CHAPTER IV

RESULTS AND DISCUSSION

Through out the experiments, temperature was kept at 30^0C and all measurements were duplicated.

4.1 Results

4.1.1 CDS Properties

CDS precipitate is white, glossy, and slippery. It has very low solubility with solubility product constant (K_{sp}) of 2.65×10^{-11} M^3 (Balasuwatthi et al., 2004). The surface tension of water and saturated solution are about 72 and 41 mN/m which correspond to the contact angles in CDS substrate of about 65 and 61 degrees respectively. The CMC values and the surface tension at the CMC are shown in Table 4.1.

Table 4.1 CDS system parameters.

	CMC (mM)	γ_{LV} at CMC (mN/m)	θ at CMC (degrees)	Adsorption at CMC (μmole/g)	$\gamma_{SL}{}^{o} - \gamma_{SL}$ (mN/m)
CDS (Pure)	-	41	61	-	-
SDeS (Pure)	30	40	-	-	-
NPE (Pure)	0.050	32	-	-	-
NaC_8 (Pure)	280	27	-	-	-
CDS + SDeS	50	39	56	70.96	1.7741
CDS + NPE	0.035	30	52	0.56	-1.4990
CDS + NaC_8	250	28	41	-	1.3635

4.1.2 Effect of Subsaturated Surfactant

4.1.2.1 The Liquid-Vapor Surface Tension and CMC Values

The CMC of surfactant solution containing saturated CDS and subsaturated NaC_8, NPE, SDeS was determined by plotting the liquid/vapor surface tension (γ_{LV}) versus logarithmic function of surfactant concentration as shown in Figure 4.1, Figure 4.2, and Figure 4.3 for pure and binary mixture. The CMC can be found as the concentration increases at which there is an abrupt change in slope.

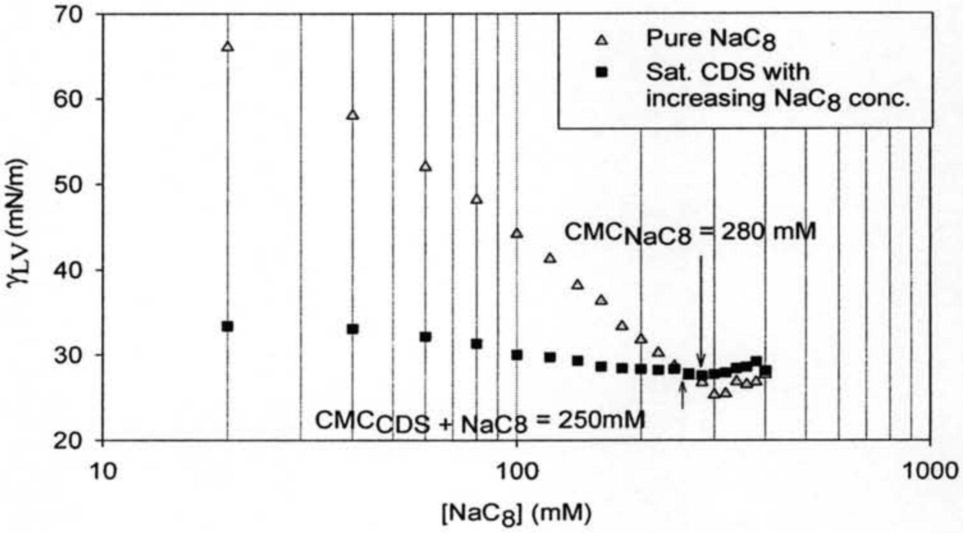

Figure 4.1. Liquid-vapor surface tension (γ_{LV}) as a function of NaC_8 concentration.

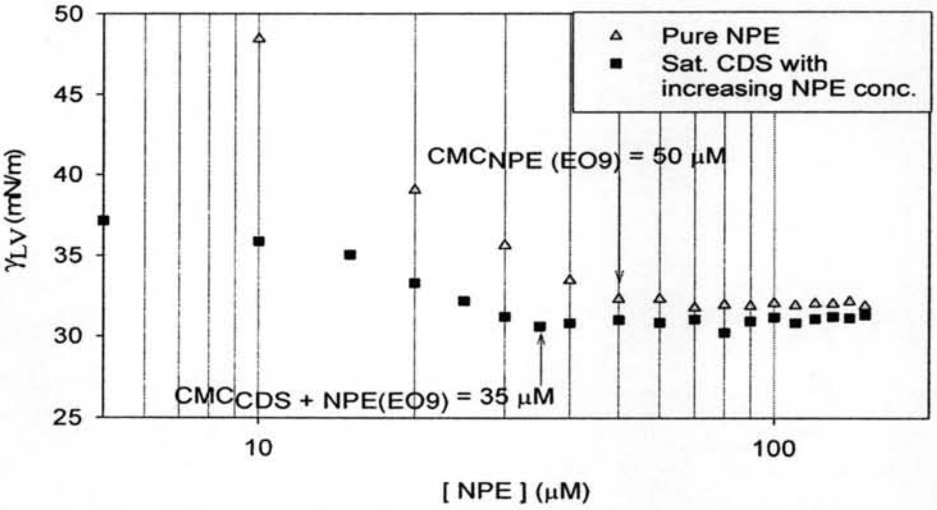

Figure 4.2. Liquid-vapor surface tension (γ_{LV}) as a function of NPE concentration.

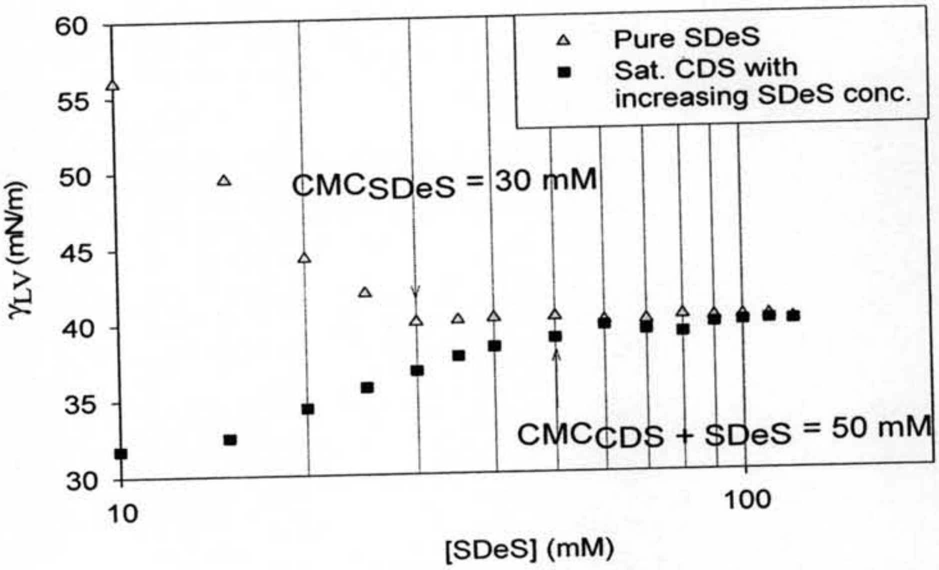

Figure 4.3. Liquid-vapor surface tension (γ_{LV}) as a function of SDeS concentration.

4.1.2.2 Contact Angle (θ)

The contact angles of saturated CDS solution containing subsaturated NaC_8, NPE, and SDeS are shown in Figure 4.4 and Figure 4.5. The contact angles tend to follow the trend of surafce tension graph. The CMC values are shown and also summarized in Table 4.1.

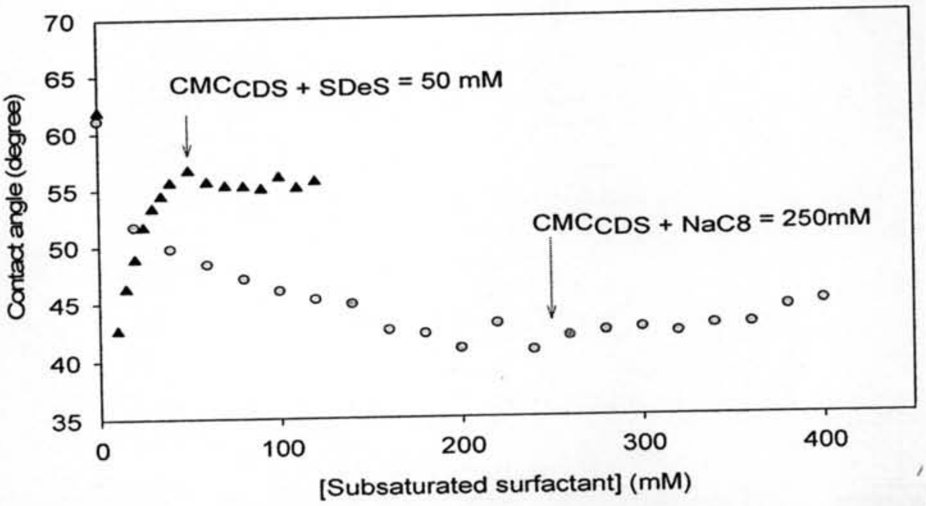

Figure 4.4. Effect of subsaturated surfactants concentration on contact angles of saturated CDS solution.

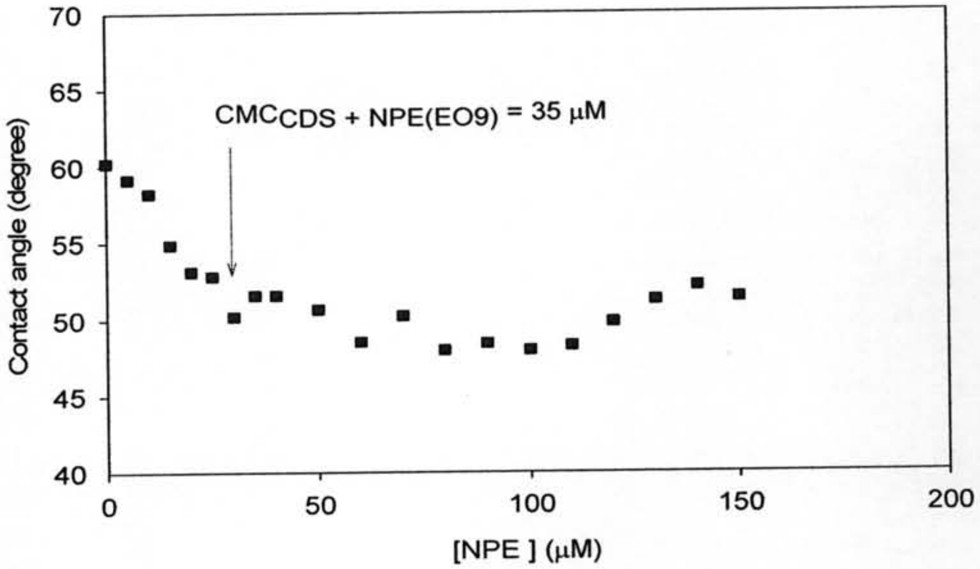

Figure 4.5. Effect of subsaturated NPE concentration on contact angles of saturated CDS solution.

4.1.2.3 Adsorption Isotherms

The adsorption isotherms of NPE and SDeS onto the CDS precipitate are shown in Figure 4.6 and Figure 4.7, respectively as a function of subsaturated surfactant concentration. In case of NaC_8, the adsorption measurement was not preceded due to turbidity problem encountered when supernatant solution was separated from the mixture of surfactant solution and adsorbate. The exact nature of precipitate wasn't pursued. The adsorption values at the CMC of the NPE and SDeS are 0.56 and 70.96 μmole/g, respectively. The relationship of peak area against subsaturated SDeS concentration before and after adsorption isotherm measurement from HPLC is shown in Figure 4.8.

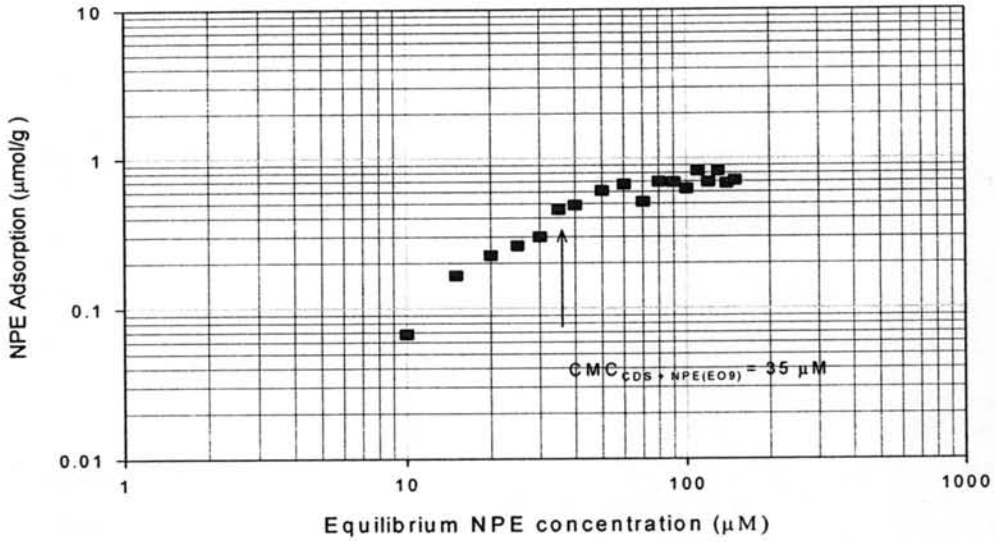

Figure 4.6. Adsorption of NPE onto CDS precipitate at various concentrations.

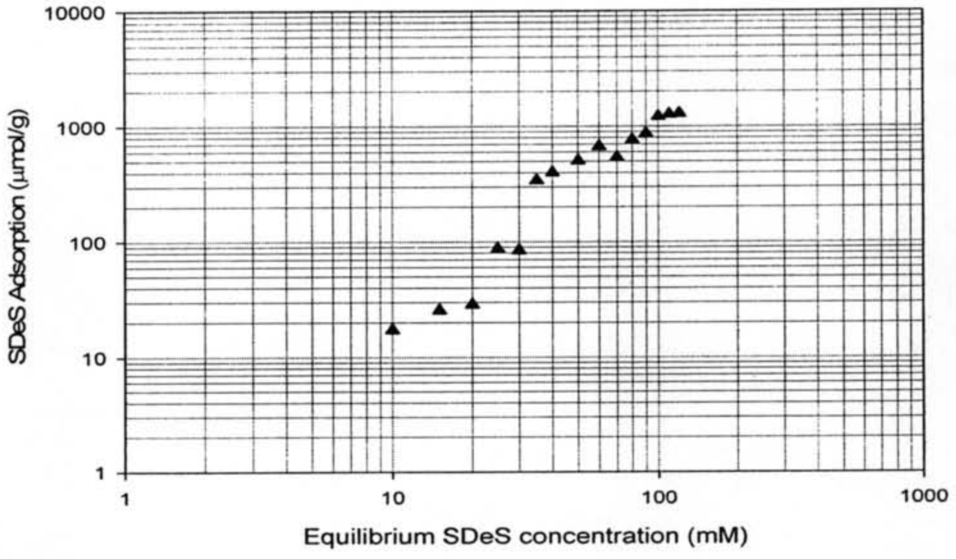

Figure 4.7. Adsorption of SDeS onto CDS precipitate at various concentrations.

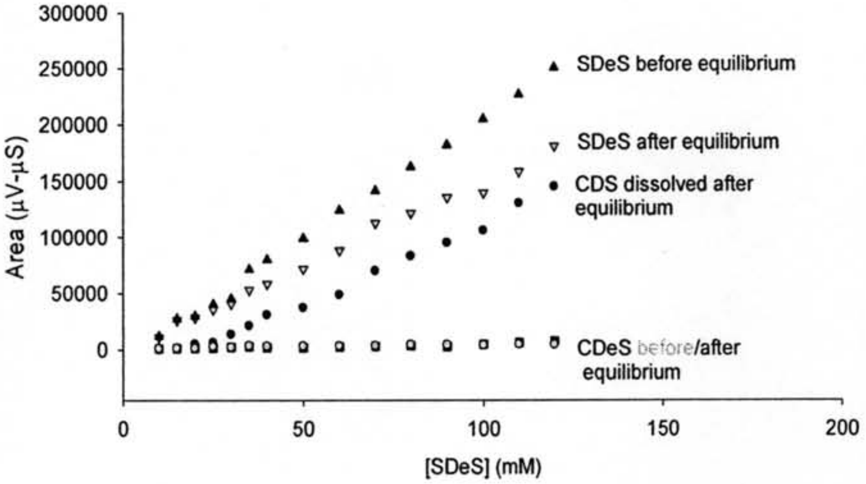

Figure 4.8. The relationship of peak area against subsaturated SDeS concentration before and after adsorption isotherm measurement.

4.1.2.4 Zisman Plot

The Zisman's plot of the three subsaturated surfactants with extrapolation of the line to cos Θ = 1 estimated the "critical surface tension ($\gamma_{LV}{}^{c}$)" of the substrate as shown in Figure 4.9. Application of the Zisman equation has been discussed for surfactant precipitate in our previous work (Balasuwatthi et al., 2003):

$$\cos\theta = 1 - \beta\,(\gamma_{LV} - \gamma_{LV}{}^{C}) \qquad (3)$$

where $\gamma_{LV}{}^{C}$ and β can be deduced from the plot of cos Θ vs. γ_{LV}.

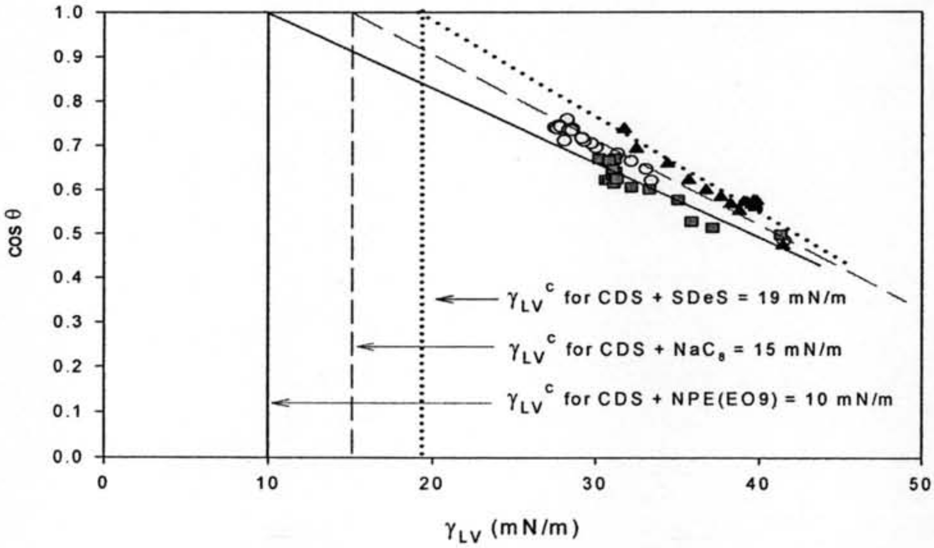

Figure 4.9 Cos θ as a function of γ_{LV}.

4.1.3 Calculation of Solid/Liquid Surface Tension

There is no method presently available for direct measurement of solid-liquid interfacial tension (γ_{SL}). However, Young's equation can still be used to describe the interactions at solid-liquid interfaces. Based on Young's equation (2), the graph plotted between cosθ and $1/\gamma_{LV}$ as shown in Figure 4.10 should be linear with a slope equal to $\gamma_{SV} - \gamma_{SL}$ provided that the solid-vapor interfacial tension (γ_{SV}) and solid-liquid interfacial tension (γ_{SL}) are constant. The slope values of NaC_8 and NPE are 20.70 and 20.40, correspondingly, while SDeS is about 27.31. The plot of SDeS shows the deviation of slope. The cluster of points in Figure 4.10 indicates the change of γ_{SV} and γ_{SL} values corresponding to the surface activities of the subsaturated surfactants.

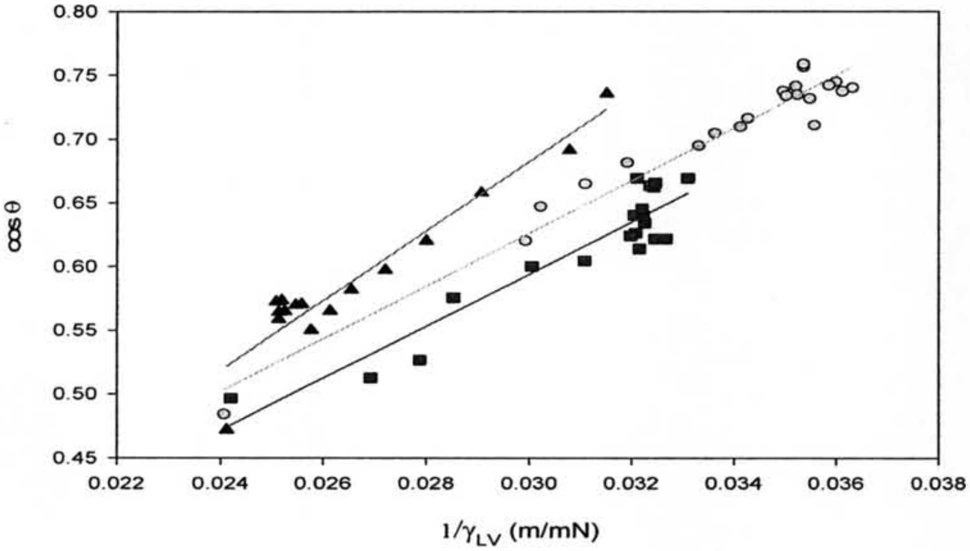

Figure 4.10. Cos θ as a function of $1/\gamma_{LV}$.

The solid/liquid spreading pressure ($\gamma_{SL}^{o} - \gamma_{SL}$), where γ_{SL}^{o} is γ_{SL} for the standard state condition of no subsaturated surfactant, can be calculated by:

$$\gamma_{SL}^{o} - \gamma_{SL} = \gamma_{LV}\cos\theta - \gamma_{LV}^{o}(\cos\theta)^{o} \qquad (4)$$

The value of $\gamma_{SL}^{o} - \gamma_{SL}$ is calculated from the γ_{LV} data in Figs. 4.1-4.2 and θ data in Fig. 4.4-4.5 and is plotted as a function of subsaturated surfactant concentration shown in Fig. 4.11-4.12. The value of $\gamma_{SL}{}^{o}$ - γ_{SL} at CMC is 1.7741 mN/m and -1.4990 mN/m, corresponding to SDeS and NPE.

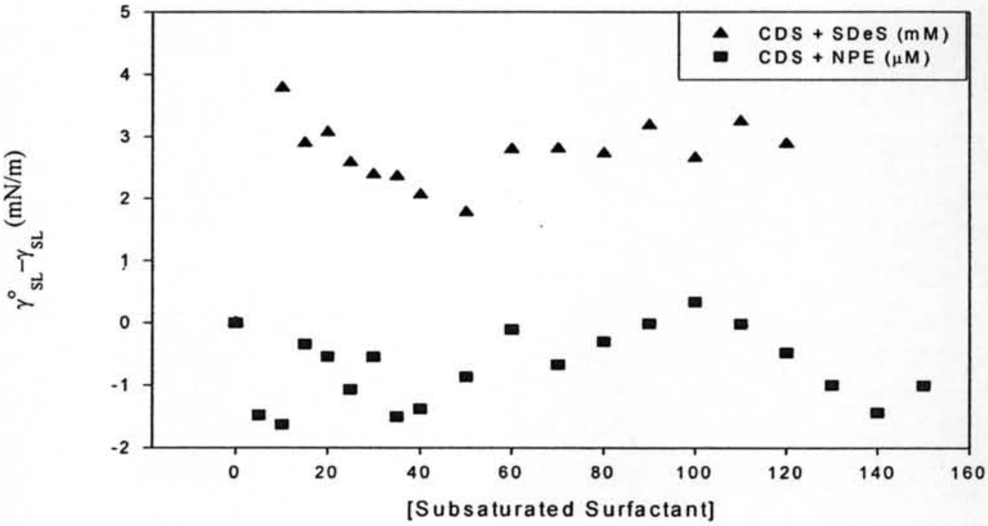

Figure 4.11. The Solid/liquid spreading pressure ($\gamma_{SL}{}^{\circ}$ - γ_{SL}) of solution of saturated CDS and subsaturated NPE and SDeS as a function of subsaturated surfactant concentrations.

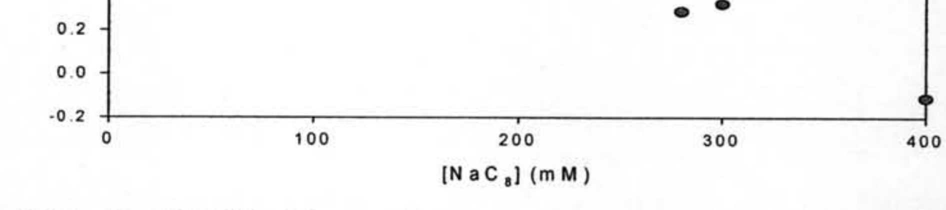

Figure 4.12. The Solid/liquid spreading pressure ($\gamma_{SL}{}^{\circ}$ - γ_{SL}) of solution of saturated CDS and subsaturated NaC_8 as a function of subsaturated surfactant concentration.

4.2 Discussion

4.2.1 Effect of Subsaturated Surfactants to Surface tension, Contact angle, and Adsorption

The plots of liquid-vapor surface tension (γ_{LV}) versus pure and mixed surfactant concentration are shown in Figures 4.1-4.3. Similarly, plots of contact angle versus logarithm of surfactant concentration are shown in Figure 4.4-4.5. The critical micelle concentration (CMC) is found in a sudden transform of slope from the surface tension and contact angle plots. The CMC signifies surface activity by adsorbing monomers to form monolayers to the liquid-vapor and solid-liquid interfaces causing an increase in surface charge density of solid to be wettable enough by the aqueous phase. The succeeding values beyond CMC are constant, which shown as a plateau in the plot. Usually, at CMC, surfactant forms micelle as well as the monolayer at the air/liquid interface that reduces γ_{LV} of the solution. The CMC's of pure surfactant were measured about 280 mM, 50 μM , and 30 mM for NaC_8, NPE(EO9), and SDeS, respectively, as illustrated in Figures 4.1-4.3. When subsaturated surfactants were added to CDS saturated solution the CMC's were measured about 250 mM, 35 μM , and 50 mM for NaC_8, NPE(EO9), and SDeS, correspondingly. The CMC of saturated CDS was not determined due to its very low solubility, however it's saturated solution alone has surface tension of about 41 mN/m and contact angle with its saturated solution of about 61°, indicating that calcium dodecyl sulfate is fairly hydrophilic. In the presence of second subsaturated surfactants, the surface tension of CDS decreases as well as the CMC of pure subsaturated surfactants, such NaC_8 decreased from 280mM to 250 mM and NPE decreased from 50 μM to 35 μM, except for SDeS which increased from 30mM to 50 mM. Subsaturated surfactants effectively decrease the surface tension of saturated CDS. The surface tension value at CMC of the mixtures was reduced to similar surface tension values of pure subsaturated surfactants at around 28, 30, and 39 mN/m for NaC_8, NPE(E09), and SDeS, respectively as summarized in Table 4.1. This reduction was due to the adsorption of subsaturated surfactant molecules at the interfaces.

The reduction of surface tension leads to better wetting and quantified by contact angle. The monolayer formed at the air/liquid interface helps to wet the solid surfaces. The contact angle of pure saturated CDS solution alone to its solid substrate is around 61°, which is not effective to act as solid hydrophobic antifoam (Garrett, 1993). The contact angles at CMC when mixed with co-surfactant are 41°, 52°, and 56° for NaC_8, NPE (EO9), and SDeS, correspondingly. The mentioned values are connected with the lower values of $\gamma_{LV.}$ As result from this experiment, NaC_8 serves as the best wetting agent compared to NPE (EO9) whereas in the case of SDeS, it is effective wetting agent as NaC_8 only at lower concentration. The reduction in γ_{SL} gives an important contribution to the reduction in the contact angle caused by adsorption of surfactant which supported by Young's equation. Therefore, plotting contact angle and surface tension are expected to have similar trend.

The tremendous importance of adsorption onto the solid and resulting reduction in γ_{SL} determines the ability of a surfactant to act as a wetting agent (Rosen, 2004).The adsorption isotherm of NPE and SDeS onto the surface of CDS precipitate is shown in Figure 4.6 and 4.7.

4.2.1.1 Effect of NaC_8

The CMC of the NaC_8 is about 280mM which much greater than that of SDeS and NPE, respectively. This is due to a very short hydrophobic tail that cannot easily aggregate to form micelles. Thus, CMC will be found at higher concentration. As subsaturated surfactant, the CMC of NaC_8 in saturated CDS solution decreased to about 30 mM as well as the saturated CDS surface tension decreased from 41 mN/m to 28 mN/m at CMC value of mixed surfactants. This phenomenon is due to the counter ion effect, which monovalent (Na^+) competes against bivalent (Ca^{2+}) ion. Calcium ion binds two anionic surfactant head groups at the micelle surface that decreases the optimal area per head group of the octanoate molecules, which promotes hydrophobic tail to combine easily leading to a reduction of CMC.

However, precipitates occurred in the supernatant solution after equilibrium, mainly due to presence of calcium octanoate (CaO_2) from the reaction of Ca^{2+} ions and deprotonated octanoate (O^-) which was also reported by Rodriguez et al. (1998). For this reason NaC_8 adsorption was not dealt further and the nature of this precipitate was not pursued.

4.2.1.2 Effect of NPE

NPE (EO9) as nonionic surfactant has longer hydrophobic tail that can easily aggregate to form micelles at very low concentration of about 50 μM. As subsaturated surfactant, its CMC decreased to around 15 μM as well as the saturated CDS surface tension decreased from 41 mN/m to 30 mN/m at CMC value of mixed surfactants. This is due to the preferential adsorption of NPE in the micelle. This CMC reduction occurred since the nonionic surfactant molecules shielded the repulsion between the negative head groups of CDS in the micelle decreasing the electrostatic repulsion that led monomers to aggregate easily to form micelles. The adsorption of NPE increased with increasing concentration until reaching a plateau. NPE serves as one of effective wetting agents in this system.

4.2.1.2 Effect of SDeS

Pure SDeS has CMC value at 30mM which increased to 50 mM when used as subsaturated surfactant of saturated CDS solution. The result of measurements didn't obey the common trend as observed from the other subsaturated surfactants in this system. As shown in Figure 4.3 and Figure 4.4, the surface tension decreased abruptly from 41mN/m to around 31 mN/m as well as the contact angle from 61° to 42° at 10 mM of subsaturated surfactant concentration then suddenly increased up to 50 mM until succeeding values were found constant.

This phenomenon is opposite to common physical insight because surface tension of the saturated surfactant solution has been known to decrease with increasing subsaturated surfactant concentration. The three types of adsorption are; (i) ion exchange, (ii) interaction of hydrophobic chain to oncoming surfactant ion, and (iii) overcoming static repulsion between the oncoming ions and similarly charged solid. In this case, the initial sudden drop in surface tension and contact angles was due to the adsorption of the low surface-energy species of SDeS molecules to saturated CDS by ion exchange of Na^+ and Ca^{2+}, yielding CDeS molecules from this reaction, which verified by HPLC at retention time of 3.1 minutes. From the abrupt reduction at 10mM, the increasing values of surface tension and contact angles until it reaches 50 mM was due to the increasing concentration of SDeS molecules, leading to form monolayer in liquid-vapor and solid-liquid interfaces as well as micelles in the solution. Considering Figure 4.3, as the SDeS concentration increases, more SDeS molecules were available to form monolayer in the interfaces until it forms micelles at 50 mM concentration. The CMC increase of SDeS was due to static repulsion of anionic head groups. The very low solubility of CDS solid provides low concentration of Ca^{2+} ions in saturated solution, yielding small amount of CDeS as a by-product, which was delimited by the mole ratio of the ion exchange reaction. The CDeS concentration was detected by HPLC and qualified by chromatogram peak area of around 1000-4500 μV-μS corresponding to increasing concentration.

SDeS has greater adsorption than NPE after sample solutions were equilibrated into the vial with 0.5 g of solid CDS. The plot of adsorption isotherm is remarkably different from NPE. This phenomenon was due to competition of two counter ions (Ca^{2+} has greater activity than Na ions) which led to ion exchange. Furthermore, as concentration of SDeS increases, more CDS solid were solubilized. Thus, SDeS solution effectively increases the solubility of CDS solid.

Results from HPLC conductivity measurement qualified the interaction of the system and quantified the mixture components of mixed solution as shown in Figure 4.8. Before equilibrium, the various concentrations of SDeS diluted by saturated CDS were measured for the calibration plot. The CDeS molecules were detected in each sample at retention time of 3.1 minutes . The retention time of SDeS was detected at 4.83 minutes. The amount of SDeS increased dramatically unlike with the CDeS. The peak of CDS was undetectable since the calcium ions were compensated with decyl sulfate. Similarly, SDS molecules as a by-product of ion exchange were undetectable and considered negligible taking into account the very low amount of dodecyl sulfate concentration in solution due to low solubility of CDS solid.

After equilibrium, HPLC revealed three components in the system (CDeS, SDeS, CDS), while increasing concentrations of SDeS, remarkable increase of the amount of CDS was detected with a retention time of 8.35 minutes. In this event, SDeS adsorbed and solubilized the solid CDS. In Figure 4.8, CDeS concentration was limited due to the mole ratio of reactants and products of this reaction. Thus it appears almost no difference of concentration from 10 to 120 mM with corresponding value of 1000 to 7500 µV-µS.

The chromatogram confirmed the retention time of the above three peaks. The mentioned peaks were calibrated by injecting individually SDeS, CDeS, and CDS in the same HPLC set-up conditions. In the case of CDS, as it is almost insoluble in water, combination of alcohol and water can be used to effectively dissolve CDS solid (Hornfeck et al., 1998). In this system, HPLC mobile phase (80% MeOH: 20% H_2O) was used as to dissolved 0.2 gram of CDS and resulted to retention time of 8.31 minutes.

It was found out that as the concentration of SDeS increases, more CDS solid was dissolved. The increasing concentration of SDeS in each sample diluted with saturated CDS solution at 20 mL equilibrated in a vial with 0.5 g of CDS precipitate resulted to noticeable increasing solubility of CDS solid surfactant. Solubilization is one of the most important properties of surfactants. It may be defined as the spontaneous dissolution of an insoluble substance by reversible interaction with the micelles of surfactants in a solvent to form a thermodynamically stable isotropic solution (Chem and Liu, 1987). In general, solubilization occurred only above the critical micelle concentration (CMC), above this value the amount of the substance solubilized increases with the concentration of surfactants. Theoretically, the factors of this phenomenon are the unequal length of the hydrophobic chains and the difference of counterion affinity. The presence of Ca^{2+} ions in the solution attributed to competitive effects which are the competition between monovalent and multivalent counter ions and the presence of short chain alkyl sulfate (SDeS) in saturated CDS solution led to solubilize the solid CDS. Moreover, Kraft temperature decreases with alkyl chain length of the surfactant molecule and it also depends on the head groups and counter ions (Rosen, 2004). Theoretically, solubility increases above Kraft temperature, thus, SDeS expected to decrease the Kraft temperature of CDS and led to solubilize more CDS solid as subsaturated SDeS concentration increases. Sodium decyl sulfate has Kraft temperature of 22°C (Tadros, 2005) while

CDS has 50°C as reported by Hornfeck et al. (1998). The synergism of this event requires further investigation.

4.2.1 The Critical Solid Surface Tension

The predictions of an interpolative nature of the subsaturated surfactants were also applied using the Zisman equation for precipitated CaC_{12} in our previous work. Zisman has shown that complete wetting (zero contact angle on the solid) can only occur when the liquid has been reduced to a critical value, $\gamma_{LV}{}^{c}$ characteristic of the substrate (Rosen, 2004). The Zisman plots (cosΘ versus γ_{LV}) of three different subsaturated surfactants (NaC_8, NPE (EO9), and SDeS) are shown in Figure 4.9. The respective critical surface tensions ($\gamma_{LV}{}^{c}$) on the solid CDS precipitate are 19, 15, and 10 mN/m for the system with the subsaturated surfactants. Hence in this work, the three binary mixture of solutions have not reduced the surface tension beyond their respective critical surface tension values, then the wetting solutions partially wet the surface of the CDS substrate. Critical surface tension values as shown are useful empirical values that characterize relative degrees of surface energy of CDS substrate but Zisman's empirical prediction fails for liquids that form hydrogen bonds or acid-base interactions with the substrate. These liquids would spread spontaneously on the substrate. . The higher critical surface tension value indicates better wetting by coating the solution onto the CDS substrate. Thus, in comparison of NPE and NaC_8, this method can also confirm that NaC_8 is better than NPE. With regards to SDeS, it is considerably effective as best wetting agent at certain 10 mM concentration but further investigation is necessary to characterize the unusual trend of surface tension and contact angle as concentration of subsaturated SDeS increases. However, Zisman emphasized that his method is only applicable to pure liquids, not solutions. Thus, the determination of critical surface tension in this paper has the risk of using Zisman equation beyond its original intention.

The graph plotted in Figure 4.10 should be linear with a slope equal to (γ_{SV}-γ_{SL}), the linear slope obtained from the plot of Cos θ as a function of 1/ γ_{LV} was based on Young's equation provided that (γ_{SV}) and (γ_{SL}) are constant as seen for the NaC_8 and NPE systems. The deviation of the slope in the plot from linearity indicates the amount of surfactant adsorbed on the solid/liquid interface changes with varying surfactant concentration because the values of γ_{SL} are not constant as it is observed for SDeS. Figure 4.8 implies the change of γ_{SL} with varying surfactant concentration.

Direct measuring of solid-liquid interfacial tension is presently unavailable (Starkweather et al., 2000). However, Young's equation can still be used to provide insight into interactions at solid-liquid interfaces by calculating γ_{SL} relative to γ_{SL}^{o} reference condition (pure saturated CDS). The difference of γ_{SL} from the reference condition gives spreading pressure, $\gamma_{LV}^{o} - \gamma_{LV}$ as illustrated in Figure 4.11 and Figure 4.12. The reduction in solid/liquid interfacial tension due to surfactant adsorption is quantified by the increase in spreading pressure with increasing surfactant adsorption. The value of spreading pressure was calculated using equation (4). Table 4.1 summarizes at the CMC of the spreading pressure increases in the order of NPE < NaC_8 < SDeS. Given the very low adsorption of NPE on the solid, the negative value of -1.4990 mN/m for $\gamma_{LV}^{o} - \gamma_{LV}$ at CMC was expected.