

CHAPTER IV

RESULTS AND DISCUSSION

In all experiments, CaC_{12} was used as saturated surfactant solution with other surfactants namely NaDS, NPE and NaC_8 as second subsaturated surfactants. The temperature of all experiments was kept constant at 30 °C.

4.1 Results

4.1.1 Contact Angle

4.1.1.1 Contact Angle of Surfactant Mixture Solution between Saturated CaC_{12} and Subsaturated NaDS

The contact angles of a saturated CaC_{12} solution containing subsaturated NaDS with varying salt concentration are shown in Figure 4.1. It was found that the contact angle decreased significantly with increasing NaDS concentration for all the systems. The decrease of contact angle in each system reached its plateau at the NaDS concentrations of 7.0, 4.5 and 3.0 mM for the systems of 0.00, 0.01, and 0.03 M NaCl respectively.

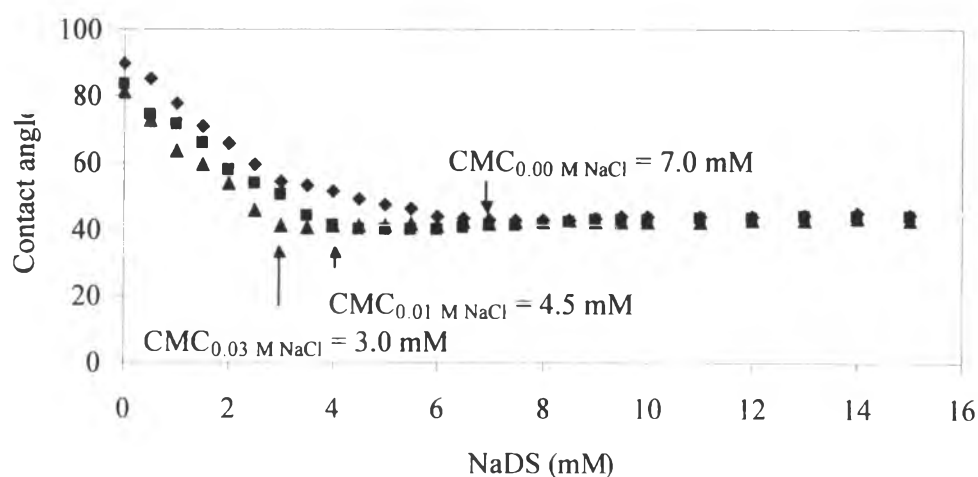


Figure 4.1 Contact angles of saturated CaC_{12} solution on its precipitate with varying NaDS concentration and different NaCl concentrations.

4.1.1.2 Contact Angle of Surfactant Mixture Solution between Saturated CaC_{12} and Subsaturated NPE

The contact angles of a saturated CaC_{12} solution containing subsaturated NPE are shown in Figure 4.2. It was found that the contact angle decreased substantially from about 90° to 60° with increase in NPE concentration and reached the plateau at the NPE concentration of $75 \mu\text{M}$.

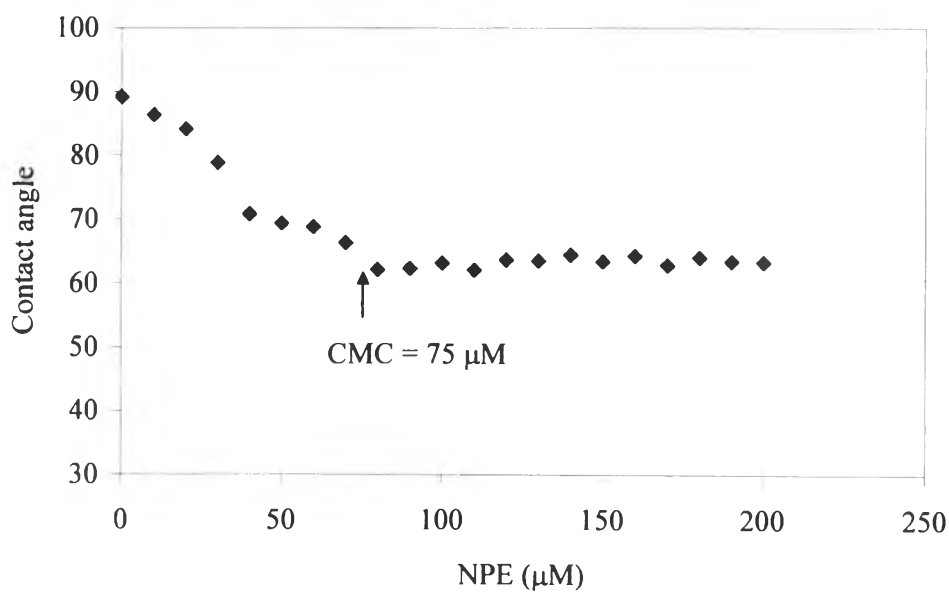


Figure 4.2 Contact angles of saturated CaC_{12} solution with varying NPE concentration.

4.1.1.3 Contact Angle of Surfactant Mixture Solution between Saturated CaC_{12} and Subsaturated NaC_8

The contact angles of a saturated CaC_{12} solution containing subsaturated NaC_8 are shown in Figure 4.3. It was found that the contact angles decreased substantially (50°C reduction) with increasing NaC_8 concentration until reaching the plateau at the NaC_8 concentration of 270 mM.

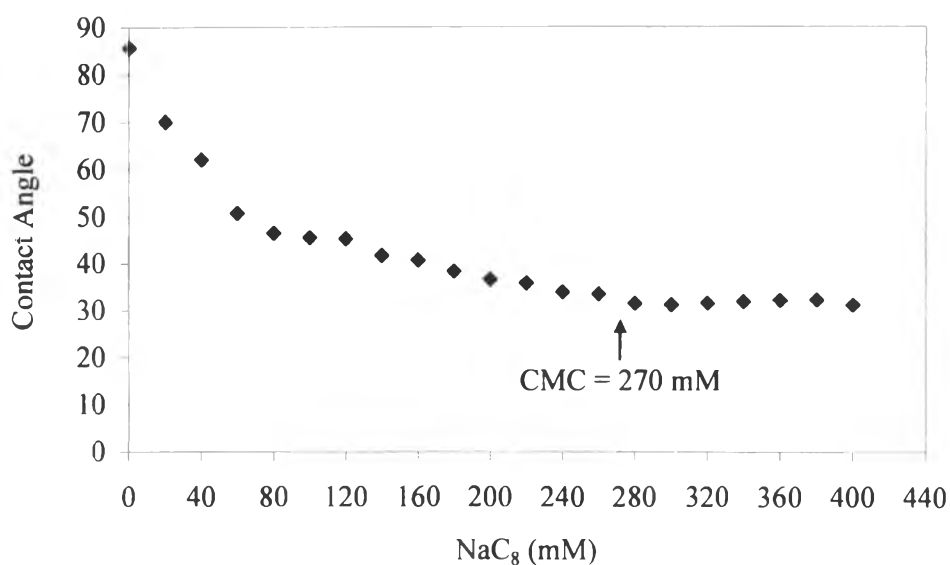


Figure 4.3 Contact angles of saturated CaC_{12} solution with varying NaC_8 concentration.

4.1.2 The Liquid-Vapor Interfacial Tension

4.1.2.1 Surface Tension of Surfactant Mixture Solution between Saturated CaC_{12} and Subsaturated NaDS

The critical micelle concentrations (CMC) of the surfactant solution containing saturated CaC_{12} and varying NaDS concentration were determined from the graphical plots between the liquid-vapor interfacial tension (γ_{LV}) and a semi logarithm of NaDS concentration as shown in Figure 4.4. An intercept of the two tangents is taken as the CMC value for each system.

The CMC value was 8.0 mM for pure NaDS solution. In the mixture of saturated CaC_{12} and subsaturated NaDS, the CMC values at 30°C were 7.0, 4.5 and 3.0 mM with 0.00, 0.01 and 0.03 M NaCl salt added, respectively. The CMC value obtained for aqueous NaDS solution corresponding to that reported in literature, i.e. 8.2 mM at 25 °C with no added salt (Rosen, 1989) and around 8.1 mM and 8.4 mM was reported by Fillipi *et al.* (1999) and Deshpande *et al.* (1999) respectively. Moreover, the CMC values for NaDS solutions with 0.01 and 0.03 M NaCl added at 21 °C equaling to 5.6 mM and 3.2 mM respectively were also reported.

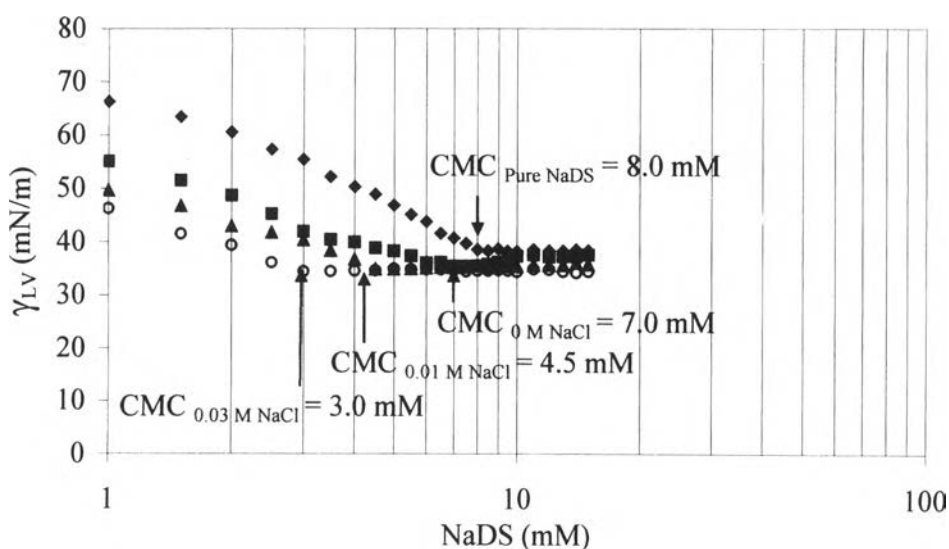


Figure 4.4 Liquid/vapor surface tension as a function of NaDS concentration.

4.1.2.2 Surface Tension of Surfactant Mixture Solution between Saturated CaC_{12} and Subsaturated NPE.

The critical micelle concentrations of the pure NPE solution and the surfactant mixture between saturated CaC_{12} and subsaturated NPE solutions were also determined as shown in Figure 4.5. The CMC values were taken at 85 μM for the former and 75 μM for the latter solution.

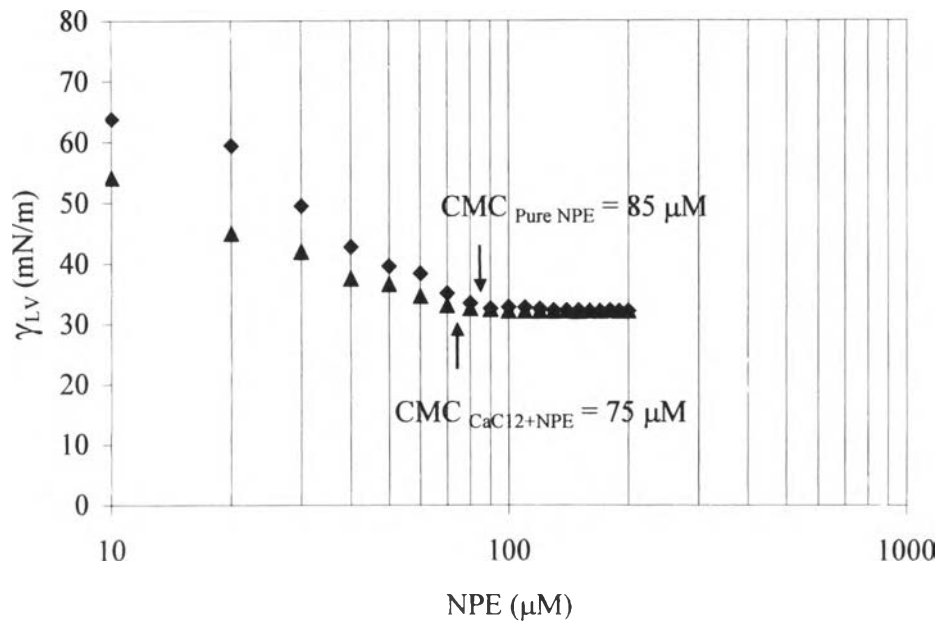


Figure 4.5 Liquid/vapor surface tension as a function of NPE concentration.

4.1.2.3 Surface Tension of Surfactant Mixture Solution between Saturated CaC_{12} and Subsaturated NaC_8

Figure 4.6 is the plot between the liquid/vapor interfacial tension and the semi-logarithm of NaC_8 concentration of the aqueous NaC_8 solution and the surfactant mixture solution of saturated CaC_{12} and subsaturated NaC_8 . The CMC values were taken at about 280 mM for both pure NaC_8 solution and the mixture of saturated CaC_{12} and subsaturated NaC_8 solution.

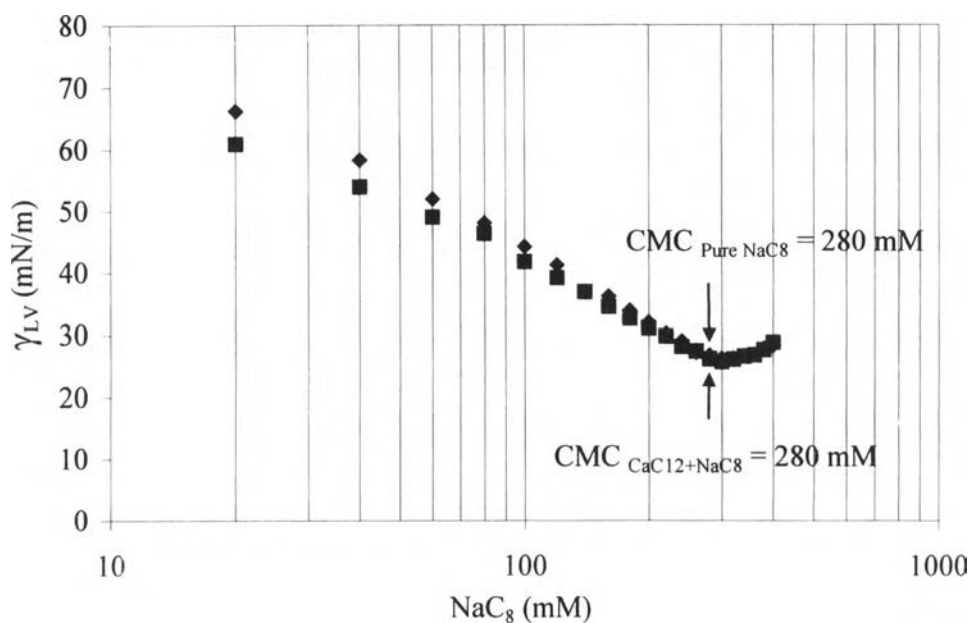


Figure 4.6 Liquid/vapor surface tension as a function of NaC_8 concentration.

4.1.3 Adsorption of Subsaturated Surfactant onto Precipitated Surfactant

4.1.3.1 Adsorption of NaDS on CaC_{12} Surface in the System with Various NaCl Concentrations

The adsorption isotherms of NaDS onto the surface of calcium dodecanoate (CaC_{12}) precipitate in the presence of various NaCl salt concentrations are shown in Figure 4.7. The adsorption increased with NaDS concentration at low concentration, reached the plateau when the NaDS concentration was around the CMC, and slightly increased beyond the CMC. The same trend of adsorption isotherm was found in every system with different salt concentrations. The amount of surfactant adsorbed increased noticeably as the concentration of NaCl increased. The amount of NaDS adsorbed in the vicinity of the CMC were 84, 77, and 71 $\mu\text{mole/g}$ for the systems with 0.00, 0.01, and 0.03 M NaCl added, respectively.

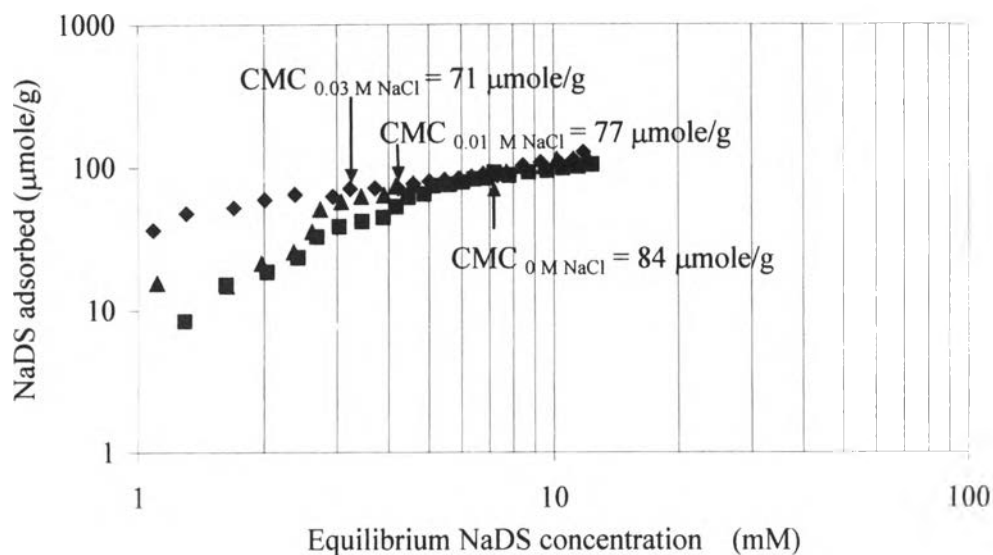


Figure 4.7 Adsorption of NaDS onto CaC_{12} precipitate at various NaCl concentrations.

4.1.3.2 Adsorption of NPE on CaC_{12} Surface

The adsorption isotherm of NPE onto the surface of CaC_{12} precipitate is shown in Figure 4.8. The result stated that the adsorption of NPE increased with increasing NPE concentration until reaching the plateau around $1.4 \mu\text{mole/g}$ of NPE adsorbed at the equilibrium NPE concentration of $75 \mu\text{M}$, corresponding to the CMC value of this system.

4.1.3.3 Adsorption of NaC_8 on CaC_{12} Surface

The adsorption of NaC_8 on the surface of CaC_{12} precipitated in the saturated solution of CaC_{12} encountered the problem in the separation of the supernatant solution from the mixture of surfactant solution and the adsorbate when the adsorption experiment was performed. The solution was very slurry as the concentration of NaC_8 increased, due not only to C_8^- ions in the surfactant solution tending to precipitate as CaC_8 , but also to the dissolution of CaC_{12} precipitate in the presence of Na^+ ions in the solution when the ratio of calcium ion/octanoate ion exceeded its K_{sp} ($K_{\text{sp}} \text{CaC}_8 = 4.53 \times 10^{-7} \text{ M}^3$ (Balasuwatthi *et al.*, 2003)). Sodium salts of both NaC_{12} and NaC_8 have much higher solubility in aqueous solution than that of calcium salts.

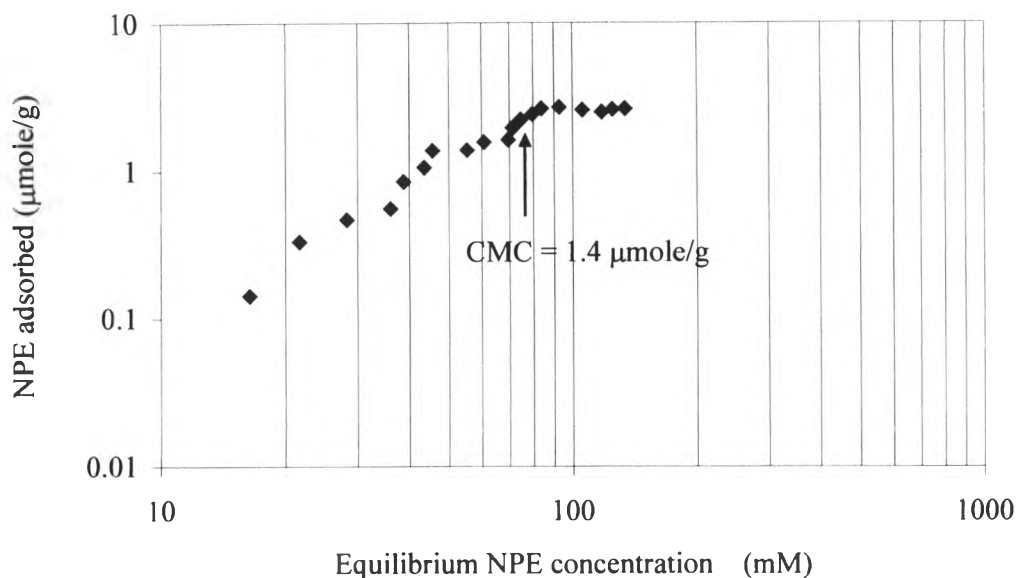


Figure 4.8 Adsorption of NPE onto CaC_{12} precipitate.

4.1.4 Calculation of Solid/Liquid Surface Tension

Young's equation (1) shows that, if the solid-vapor interfacial tension (γ_{SV}) and solid-liquid interfacial tension (γ_{SL}) were constant, the graph plotted between $\cos \theta$ and $1/\gamma_{LV}$ should be linear with slope equal to $\gamma_{SV} - \gamma_{SL}$. The deviation of the slope of the plot from linearity indicates that the amount of surfactant adsorbed on the solid/liquid interface changes with varying surfactant concentration thereby changing in the value of solid/liquid interfacial tension. For the system of the subsaturated NaDS and saturated CaC_{12} as shown in Figure 4.9 with various NaCl concentrations, the results showed good correlation, however, it did not imply that the γ_{SL} was constant with varying NaCl concentration. The results for the subsaturation systems of NPE as shown in Figure 4.10 and NaC_8 in Figure 4.11 obviously show the deviation of the slope from linearity implying the change of γ_{SL} with varying surfactant concentration.

Even though no method is presently available for directly measuring solid-liquid interfacial tension (Starweather *et al.*, 2000), however, equation (1) can still be used to provide insight into the interactions at solid-liquid interfaces by calculating γ_{SL} relative to γ_{SL}^0 at a reference condition, where there is no second subsaturated surfactant. The difference of γ_{SL} from the reference condition gives the spreading pressure, $\gamma_{SL}^0 - \gamma_{SL}$.

$$\gamma_{SL}^0 - \gamma_{SL} = \gamma_{LV} \cos\theta - \gamma_{LV}^0 \cos\theta^0 \quad (4)$$

Rearrangement of equation (2) yields

$$(\gamma_{LV}^0/\gamma_{LV})(\cos\theta^0) - \cos\theta = (\gamma_{SL}/\gamma_{LV}) - (\gamma_{SL}^0/\gamma_{LV}) \quad (3)$$

The dependences of the spreading pressure for the solid/liquid interface indicates the reduction in surface tension induced by the adsorption of the subsaturated surfactants as shown for NaDS in Figures 4.12 and 4.13, for the surfactant mixture solution systems of NPE/CaC₁₂ in Figures 4.14 and 4.15, and NaC₈/CaC₁₂ in Figure 4.16. The spreading pressure increase with increase of the subsaturated surfactant concentration and plateauing at the CMC. The subsaturated NaDS provided the greatest spreading pressure at the CMC (26 mN/m) and its value decreased with increase of NaCl concentration, while the subsaturated NPE gave the lowest value (14 mN/m).

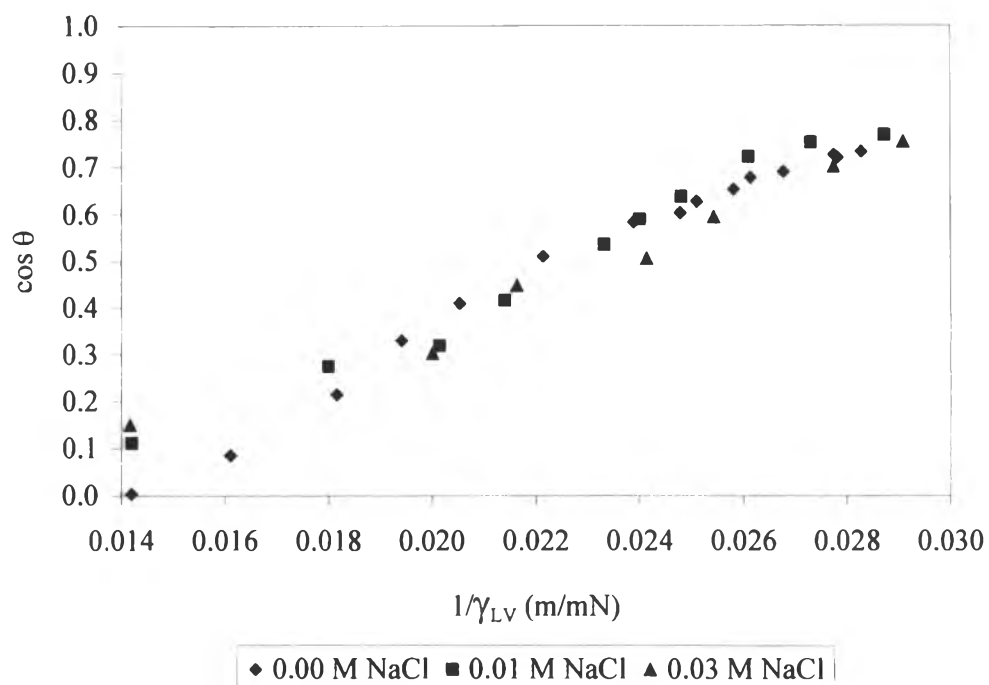


Figure 4.9 The relationship between contact angle and liquid-vapor interfacial tension of mixed solution of saturated CaC_{12} and NaDS.

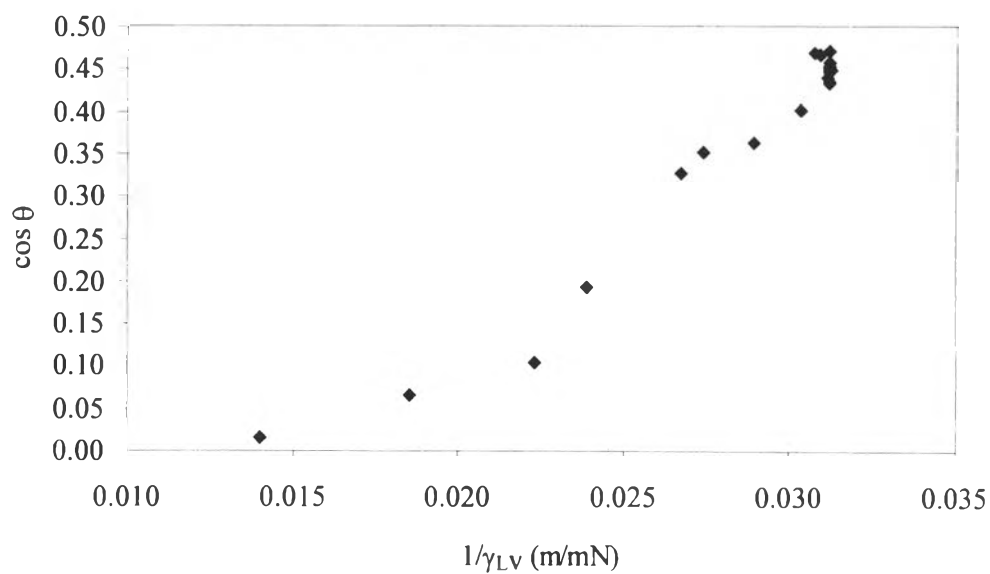


Figure 4.10 The relationship between contact angle and liquid-vapor interfacial tension of mixed solution of saturated CaC_{12} and NPE.

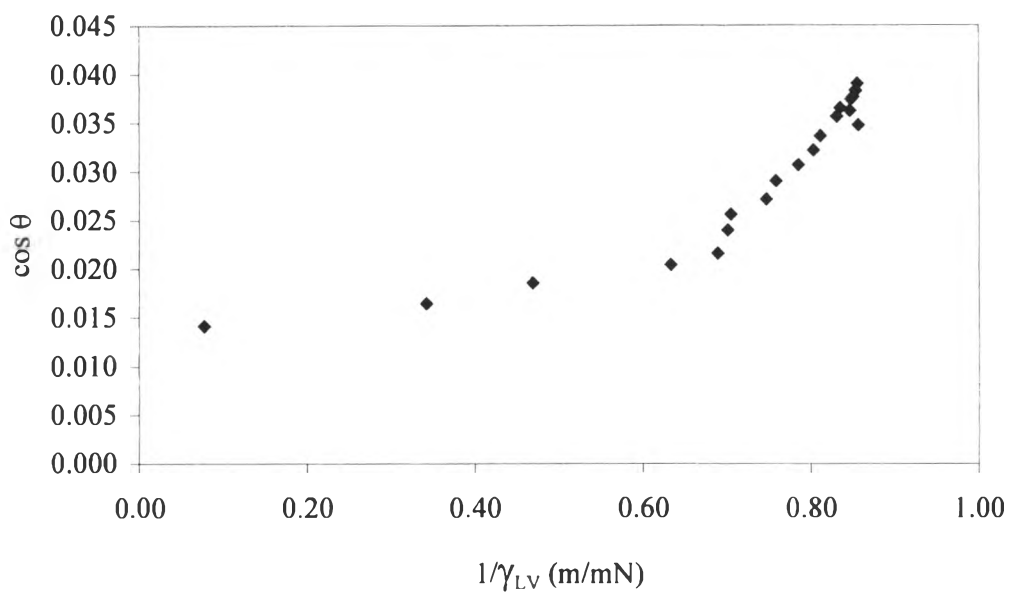


Figure 4.11 The relationship between contact angle and liquid-vapor interfacial tension of mixed solution of saturated CaC_{12} and NaC_8 .

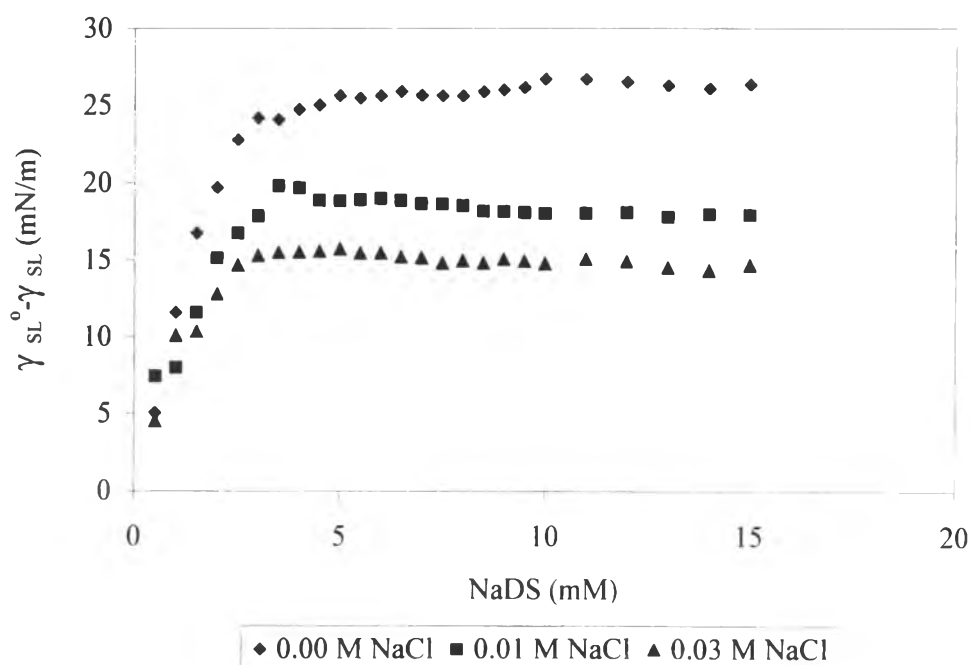


Figure 4.12 Solid-liquid spreading pressure of mixed solution of saturated and subsaturated NaDS as a function of NaDS concentration.

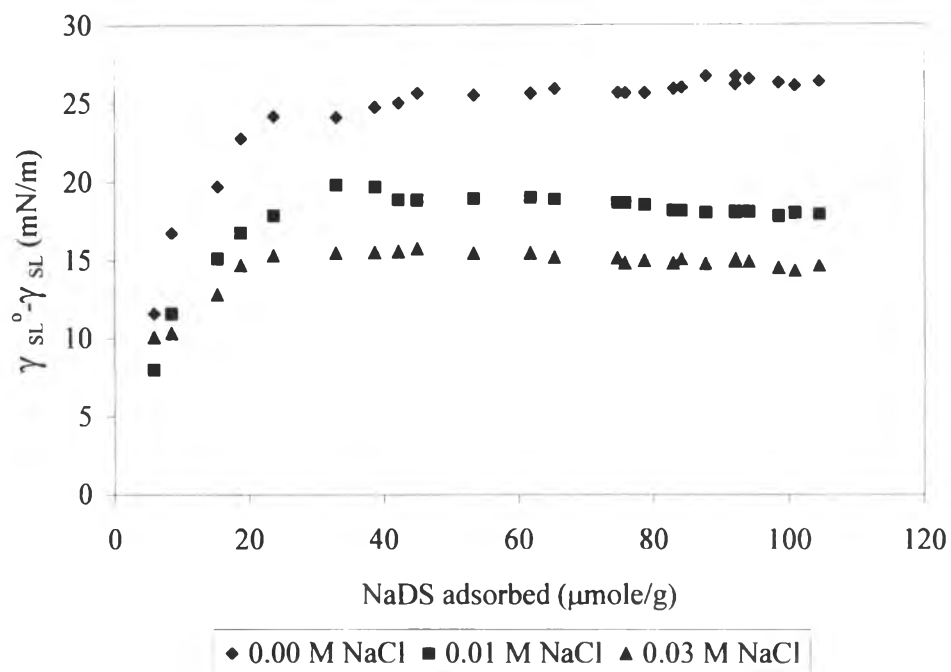


Figure 4.13 Solid-liquid spreading pressure of mixed solution of saturated CaC_{12} and subsaturated NaDS as a function of NaDS adsorption.

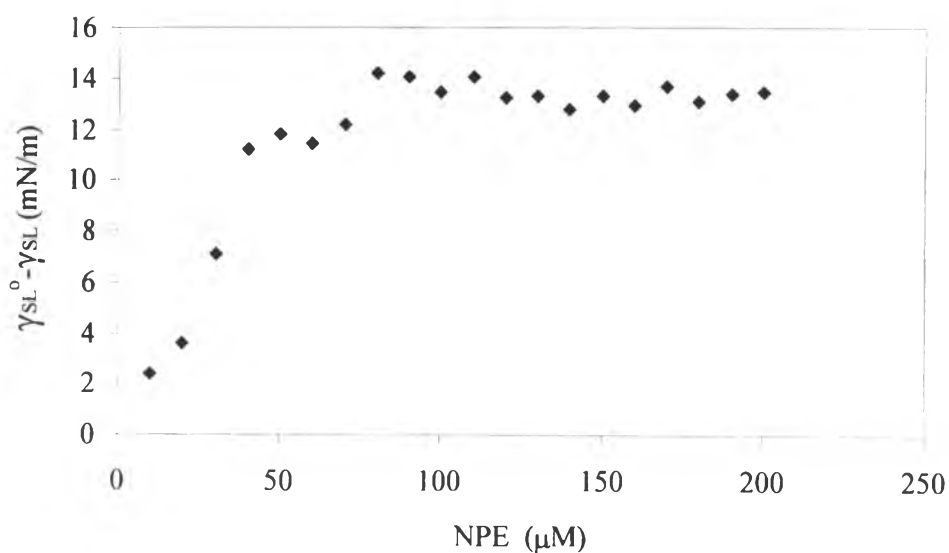


Figure 4.14 Solid-liquid spreading pressure of mixed solution of saturated CaC_{12} and subsaturated NPE as a function of NPE concentration.

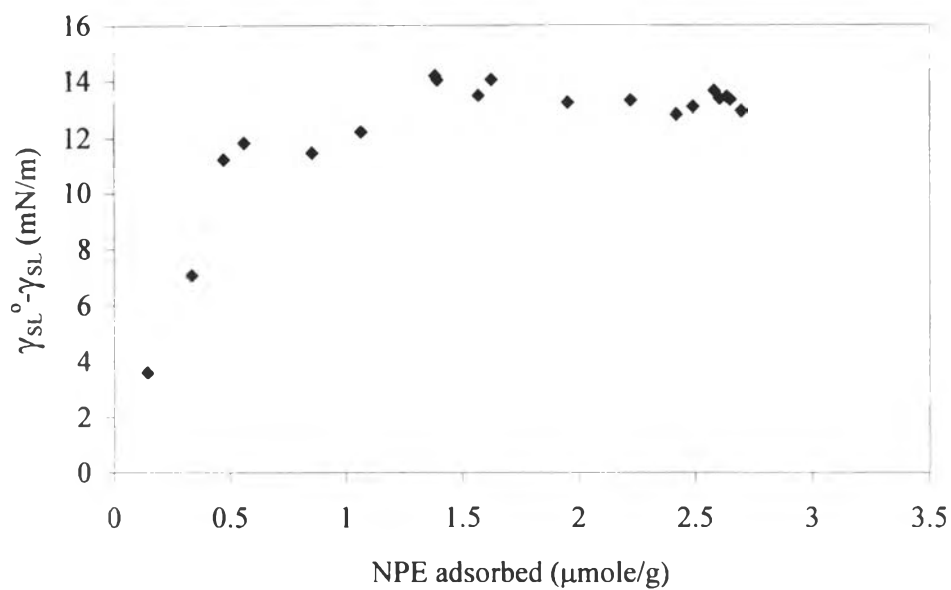


Figure 4.15 Solid-liquid spreading pressure of mixed solution of saturated CaC_{12} and subsaturated NPE as a function of NPE adsorption.

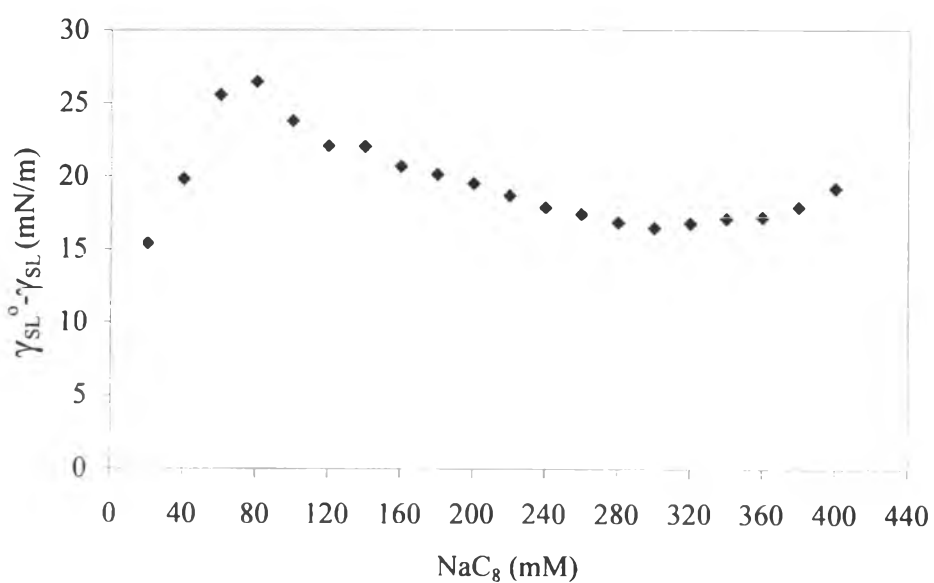


Figure 4.16 Solid-liquid spreading pressure of mixed solution of saturated CaC_{12} and subsaturated NaC_8 as a function of NaC_8 concentration.

4.1.5 Calculation of Critical Solid Surface Tension

The Zisman plots of $\cos\theta$ against γ_{LV} of three different subsaturated surfactants (NaDS, NPE, and NaC₈) are shown in Figures 4.17, 4.18, and 4.19. The critical surface tension (γ_{LV}^c) of the solid CaC₁₂ precipitate are 26.0, 13.7, and 20.0 mN/m for the system with subsaturated NaDS, NPE, and NaC₈, respectively.

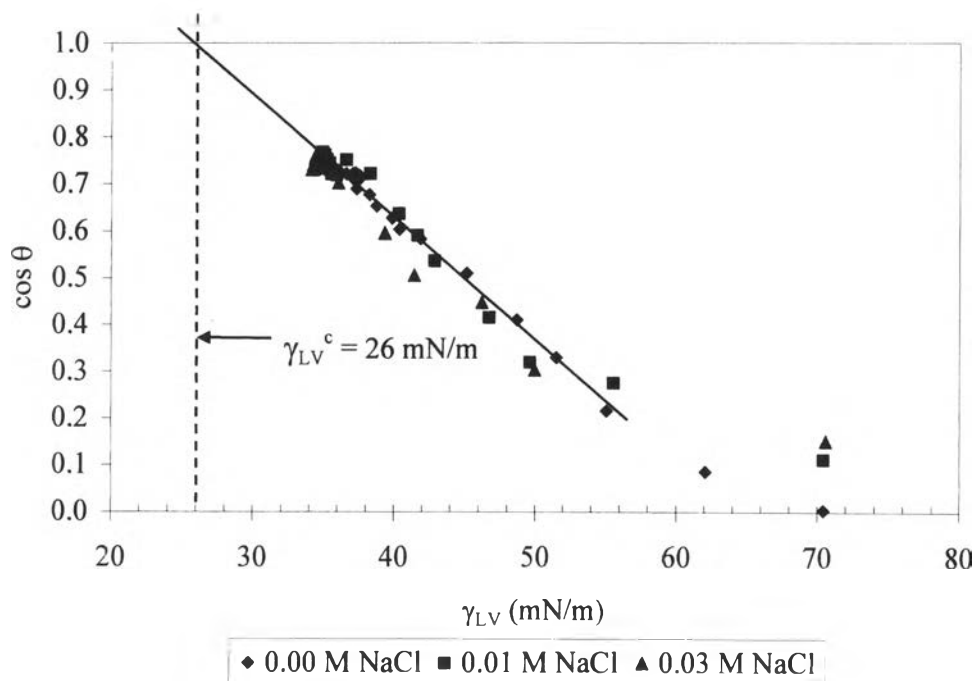


Figure 4.17 Zisman plot of the data from the surfactant mixture solution between saturated CaC₁₂ and NaDS.

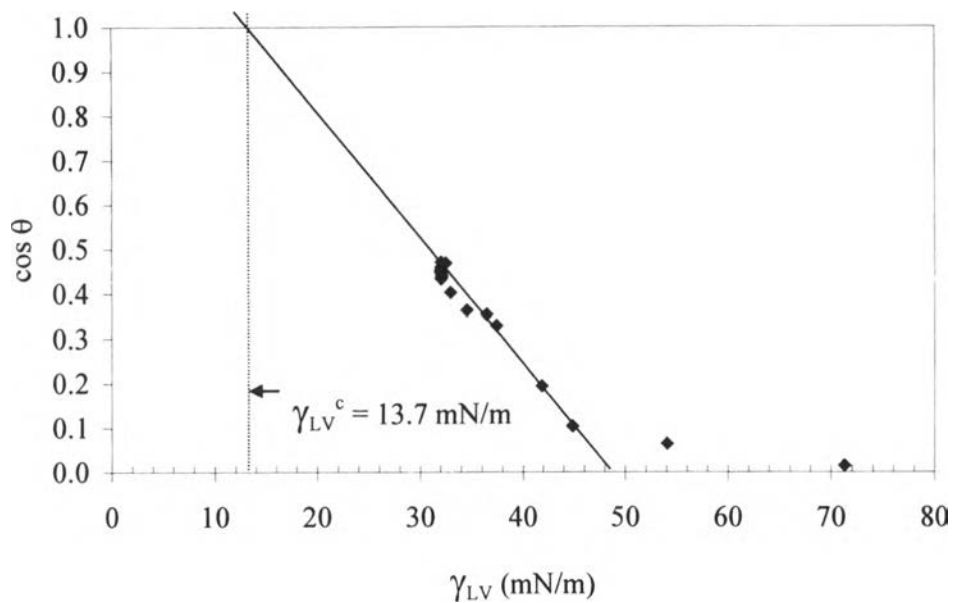


Figure 4.18 Zisman plot of the data from the surfactant mixture solution between saturated CaC_{12} and NPE.

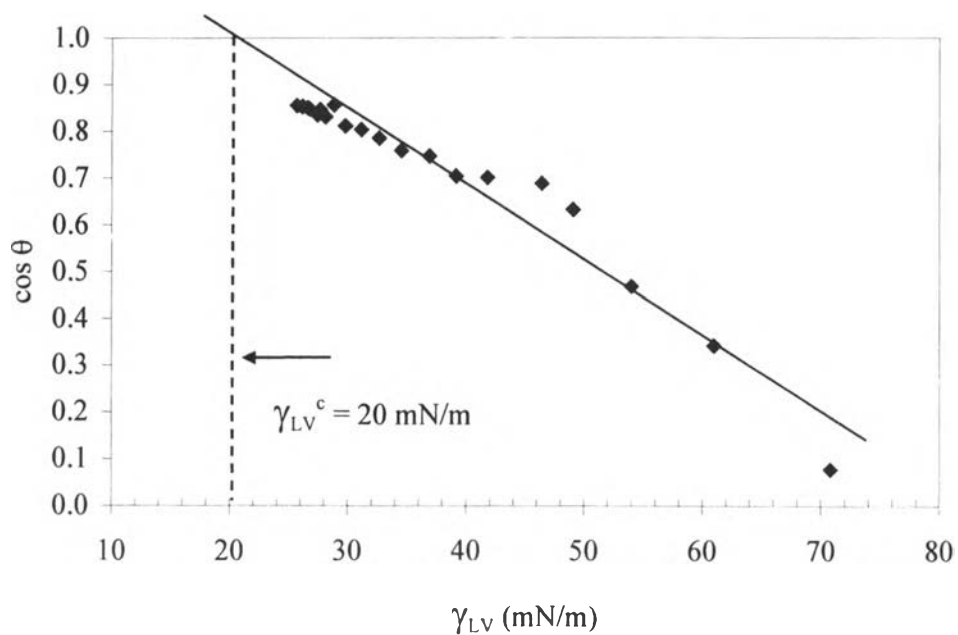


Figure 4.19 Zisman plot of the data from the surfactant mixture solution between saturated CaC_{12} and NaC_8 .

4.2 Discussion

4.2.1 Effect of Subsatuated NaDS and NaCl

The results of contact angle, surface tension, and adsorption measurements (Figures 4.1, 4.2, and 4.3) show that NaDS can act as an effective wetting agent by adsorbing at both liquid/vapor and solid/liquid interfaces. The value of contact angle in the vicinity of the CMC is about 40°, indicating that calcium dodecanoate precipitated surface is fairly hydrophilic in the presence of a second subsaturated surfactant. It implies that NaDS should adsorb by figuring their head groups out as already seen in the previous work (Balasuwatthi *et al.*, 2003). The adsorption of ionic surfactants in this manner causes an increase in surface charge density of the solid, making it more wettable by the aqueous phase.

The effect of NaCl salt addition to the system of the subaturated NaDS and saturated CaC_{12} on CaC_{12} precipitate illustrated by the reduction in the liquid/ vapor interfacial tension and the CMC of the mixture of the surfactant solution (Figure 4.4) is due mainly to the decrease in the ionic atmosphere surrounding the ionic head groups in the presence of the additional electrolyte (Rosen, 1989). The addition of NaCl increases efficiency of NaDS adsorption without affecting the effectiveness of NaDS adsorption at the vicinity of its CMC (Figure 4.7). As the efficiency term is used as a measure of the equilibrium concentration of surfactant in the liquid phase necessary to produce a given amount of effect (Rosen, 1989), in this case it is the amount of surfactant adsorbed, and effectiveness is used as a measure of the maximum effect. The increase in the amount of NaDS adsorbed with NaCl concentration should be due to the reduction in electronic repulsion between surfactant molecules. However, increased NaDS concentration also increases the amount of CaDS precipitation as already seen in the previous work (Balasuwatthi *et al.*, 2003). As the micelle formation phenomenon takes place when the concentration of surfactant mixture solution is greater than mixed CMC, there is a mixed micelle that is composed of both the dodecyl sulfate (DS^-) and dodecanoate (C_{12}^-) anionic surfactants. The higher the concentration of NaDS, the more the mixed micelles are formed. This occurrence causes some precipitated CaC_{12} to dissolve, allows the dodecanoate to micellize, and causes some of the dissolved calcium ion (Ca^{2+}) to end up

as unassociated in the solution. When the concentration of calcium ion is high enough until the ratio of calcium ion/ dodecyl sulfate ion exceeds its K_{sp} ($K_{sp_{CaDS}} = 2.65 \times 10^{-11} \text{ M}^3$, (Balasuwatthi *et al.*, 2003)), the precipitation of dodecyl sulfate ion occurs as the calcium salt. The more NaDS added, the more CaC_{12} dissolves and the more CaDS precipitates. Unfortunately, the solution depression method that determines the amount of NaDS adsorbed from the difference between the initial and final concentrations cannot distinguish the NaDS adsorption from the NaDS precipitation. Therefore, only the apparent adsorption of the surfactant was reported. Furthermore, the determination of the spreading pressure of the surfactant mixture between subsaturated NaDS and saturated CaC_{12} solution (Figure 4.12) shows that the spreading pressure decreases as NaCl concentration increases, which implies that the value of γ_{SL} does not decrease as the amount of NaDS adsorbed on the solid/liquid interface increases (Figure 4.7). The depletion of NaDS in the solution to the solid surface is due not only to the NaDS adsorption, but also to the precipitation. This combination of adsorption and precipitation was defined as “abstraction” by Hanna and Somasundaran (Hanna and Somasundaran, 1979). According to the linear slope obtained from the plot of $\cos \theta$ against $1/\gamma_{LV}$ based on Young’s equation (Figure 4.9), the results confirm no change of γ_{SL} as NaDS adsorption at the solid/liquid interface increases due to the precipitation of DS^- with Ca^{2+} ions on the solid surface. However, the determination of the effect on the solid spreading pressure shows that NaDS provides the greatest spreading pressure compared with NPE and NaC_8 , which are also used as second subsaturated surfactants.

4.2.2 Effect of NPE Nonionic Surfactant

The subsaturated NPE nonionic surfactant can also act as an effective wetting agent in the system of saturated CaC_{12} solution and CaC_{12} precipitate and cause 30° contact angle reduction as compared to that of the saturated CaC_{12} solution alone. The mixed CMC ($\sim 75 \mu\text{M}$) values obtained from both the surface tension (Figure 4.5) and adsorption measurements (Figure 4.8) agree well. The precipitated surface of CaC_{12} becomes moderately hydrophilic in the presence of NPE nonionic surfactant adsorbed by figuring their head groups outward. However, in the case of polyoxyethyleneated nonionic surfactants, adsorption may produce a steric barrier to the close approach of

another similarly covered particle (Rosen, 1989). In addition, the low amount of NPE adsorbed should be due to the structure of NPE nonionic surfactant, *i.e.* branched molecular structure and also aromatic nucleus causing looser packing of the surfactant molecules at the surface. The even stronger evidence for this assumption is the lowest effect on the solid spreading pressure compared with the other two second subsaturated surfactants (NaDS and NaC₈).

4.2.3 Effect of NaC₈

The effect of a second subsaturated surfactant of NaC₈ in the system of saturated CaC₁₂ solution and its precipitate (Figure 4.3 and Figure 4.6) indicates that NaC₈ is the most effective wetting agent, which causes 50° contact angle reduction. The spreading pressure of NaC₈ increases with increasing in NaC₈ concentration at the low NaC₈ concentration range, the value decreases with the NaC₈ concentration higher than 100 mM, and tends to be constant at the CMC. This should be due to the NaC₈ adsorption playing a major role in decreasing the solid/liquid interfacial tension of the solid surface at low concentration until the precipitation phenomenon occurs.

4.2.4 The Critical Solid Surface Tension

Zisman has introduced an empirical procedure to estimate the wettability of solid surface (Nylund *et al.*, 1998; Shafrin and Zisman, 1967; Siboni *et al.*, 2004). The method is based on the measurement of the surface tension of the liquid and the contact angle of the liquid on a solid surface. A critical surface tension, γ_c , for the solid surface is defined as the surface tension of the reference liquid which fully wets the solid surface or the surface tension needed to give a zero contact angle on the solid. Zisman emphasized that his method is only applicable to pure liquids, not solutions (Zdziennicka *et al.*, 2003). He especially warned against using solutions due to the large probability for specific, selective, or preferential adsorption of the components constituting the solution. However, in most practical applications, mixtures of surfactants rather than individual surfactants are used. In some cases this is involuntary since the commercial surfactants used, even when designated by the name of an individual surfactant, are mixture of surface-active

materials as a result of non-homogeneous raw materials used in their manufacture and/or the presence of unreacted raw materials and formed by-products.

Wetting enhancement by surfactants is commonly attributed primarily to a reduction in liquid/vapor surface tension (Balasuwatthi *et al.*, 2003), as its effect is also seen with a second subsaturated surfactant. Increasing adsorption of the second subsaturated surfactant onto the CaC_{12} precipitate is the cause of the decrease in γ_{SL} as the second subsaturated surfactant concentration increases, just as the second subsaturated surfactant adsorption at the liquid/vapor interface is responsible for the reduction in γ_{LV} as the subsaturated surfactant concentration increases.

The Zisman equation is as follows:

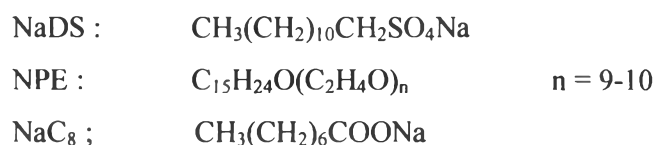
$$\cos \theta = a + b\gamma_{\text{LV}} \quad (4)$$

or

$$\cos \theta = 1 - \beta(\gamma_{\text{LV}} - \gamma_{\text{LV}}^{\text{C}}) \quad (5)$$

where $\gamma_{\text{LV}}^{\text{C}}$ is the critical surface tension characteristic of the solid (Balasuwatthi *et al.*, 2003). The Zisman plots of the experimental results obtained for NaDS/ CaC_{12} , NPE/ CaC_{12} , and NaC_8 / CaC_{12} (Figures 4.17-4.19) show that the Zisman equation is not obeyed over the range of conditions studied. Evaluation the linear region of the Zisman plot for the system of NaDS/ CaC_{12} gives the value of critical surface tension, γ_{c} , of about 26 mN/m and $\beta = 0.028$ which are comparable with the results from the previous work, $\gamma_{\text{c}} = 25.5$ mN/m and $\beta = 0.045$ (Balasuwatthi *et al.*, 2003). The addition of NaCl does not affect the value of the critical surface tension (Figure 4.17). For the NPE/ CaC_{12} system, the critical surface tension is 13.7 mN/m and $\beta = 0.029$ and $\gamma_{\text{c}} = 20.0$ mN/m and $\beta = 0.019$ for the NaC_8 / CaC_{12} system. Similar results illustrating the distinction of the critical surface tension by using solutions were reported by Nylund and co-worker (1998), for a resin and a stainless steel surfaces with different liquids. They used diiodomethane and α -bromonaphtalene as pure probe liquids and other solutions for the determination. They found that γ_{c} was approximate 42.0 mN/m and 40.3 mN/m for the resin surface and the stainless steel surface, respectively, by using the probe liquid, whereas when using acetic acid solution, γ_{c} were 25.4 mN/m for the resin surface and 23.7 mN/m for the stainless

steel surface. They considered the discrepancy in this critical surface tension values as the result from specific adsorption effects, and although the determination of critical surface tensions is justified with pure liquid only, the use of specific set of solutions for characterizing surfaces of similar kind might be applicable if only relative values for the critical surface tensions are aimed at. The differences in the results of CaC_{12} critical surface tension determined by using surfactant mixture solutions received from this work is due to the dissimilarity in the interactions of each surfactant mixture solution and the solid surface. The total surface tension of liquids and solids can be composed of sub-part of surface tension, *i.e.* polar parts of surface tension (dipole-dipole interaction and Lewis acid-base interaction), disperse parts of surface tension (van der Waals interaction), and hydrogen bonding parts of surface tension. The composition of these parts of surface tension for each substance depends on its molecular structure. In the case of subsaturated surfactants NaDS, NPE, and NaC_8 , the molecular structure of each subsaturated surfactant is as follows;



NPE should have the highest van der Waals interaction as it has the largest hydrophobic portion while NaC_8 with the shortest chain length should provide the lowest value. The polar part contribution to surface tension of NPE is hydrogen bonding mainly from EO groups ($n = 9-10$), while NaDS and NaC_8 , both an anionic and carry the same charge can have the contribution from the dipole-dipole interaction and Lewis acid-base interaction. Therefore, the second subsaturated surfactant that has different molecular structure from the others will interact differently on the solid precipitated of CaC_{12} surface. The linear relationship of Zisman plot only applies when the relationship between the disperse and polar interactions is the same between the solid and the liquid. This particular case occurs when a purely disperse interactive solid and liquid are involved. Therefore, only some ranges determined from the Zisman plot obey the linear relationship. This fact indicates that the use of solutions for determination of the critical surface tension is seldom acceptable and also illustrates the risk of using the Zisman equation beyond its original intention as Zisman seriously pointed out.