CHAPTER IV
RESULTS AND DISCUSSION

All of the surfactant solutions used in the experiment were saturated except sodium dodecylsulfate (SDS), sodium octanoate (NaC_8) and sodium dodecanoate (NaC_{12}). The reason for these latter exceptions is that their saturated solutions are a viscous solution. Therefore, they were prepared at near saturation, [SDS] = 1 M, [NaC_8] = 2 M, [NaC_{12}] = 0.1 M.

4.1 Solubility Product

The precipitated surfactant can be in equilibrium with different ratios of surfactant and counterion (calcium, sodium, or hydrogen) below the CMC as long as the solubility product is satisfied. If distilled water is equilibrated with a pure ionic surfactant crystal, the surfactant ion and the counterion (e.g.. cation for anionic surfactant) will be present in solution at their stoichiometric proportions. This surfactant/ counterman ratio could be different if. for example, hard water were equilibrated with anionic surfactant crystal at low ionic strength used in this study, activity coefficients were ignored in calculating and using K_{SP} values. These concentration-based K_{SP} values are shown in Table 2.

Table 2 Ksp values for calcium of dodecylsulfate, octanoic acid. and dodecanoic acid at 30 ^{o}C.

Surfactant	K_{SP} (experiment)	K_{SP}
$Ca(DS)_2$	$3.69 \times 10^{-12} M^3$	$6.0 \times 10^{-10} M^3$
CaC_8	$6.62 \times 10^{-8} M^3$	$1.5 \times 10^{-6} M^3$
CaC_{12}	$7.49 \times 10^{-14} M^3$	$1.0 \times 10^{-12} M^3$

* data from literature (Riviello, A. E., 1997)

4.2 Kinetics of Wetting

The advancing contact angles for sodium dodecyl sulfate (SDS). sodium octanoate (SO) and sodium dodecanoate are shown in Figure 4.1. It was found that the advancing contact angles for all three surfactant solutions did not change measurably with time. The relationship between receding contact angle and time for sodium octanaote is shown in Figure 4.1 The receding contact angle decreases substantially $(9\text{-}10^{o})$ with time, and reaches an equilibrium value after about 10 min. Remarkably, all data which are represented in Figure 4.1 were obtained by using video recorder. Therefore. these values would be deviated from taking photograph because of resolution on screen.
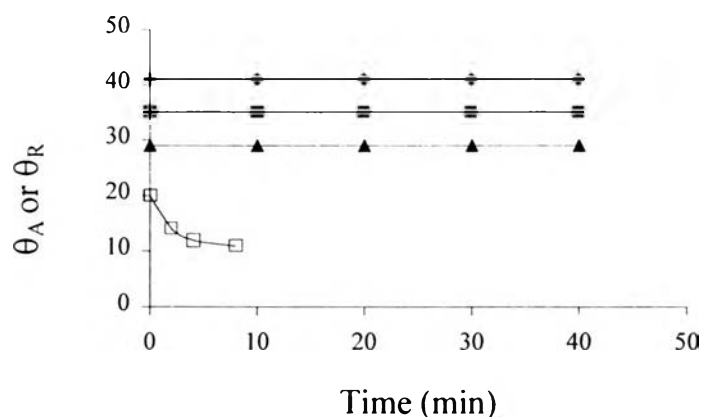

Figure 4.1. Advancing or receding contact angle as a function of time, ($\blacklozenge$) SDS, ($\blacksquare$, $\square$) NaC$_8$, ($\blacktriangle$) NaC$_{12}$. Solid points: advancing; open point: receding.

4.3 Effect of Liquid Volume

The value of θ_A and of θ_R were measured by taking photograph when volume of the drop of liquid was varied. The three-phase contact line of the liquid drop was made to advance or retreat by adding or withdrawing a small

volume of liquid. Figure 4.2 shows θ_A and θ_R for saturated HC_{10} solution on HC_{10} precipitate. It was found that the advancing contact angle remained unchanged ($\pm 3\text{-}5^{\circ}$) when the solution volume was increased. The receding contact angle decreased from 63° to 30° when the solution volume decreased from 90 μl. to 40 μl. Similar variation of θ_R with drop volume is reported in Table 3 whereas the values of θ_A are invariant with drop volume for all systems.
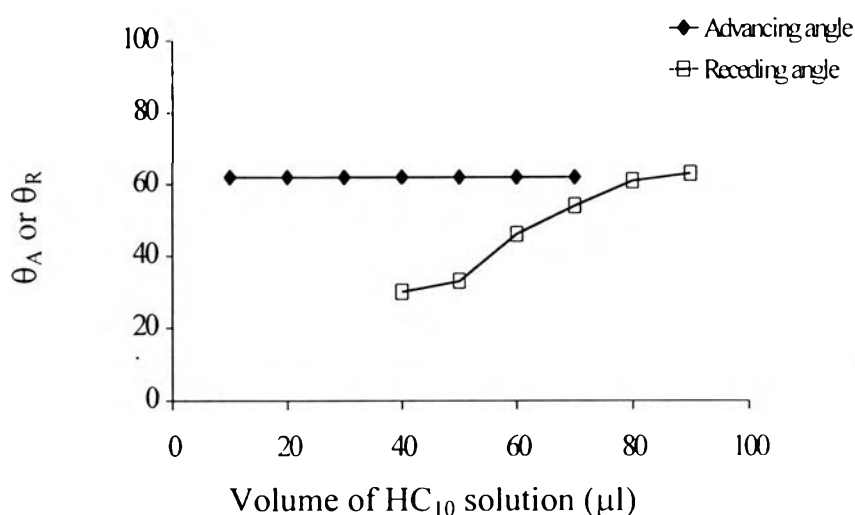

Figure 4.2. The advancing and receding angles of decanoic acid (C_{10}).

Table 3 Fresh surface contact angles of saturated surfactant solutions on precipitated surfactant as drop volume was varied from 60-80 μl.

Surfactant	Average θ_A (degree)	θ_R (degree)
HC_{10}	62	46-61
HC_{12}	82	59-77
HC_{14}	87	57-74
HC_{16}	87	55-63
HC_{18}	91	75-88
NaC_8	45	22-34
NaC_{10}	28	17-26
NaC_{12}	55	37-47

Table 3 (Cont'd) Fresh surface contact angles of saturated surfactant solutions on precipitated surfactant as drop volume was varied from 60-80 µl.

Surfactant	Average θ_A (degree)	θ_R (degree)
NaC_{14}	59	30-48
NaC_{16}	80	46-78
NaC_{18}	80	49-67
CaC_8	87	84-87
CaC_{10}	43	21-32
CaC_{12}	85	66-84
CaC_{14}	81	58-73
CaC_{16}	81	61-70
CaC_{18}	85	64-79
SDS	98	58-72
$Ca(DS)_2$	55	39-52

The solution contains a stoichiometric proportion of surfactant ion and counterion except SDS, NaC_8 and NaC_{12}.

4.4 Non-Stochiometric Ratio of Surfactant and Counterion

As discussed under K_{SP} determination, ignoring activity coefficients, when the monovalent surfactant ion concentration and the monovalent (e.g., Na^+) counterion concentration equal the K_{SP}, the solution is saturated and in equilibrium with the solid precipitate. For divalent counterions, the K_{SP} equal (surfactant ion concentration)^2 times counterion concentration. Table 4 shows advancing contact angles for $Ca(DS)_2$, CaC_8 and CaC_{12}. The data in this experiment were obtained by using video recorder. The results show little difference in θ_A as a function of counterion/ surfactant ratio.

Table 4 Advancing contact angles for non-stochiometric saturated solutions.

Surfactant	Average θ_A (degree)
$Ca(DS)_2$	
$[DS^-] = 2.35 \times 10^{-4}$ M, $[Ca^{2+}] = 1.15 \times 10^{-4}$ M	33
$[DS^-] = 4.82 \times 10^{-4}$ M, $[Ca^{2+}] = 2.37 \times 10^{-4}$ M	35
$[DS^-] = 5.15 \times 10^{-4}$ M, $[Ca^{2+}] = 4.19 \times 10^{-4}$ M	30
$[DS^-] = 9.29 \times 10^{-4}$ M, $[Ca^{2+}] = 2.11 \times 10^{-4}$ M	37
CaC_8	
$[C_8^-] = 0.023$ M, $[Ca^{2+}] = 1.94 \times 10^{-4}$ M	52
$[C_8^-] = 0.056$ M, $[Ca^{2+}] = 4.23 \times 10^{-4}$ M	53
$[C_8^-] = 0.081$ M, $[Ca^{2+}] = 6.68 \times 10^{-4}$ M	50
$[C_8^-] = 0.097$ M, $[Ca^{2+}] = 3.13 \times 10^{-4}$ M	52
CaC_{12}	
$[C_{12}^-] = 1.11 \times 10^{-4}$ M, $[Ca^{2+}] = 2.08 \times 10^{-6}$ M	55
$[C_{12}^-] = 1.23 \times 10^{-4}$ M, $[Ca^{2+}] = 1.76 \times 10^{-6}$ M	55
$[C_{12}^-] = 2.30 \times 10^{-4}$ M, $[Ca^{2+}] = 1.54 \times 10^{-6}$ M	54
$[C_{12}^-] = 2.88 \times 10^{-4}$ M, $[Ca^{2+}] = 2.00 \times 10^{-6}$ M	55

4.5   Effect of Cycling

The advancing and receding contact angles were repeatedly determined in a cyclic manner. Firstly, the advancing contact angle was measured on fresh precipitate and followed by a measure of receding contact angle as usual. However, then solution was injected back into the drop to cause it to advance over the same area again, liquid withdrawn from the drop as θ_R is measured and their cycle repeated as many times as needed. Figure 4.3 shows θ_A and θ_R of CaC_{12} under cycling. For the first cycle, θ_A is independent of drop volume as already discussed. Not only does the value of θ_A depend on

drop volume for the second and subsequent cycles, but these values of θ_A nearly correspond to those of θ_R at the same volume.
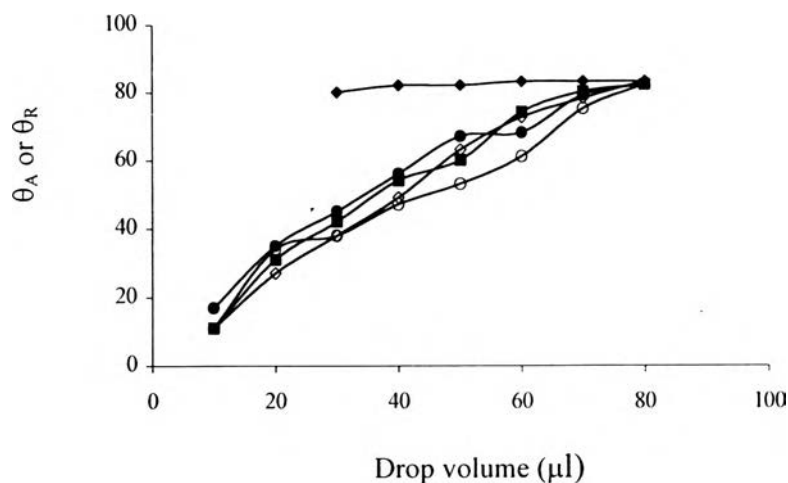

Figure 4.3 Effect of cycling on θ_A and θ_R for CaC_{12} $\diamond$–1st, $\bigcirc$–2nd, $\boxminus$–3rd, solid point: θ_A, open point: θ_R.

4.6   Effect of Surfactant Structure and Counterion Type

Figure 4.4 and Table 3 show the relationship between average fresh surface advancing contact angle and number of carbons in the hydrophobe (n) for fatty acid soaps, sodium and calcium soaps. The value of θ_A for all three surfactants increased mildly when the number of carbon increased from 10 to 18. The value of θ_A for calcium soaps was slightly lower than the fatty acid with that of sodium soaps being the lowest. The octanoic acid and sodium octanoate show anomalously high θ_A compare to the other hydrophobe lengths.
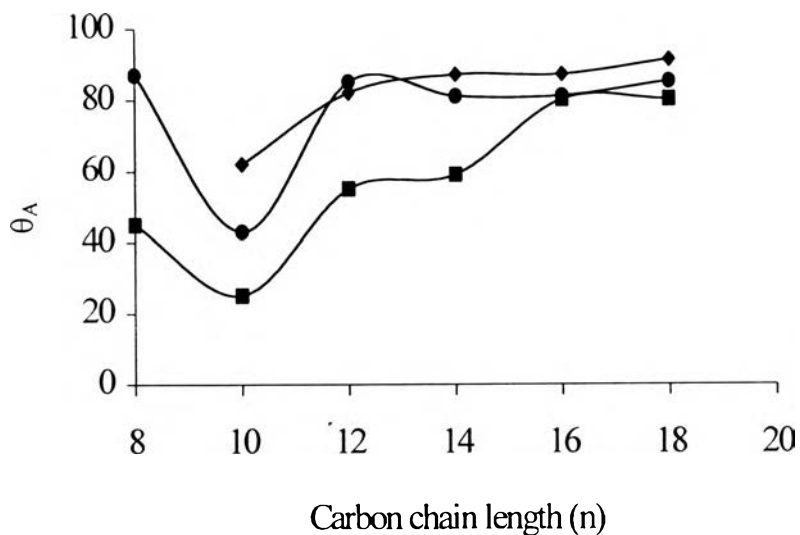
Figure 4.4. Fresh surface advancing contact angles of soaps, (♦) fatty acids, (■)sodium soap, (●) calcium soap as a function of carbon chain length.

Table 5 presents the average advancing contact angle of sodium and calcium salts of dodecylsulfate and dodecanoic acid, as well as dodecanoic acid in order to compare surfactants with the same hydrophobe.

Table 5. The average advancing contact angle of sodium and calcium salts of dodecylsulfate and sodium and calcium salts of dodecanoic acid.

Chemicals	Average θ_A (degree)
$Ca(DS)_2$	55
$Na(DS)$	98
CaC_{12}	85
NaC_{12}	55
HC_{12}	82

4.7 Dynamic Effect and Hysteresis

Advancing contact angles on fresh surfaces show no significant time dependence (on the scale of minutes) and give the most important information

on surface energetics. However, in application (e.g., detergency), the precipitated surfactant may be immerse in liquid prior to interaction at an air/ water interface (e.g., foam lamellae), so receding contact angles or advancing contact angles on already wet surfaces (as seen in cycling experiments here) may be of pragmatic importance.

The value of θ_R are less than θ_A (as is often observed in wetting), but θ_A in cycling experiments is also less than on fresh surfaces. Both effects can be explained by a residual more hydrophilic surface film left behind after the surfactant solution has contacted a surface. This may just be a thin film of water as shown schematically in Figure 4.5. An adsorbed surfactant bilayer (admicelle-ref) may be left behind as illustrated in Figure 4.6 with the heads in the upper layer importing hydrophilicity to the surface. Dissimilar surfactants have been shown to adsorb onto the surface of precipitated surfactants (ref), so it is quite reasonable that surfactants could adsorb on their own crystals. In any case, imaged θ_R can be over 30 degrees less than θ_A, while aged θ_R can approach θ_A. The dependence of θ_R on drop size would imply that the thin liquid film mechanism operating over a wider area of surface may explain θ_R hysteresis effects better than the admicellar explanation, but no definitive conclusions are possible from the available data. A thorough study of the dynamics of the wetting and dewetting phenomena would be needed to sort out these factors and is well beyond the scope of this work.

✕✕✕✕ More hydrophobic virgin surface

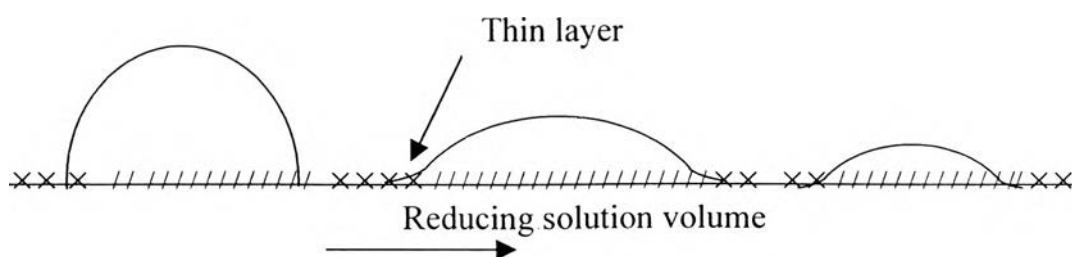⫲⫲⫲⫲ More hydrophilic surface with a thin film of water

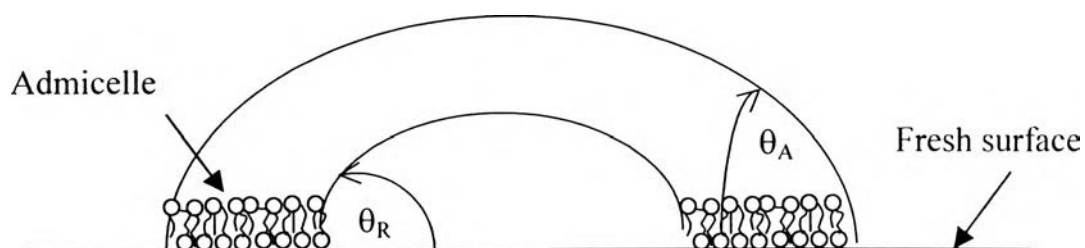Figure 4.5 The shape of droplet as withdrawn solution volume.

Figure 4.6 Admicelle formation causing contact angle hysteresis.

4.8 Surfactant Structure and Counterion Type

The surface of the precipitate is more hydrophobic as the length of the hydrophobic group is increased (Figure 4.4), ignoring the anomalous behavior of the octanoate. This implies that same portion of the hydrophobic region of the presumably bilayered surfactant crystal is exposed to the surface. Otherwise, the size of the surfactant hydrophobe should have little effect on θ_A. So, the greater antifoam behavior of the higher molecular weight soaps may be due to wetting effects as well as lower solubility.

As seen in Table 5, neither the surfactant type (sulfate or carboxylate) or the counterion type is determining, but the combination of the two is important. The calcium salt of the fatty acid and free fatty acid show high contact angle, but surprisingly the sodium salt of the alkylsulfate was the most hydrophobic solid studied. A well-crystallized salt which does not feel greasy (SDS) actually has a higher contact angle than soap scum (calcium fatty acid) which is greasy to the touch. We have been unable to find any literature measurements of contact angle on soap scum (or any precipitated surfactant), so the common attribution of soap scum as hydrophobic (high contact angle) commonly encountered seems to be presumptive based on its slippery feel. A greasy feel may be due to an ease of precipitate layers to slide past each other. This increased lubricity may be due to less structured hydrophobic regions

compared to an alkyl sulfate while the surface exposed to a liquid droplet may be ordered.

4.9   Surfactant/ Counterion Ratio

The ion activity products which equal the K_{SP} for a saturated solution also generally determine adsorption of a surfactant/ counterion in stoichiometric proportions at the vapor/ liquid interface (determining surface tension) or at the solid/ liquid interface. As a result, the surface tension at a vapor/ liquid interface and the plateau adsorption level, both above the CMC. for an ionic surfactant are relatively independent of concentration of an added simple salt, even though the surfactant monomer ion concentration is highly dependent on the added salt level. Therefore, it is not surprising that little dependence of θ_A on surfactant ion (or counterion) concentration is seen in Table 3. This indicated that the precipitating counterion concentration (e.g., water hardness) will have little effect on wettability as long as the K_{sp} is attained or exceeded.