

CHAPTER IV

RESULTS AND DISCUSSION

In all experiments, CaC_{12} was used as saturated surfactant and NaDS was used as a second subsaturated surfactant. The temperature of all experiments was kept constant at 30°C .

4.1 Results

4.1.1 Kinetics of Wetting

The study of the contact angles with time for saturated CaC_{12} solution containing NaDS at concentrations of 0, 5, 10, and 100 mM is shown in Figure 4.1. It is found that the advancing contact angles have little time dependence for the mixed surfactant solutions of different NaDS concentrations.

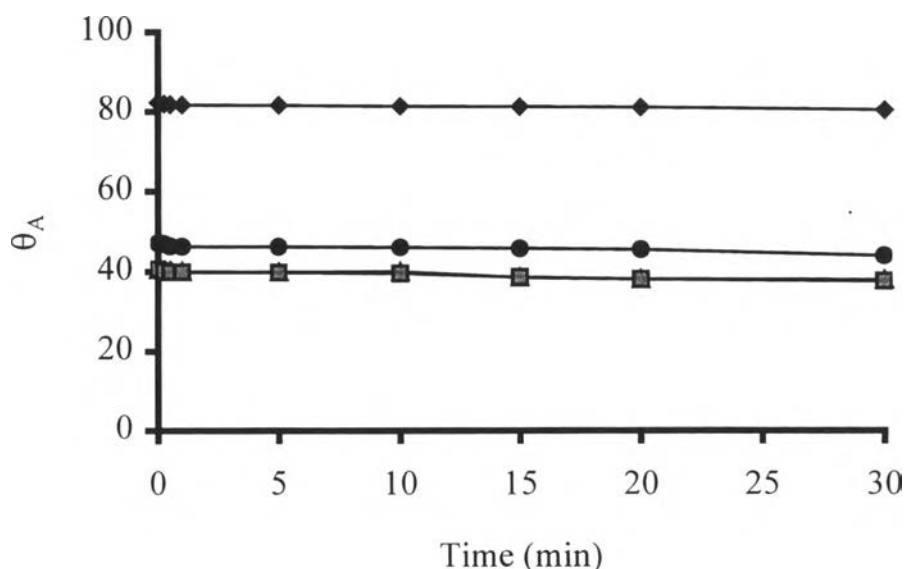


Figure 4.1 Advancing contact angle of saturated CaC_{12} solution containing NaDS as a function of time, (◆) 0 mM, (●) 5 mM, (▲) 10 mM, and (■) 100 mM at 30°C .

Contact angles reached their equilibrium within a first minute, therefore the contact angles were measured after 15 second for all experiments. The results confirmed that this method can be a good way to determine wettability because it is rapid and convenient.

4.1.2 The Contact Angle

The advancing contact angles of a saturated CaC_{12} solution containing subsaturated NaDS are shown in Figure 4.2. It was found that the contact angles decreased significantly with increasing NaDS concentration until reaching a plateau above a NaDS concentration of 6.5 mM..

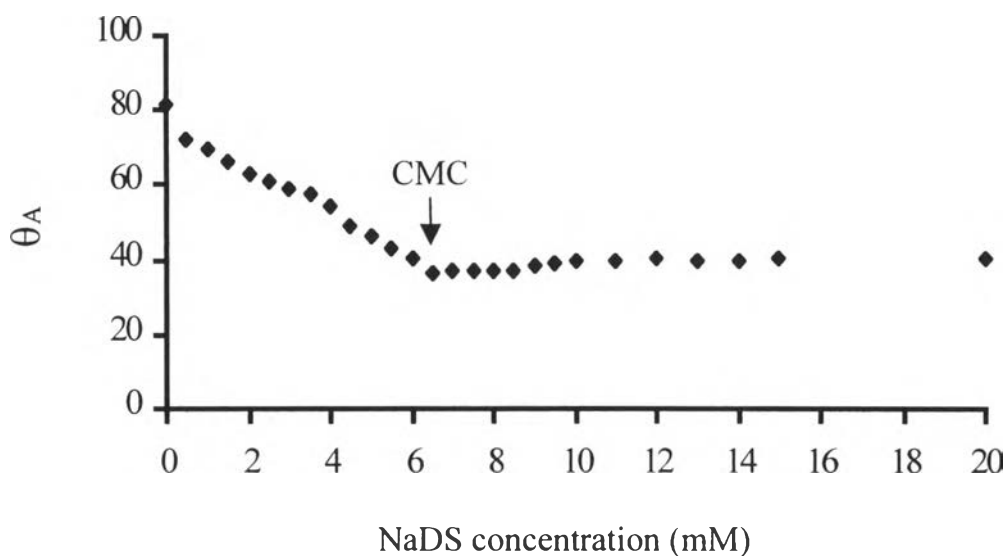


Figure 4.2 The advancing contact angles of saturated CaC_{12} solution with varying NaDS concentrations.

4.1.3 The Liquid/Vapor Surface Tension

The CMC of the surfactant solution containing saturated CaC_{12} and variable NaDS were determined by plotting the liquid/vapor surface tension (γ_{LV}) as a semilogarithmic function of NaDS concentration as shown

in Figure 4.3. The break point in the slope is the CMC. The CMC values were taken at 7.8 mM for the pure NaDS solution and 6.5 mM for the mixture of saturated CaC_{12} and NaDS at 30°C. The CMC value obtained for the pure NaDS solution at 30°C was corresponding to the values reported in literatures (Mukerjee and Mysel, 1970; Vora *et al.*, 1999). The CMC of CaC_{12} cannot be measured because the solubility of CaC_{12} is too low.

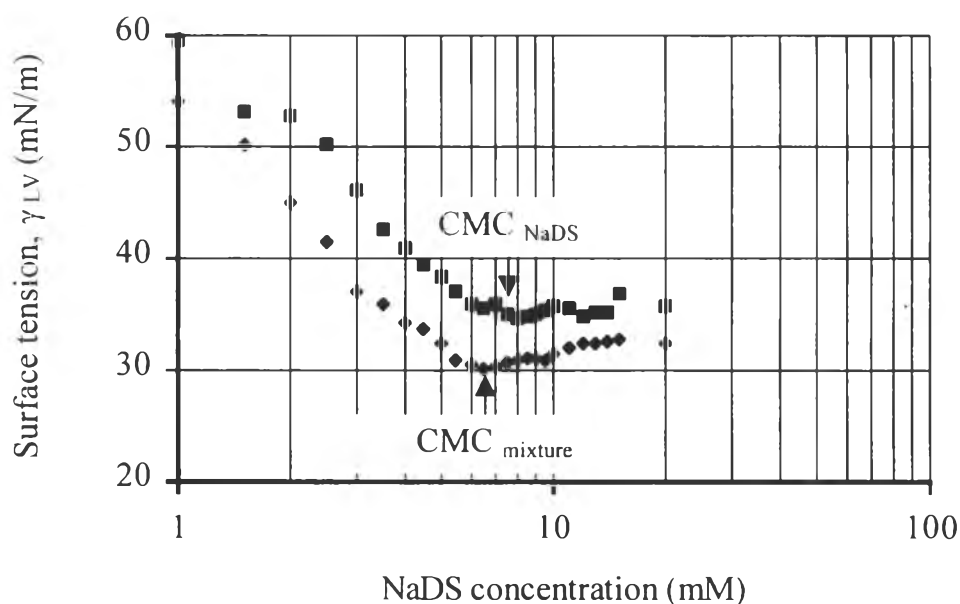


Figure 4.3 Liquid/vapor surface tension as a function of NaDS concentration, pure NaDS (■) and mixed solution of saturated CaC_{12} and NaDS (◆).

4.1.4 Adsorption of Subsaturated Surfactant onto Precipitated Surfactant

The adsorption isotherm of NaDS onto CaC_{12} precipitate is shown in Figure 4.4. At low concentration of surfactant, the adsorption increased with surfactant concentration is a less-than-proportional increase (for the typical plot of adsorption and equilibrium concentration, the slope on a log-log plot is unity). At concentration above the CMC, after a plateau

region the adsorption appeared to show sharply increase. The amount of NaDS adsorbing in the neighborhood of the CMC is $70 \mu\text{mole/g}$ or $20 \mu\text{ mole/m}^2$ or $8.3 \text{ \AA}^2/\text{molecule}$.

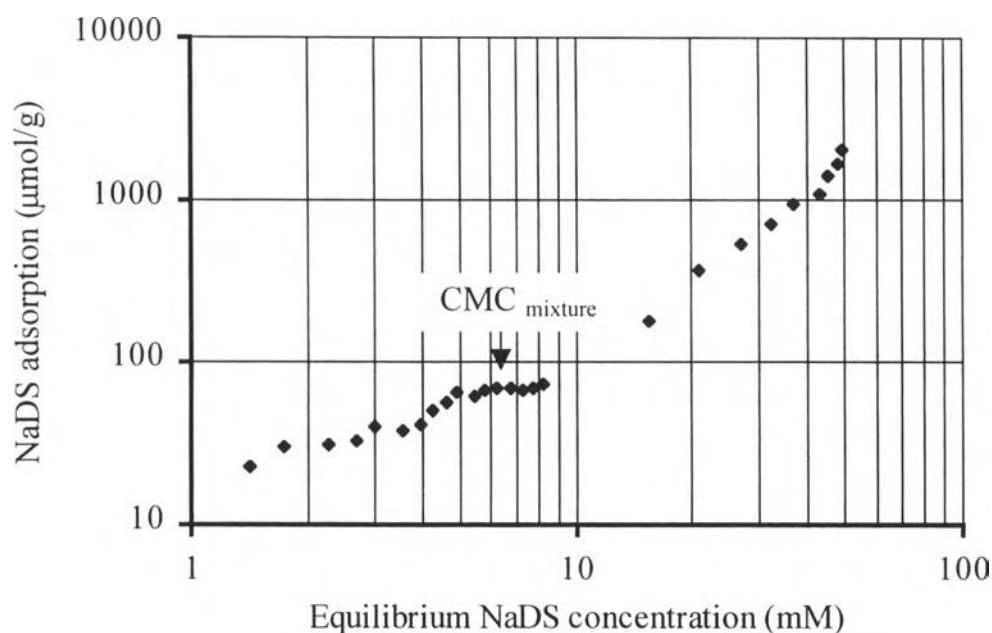


Figure 4.4 Adsorption of NaDS onto CaC_{12} precipitate.

4.1.5 Calculation of Solid/Liquid Surface Tension

From equation (1), if the γ_{SV} and γ_{SL} were constant, the plot of $\cos \theta$ vs. $1/\gamma_{\text{LV}}$ should be linear and slope = $(\gamma_{\text{SV}} - \gamma_{\text{SL}})$. The results in Figure 4.5 do not show this linear relationship, indicating that γ_{SL} varies with surfactant concentration since γ_{SV} can reasonably be assumed to be independent of the surfactant concentration since the dry solid has not been contacted by the liquid yet in an advancing contact angle. Even if the NaDS adsorbed as a complete bilayer on the flat surface of the precipitated surfactant, the reduction in NaDS concentration due to adsorption induced depletion is 22 % maximum and an initial concentration is assumed to be the same as equilibrium concentration. There is no simple way to measure or

calculate the absolute value of γ_{SL} . However, we can calculate γ_{SL} relative to γ_{SL}^0 at a reference state (γ_{SL}^0). This reference state is chosen as that corresponding to no NaDS being present. Subtracting eq. (1) for the standard state condition from eq. 1 for condition of interested yields.

$$\begin{aligned} \cos \theta - (\cos \theta)^0 &= (\gamma_{SV} - \gamma_{SL})^0 - (\gamma_{SV} - \gamma_{SL}) \\ &= (\gamma_{SL} - \gamma_{SL}^0) \end{aligned} \quad (2)$$

where the superscript 0 refers to the standard state when no NaDS is added into the solution, i.e. the CaC_{12} saturated solution. The γ_{SL} is the solid/liquid surface tension of mixed surfactant solution at a given NaDS concentration.

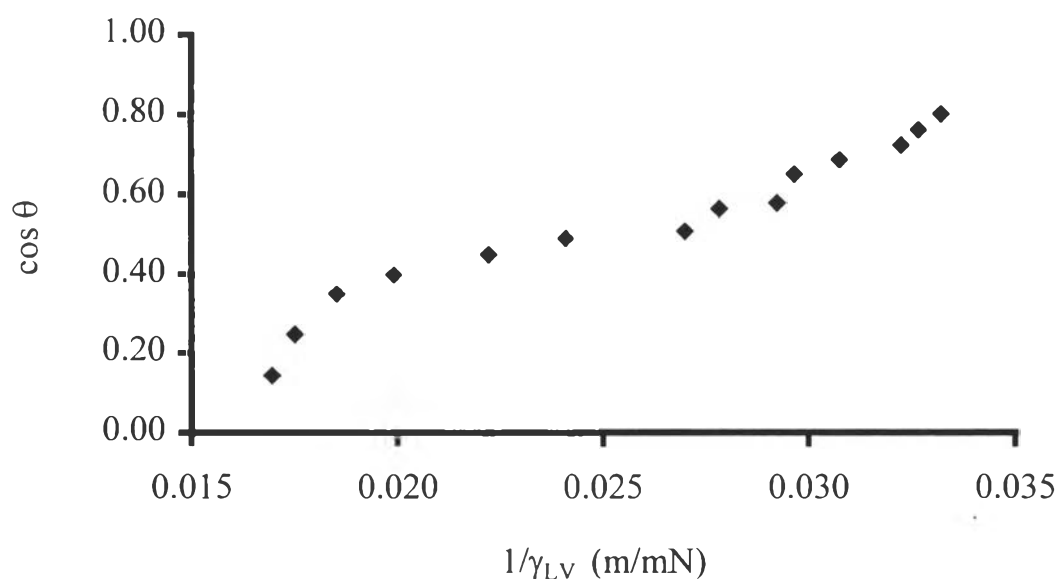


Figure 4.5 The contact angle as related to liquid/vapor surface tension (γ_{LV}) of mixed solution of saturated CaC_{12} and NaDS.

Using the adsorption data from Figure 4.4, the relative solid/liquid surface tension ($\gamma_{SL} - \gamma_{SL}^0$) can be correlated to surfactant adsorption density on the solid as well as surfactant concentration. The value of γ_{LV} can be obtained

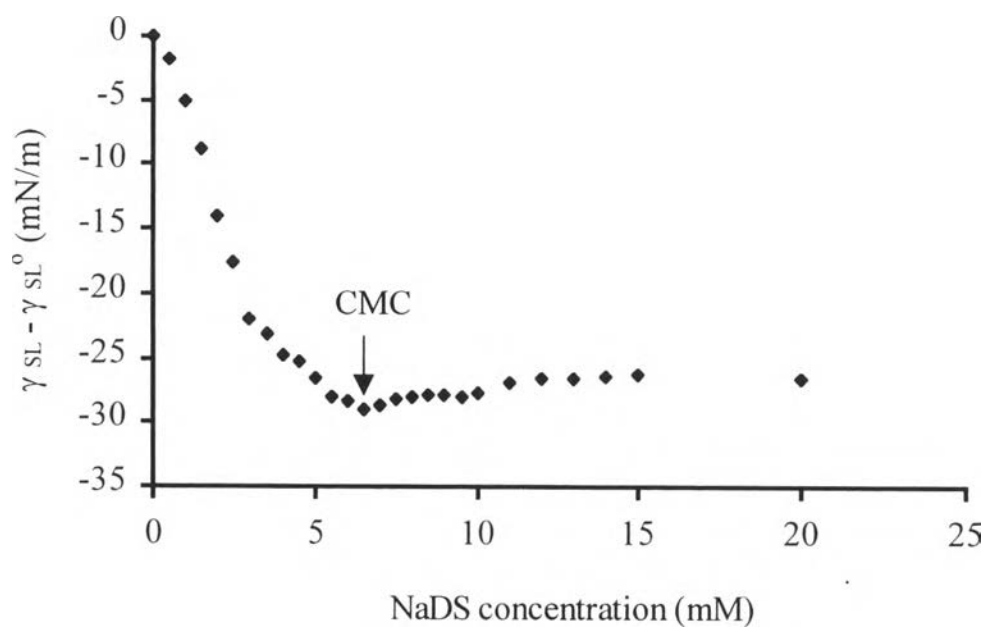


Figure 4.6 The reduction of solid/liquid surface tension of mixed solution of CaC_{12} and NaDS as a function of NaDS concentrations.

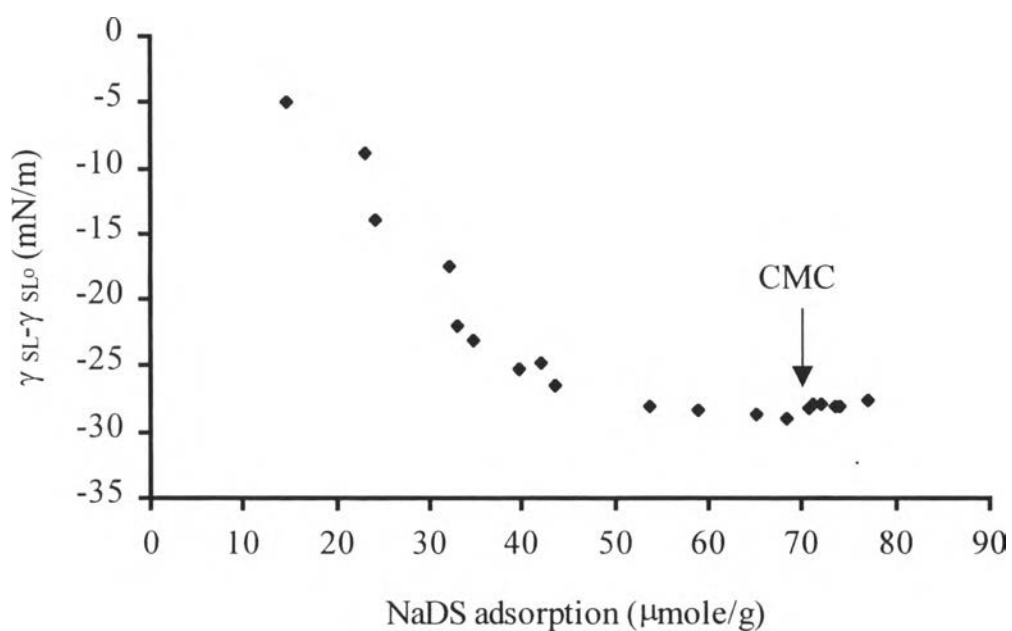


Figure 4.7 The reduction of solid/liquid surface tension of mixed solution of CaC_{12} and NaDS as a function of NaDS adsorption.

from the data on Figure 4.3. The reduction of solid/liquid surface tension ($\gamma_{SL} - \gamma_{SL}^0$) of saturated CaC_{12} containing NaDS as a function of NaDS concentrations and NaDS adsorption are shown in Figure 4.6 and Figure 4.7, respectively.

4.2 Discussion

Figure 4.2 shows that the subsaturated surfactant acts as an effective wetting agent on the precipitated CaC_{12} with more than 40° decrease in contact angle due to added NaDS, despite the fact that the solution was already saturated with CaC_{12} . In part I of this series (Dechabumphen *et al.*, 2000), it was shown that saturated solution of sodium alkyl sulfates, calcium alkyl sulfates, sodium salts of fatty acids, calcium salts of fatty acids, and free fatty acids very rarely had a contact angle which exceeded 90° with precipitate of that surfactant. This was interpreted to not support the concept that soaps act as defoamers/antifoams in hard water via the mechanism of dewetting of “hydrophobic” soap precipitates. This work provides even more evidence against the dewetting theory of foam regulation since in applications like detergency where soluble surfactants are present with the soap, it is an effective foam control agent. As shown for the calcium soap used here, a contact angle of $< 40^\circ$ in the presence of the subsaturated surfactant was observed, resulting in a fairly hydrophilic solid. Such a low contact angle implies that the NaDS is adsorbing in a head group out configuration (e.g., a bilayer a tail-down/head-out).

The adsorption isotherm shown in Figure 4.4 shows a slope of less than unity on a log/log plot, indicating a lack of cooperativity between adsorbed surfactant molecules. This indicates that adsorption increases gradually without a 2-D phase change to form admicelles as is often observed on highly hydrophilic surfaces like metal oxides (Scamehorn *et al.*, 1982). The

adsorption density of NaDS in the vicinity of CMC was used to calculate the area per adsorbed surfactant molecule of 8.3 \AA^2 . The area occupied per molecule for DS^- in the compact monolayer reported by Dahanayake *et al.* (1986) is 53 \AA^2 . The calculated result indicated that there were approximately six layers of DS^- adsorbing on the solid surface. Unless surfactant precipitation were simultaneously occurring, more than two adsorbing layers are not generally thought to occur in surfactant adsorption (Harwell and Scamehorn, 1993). Below the CMC, the NaDS did not exceed its K_{sp} ($K_{sp_{\text{NaDS}}} = 2.63 \times 10^{-4} \text{ M}^2$; $K_{sp_{\text{CaDS}}} = 2.65 \times 10^{-11} \text{ M}^3$) with either sodium or calcium. It is suspected that the surface of CaC_{12} precipitate was modified during the drying process at 40°C in an oven and possibly changed the surface area of the precipitate because the CaC_{12} precipitate has a low melting point (48°C). As the result, the surface area of precipitated CaC_{12} is reduced and the area/adsorbed molecule calculation inaccurate. As seen in Figure 4.4, after plateauing at the CMC, surfactant adsorption increases dramatically. As micelles are formed above the mixed system CMC, these mixed micelles are composed of both the dodecyl sulfate and dodecanoate anionic surfactants. As NaDS concentration increases above the CMC, a higher concentration of micelles are formed, causing some precipitated CaC_{12} to dissolve to allow the dodecanoate to micellize. While a stoichiometric ratio of calcium/surfactant dissolves less than a stoichiometric amount of counterions bind onto micelles (Rathman and Scamehorn, 1984), so some of the dissolved calcium ends up unassociated in solution. When this calcium concentration gets high enough, the calcium/dodecyl sulfate K_{sp} is exceeded and precipitation of the DS^- occurs as the calcium salt. As more NaDS is added, more CaC_{12} dissolves and more CaDS precipitates. Since the solution depletion method of measuring adsorption used here cannot differentiate adsorption from precipitation, the “apparent” adsorption reported in Figure 4.4 increases with NaDS concentration above the CMC. This combination of adsorption and

precipitation has been defined as “abstraction” by Somasundaran and Hanna (1982) and observed by Smith *et al.* (1996). Therefore, in Figure 4.7 where the relative solid/liquid interfacial tension is plotted against surfactant adsorption, the concentration range where CaDS precipitation is occurring was not included since we wish to correlate surface parameters to true adsorption. As shown in Figure 4.5, the contact angle decreases as γ_{LV} decreases due to an increasing NaDS concentration below the CMC. Both γ_{LV} (Figure 4.3) and θ_A (Figure 4.2) become nearly constant above the CMC. Normally, surfactant adsorption on a solid changes little above the CMC (Harwell and Scamehorn, 1993); the increase observed here (Figure 4.4) is believed to be due to NaDS precipitation. Therefore, further discussion will focus on the sub-CMC region.

Wetting enhancement by surfactants is commonly primarily attributed to liquid/vapor surface tension reduction. For example, the well-known Zisman equation (Zisman *et al.*, 1964) attributes contact angle changes of pure fluids on low-energy surfaces solely to liquid/vapor surface tension. From eq. (1), this implies that γ_{SL} is constant. Even though the Zisman equation was confined to pure liquids originally, it is now widely used (or misused) for surfactant solutions. As seen in Figure 4.6, γ_{SL} decreases by approximately 30 mN/m between no added NaDS and the CMC. Yet, γ_{LV} only decreases by about 30 mN/m (γ_{LV} of CaC_{12} = 59 mN/m) over this same range, all with saturated CaC_{12} . Increasing adsorption of the NaDS onto the CaC_{12} precipitate is the cause of the decrease in γ_{SL} as the NaDS concentration increases.