows the adhesion tension plot which illustrates the adhesion tension,  $\gamma_{LV}\cos\theta$ , related to the  $\gamma_{LV}$  of MES solution. From Equation 2.11, if  $\Gamma_{SV}$  for a surfactant was assumed to be zero, this plot should have slope of  $-(\Gamma_{SL}/\Gamma_{LV})$  which was the ratio of surface excess concentration at solid/liquid to liquid/vapor interface.

For pure MES solution, the plots show the straight line with slope in the range of  $-1/2$  and  $0$  which indicates that the  $\Gamma_{LV}$  is higher than  $\Gamma_{SL}$ . For the effect of hydrophobicity of surface, the slope approaches to zero as the hydrophobicity decreases meaning that  $\Gamma_{SL}$  increases compared with  $\Gamma_{LV}$ . It is concluded that surfactant can adsorb at solid/liquid interface at lower hydrophobic surface better than at higher hydrophobic surface. The result is in line with the result from the adsorption isotherm (Figures 4.44).





**Figure 4.50** Adhesion tension plot for methyl ester sulfonate (MES) on polymers.



**Figure 4.51** Cosine of contact angle for methyl ester sulfonate (MES) on polymer surfaces related to its  $\gamma_{LV}$ .

#### **4.8 Comparison of The Liquid/Vapor Surface Tension and CMC of the studied Surfactants**

Nonionic surfactants—AEs and NPE-9—have both critical micelle concentration (CMC) and equilibrium surface tension ( $\gamma_{LV}$ ) lower than anionic surfactant. It is in agreement with previous results (xxx) because nonionic surfactant has no electrical charge on head group resulting in low repulsion among the surfactant molecules, so they could pack at the interface with more amount than anionic surfactant which have negative charge, and high repulsion (xxx). Therefore, nonionic surfactant has lower equilibrium surface tension. For CMC, nonionic surfactant has less hydrophilic character which is only polar charge, while anionic surfactant has more hydrophilic character which is electrical charge. Therefore, nonionic surfactant tries to arrange its hydrophilic part far from water as far as possible. In other words, nonionic surfactants tend to form micelle easier than anionic surfactant.

Among nonionic surfactants, the studied AEs have both critical micelle concentration (CMC) and equilibrium surface tension ( $\gamma_{LV}$ ) lower than NPE-9 because most studied AEs have hydrophilic part smaller than NPE-9 resulting in more amount of surfactant packing at the liquid/vapor interface (xxx). Another reason is due to structure of NPE-9 which is more rigid hydrophilic component and is therefore unable to arrange its structure to obtained smaller area occupied in adsorption at the liquid/vapor interface.

#### **4.9 Comparison of Adsorption of Studied Surfactants and Their Wetting on Plastics**

Nonionic surfactants—AEs and NPE-9—have surface concentration higher than anionic surfactant. It is in agreement with previous results (xxx) because nonionic surfactants have no electrical charge resulting in low repulsion among the surfactant molecules, so they could pack at the interface with more amount than anionic surfactant which have negative charge and, hence, high repulsion. For concentration at maximum adsorption which is normally at the CMC, that of nonionic surfactants

are lower than that of ionic surfactant with the same explanation as in the previous part. Another reasonable explanation is that ionic surfactant has higher water solubility due to its electrical charge of surfactant with which polar group in water molecule interact. Therefore, the amount of energy required to dehydrate the molecule during its incorporation into the micelle would be higher and then would have higher CMC (xxx).

Among nonionic surfactants, alcohol ethoxylates except AE9 have surface concentration higher than NP9 because AEs have hydrophilic part smaller than NP9 resulting in more amount of surfactant packing at the liquid/vapor phase.

The contact angle and the wetting enhancement among the studied surfactants are the same trend with the adsorption results.