

CHAPTER IV

RESULTS AND DISCUSSION

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/counterion ratio could be different if, for example, hard water were equilibrated with an anionic surfactant crystal. In this study, activity coefficients were ignored in calculating and using apparent or concentration-based K_{sp} values; therefore, in the range of high salt concentrations, the apparent K_{sp} values for the solutions in this study are not comparable to activity-based values from the literature. For divalent counterion calcium, the K_{sp} is defined as

$$K_{sp} = [Ca^{2+}][S^-]^2 \quad (4.1)$$

and for monovalent sodium:

$$K_{sp} = [Na^+][S^-] \quad (4.2)$$

for the solution in equilibrium with the precipitate where $[S^-]$ is surfactant anion concentration. These apparent concentration-based K_{sp} values are shown in Table 4.1.

Table 4.1 K_{sp} values for sodium and calcium salts of alkyl sulfates, calcium octanoate, and calcium dodecanoate at 30 °C

Surfactant	K_{sp} (concentration-based)
NaDS (sodium dodecyl sulfate)	$2.63 \times 10^{-4} \text{ M}^2$
CaDS (calcium dodecyl sulfate)	$2.65 \times 10^{-11} \text{ M}^3$
NaTS (sodium tetradecyl sulfate)	$2.59 \times 10^{-6} \text{ M}^2$
CaTS (calcium tetradecyl sulfate)	$6.3 \times 10^{-12} \text{ M}^3$
NaOS (sodium octadecyl sulfate)	$7.82 \times 10^{-8} \text{ M}^2$
CaOS (calcium octadecyl sulfate)	$1.09 \times 10^{-13} \text{ M}^3$
CaC ₈ (calcium octanoate)	$4.53 \times 10^{-7} \text{ M}^3$
CaC ₁₂ (calcium dodecanoate)	$1.43 \times 10^{-12} \text{ M}^3$

4.2 Effect of Surfactant Structure and Counterion Type

The values of the advancing contact angles (θ_A) are shown in Table 4.2. The contact angles of sodium and calcium salts of alkyl sulfates (C_{12} , C_{14} and C_{18}) are in the range of 46° to 96° and increase when the alkyl chain length increases, particularly when the alkyl chain length is above 14. The alkyl trimethylammonium bromides (C_{14} , C_{16} and C_{18}) have contact angles between 0° to 34° with little dependence on the alkyl chain length. The contact angles for C_{18} TAB are not very accurate since there was penetration from the solution into the precipitated surface which reduces the contact angle. Therefore, the contact angles of this surfactant shown in Table 4.2 are the approximate values provided in order to see the trend with varying alkyl chain lengths of these series of cationic surfactants. Figure 4.1 shows plots of advancing contact angles vs carbon chain lengths of the surfactant hydrophobe.

Table 4.2 The contact angles of the saturated surfactant solutions on precipitated surfactants at 20-70 μL drop volumes

Surfactant	Average θ_A (degree)
NaDS	56
NaTS	56
NaOS	72
CaDS	46
CaTS	47
CaOS	96
C14TAB (tetradecyl trimethyl ammonium bromide)	0-2
C16TAB (hexadecyl trimethyl ammonium bromide)	16
C18TAB (octadecyl trimethyl ammonium bromide)	34

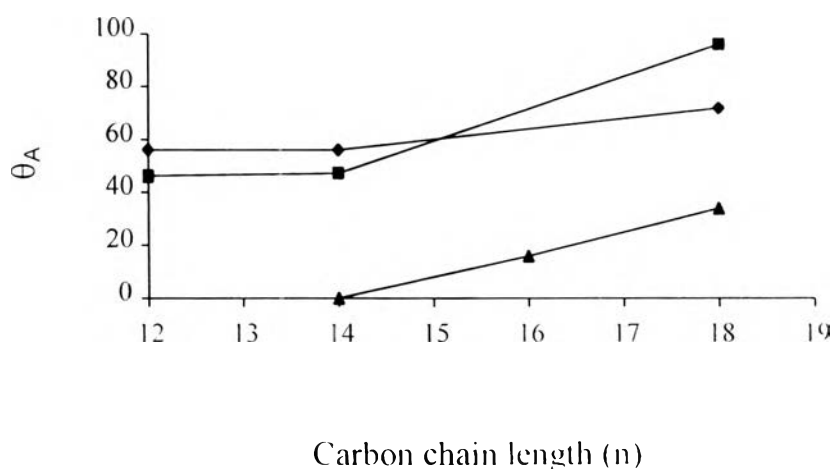


Figure 4.1 The advancing contact angle of (♦) sodium alkyl sulfate, (■) calcium alkyl sulfate, (▲) alkyl trimethylammonium bromide

The contact angles of the sodium and calcium salts of alkyl sulfates are high compared to those of alkyl trimethylammonium bromides with similar hydrophobic sizes. Cationic surfactants (e.g., quaternary ammonium head groups) generally have a higher CMC than anionic surfactants (e.g., sulfate head groups) with the same hydrophobic group size, even if the cationic and anionic surfactants are compared on the basis on similar critical micelle concentration values ($C_{18}TAB$ is roughly equivalent to a sodium alkyl sulfate with 15 carbons based on the CMC). This may be related to the larger hydrophilic group of the trimethylammonium group compared to the sulfate group.

4.3 Non-Stoichiometric Ratio of Surfactant and Counterion

From equations 4.1 and 4.2, the solubility product can be satisfied at different ratios of counterion/surfactant ion for a given counterion and surfactant. Table 4.3 shows advancing contact angles for sodium and calcium salts of alkyl sulfates, calcium octanoate and calcium dodecanoate. The results show that θ_A has little systematic dependence on surfactant/counterion ratio for all systems. However, for the most water soluble surfactant studied (NaDS), the contact angle was less reproducible (more data scatter) than less soluble surfactants. These results indicate 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 for these systems.

Table 4.3 Advancing contact angles for non-stoichiometric saturated solutions

Surfactant	Average θ_A (degree)
NaDS [DS ⁻] = 1.44×10^{-4} M, [Na ⁺] = 4.057 M	67

$[\text{DS}^-] = 1.54 \times 10^{-4} \text{ M}$. $[\text{Na}^+] = 1.509 \text{ M}$	54
$[\text{DS}^-] = 1.72 \times 10^{-4} \text{ M}$. $[\text{Na}^+] = 1.326 \text{ M}$	54
$[\text{DS}^-] = 1.85 \times 10^{-4} \text{ M}$. $[\text{Na}^+] = 2.543 \text{ M}$	56
$[\text{DS}^-] = 2.10 \times 10^{-4} \text{ M}$. $[\text{Na}^+] = 1.252 \text{ M}$	50
$[\text{DS}^-] = 2.39 \times 10^{-4} \text{ M}$. $[\text{Na}^+] = 2.839 \text{ M}$	58
CaDS	
$[\text{DS}^-] = 1.94 \times 10^{-4} \text{ M}$. $[\text{Ca}^{2+}] = 9.23 \times 10^{-4} \text{ M}$	45
$[\text{DS}^-] = 2.11 \times 10^{-4} \text{ M}$. $[\text{Ca}^{2+}] = 4.49 \times 10^{-4} \text{ M}$	49
$[\text{DS}^-] = 3.64 \times 10^{-4} \text{ M}$. $[\text{Ca}^{2+}] = 2.00 \times 10^{-4} \text{ M}$	46
$[\text{DS}^-] = 4.72 \times 10^{-4} \text{ M}$. $[\text{Ca}^{2+}] = 8.38 \times 10^{-4} \text{ M}$	43
$[\text{DS}^-] = 5.60 \times 10^{-4} \text{ M}$. $[\text{Ca}^{2+}] = 7.06 \times 10^{-4} \text{ M}$	47
$[\text{DS}^-] = 1.01 \times 10^{-3} \text{ M}$. $[\text{Ca}^{2+}] = 8.73 \times 10^{-4} \text{ M}$	48
NaTS	
$[\text{TS}^-] = 6.51 \times 10^{-4} \text{ M}$. $[\text{Na}^+] = 5.65 \times 10^{-3} \text{ M}$	58
$[\text{TS}^-] = 6.66 \times 10^{-4} \text{ M}$. $[\text{Na}^+] = 7.83 \times 10^{-3} \text{ M}$	56
$[\text{TS}^-] = 8.54 \times 10^{-4} \text{ M}$. $[\text{Na}^+] = 2.17 \times 10^{-3} \text{ M}$	54
$[\text{TS}^-] = 8.65 \times 10^{-4} \text{ M}$. $[\text{Na}^+] = 1.48 \times 10^{-3} \text{ M}$	54
$[\text{TS}^-] = 1.06 \times 10^{-3} \text{ M}$. $[\text{Na}^+] = 1.13 \times 10^{-3} \text{ M}$	67
$[\text{TS}^-] = 1.10 \times 10^{-3} \text{ M}$. $[\text{Na}^+] = 2.09 \times 10^{-3} \text{ M}$	50
CaTS	
$[\text{TS}^-] = 9.58 \times 10^{-5} \text{ M}$. $[\text{Ca}^{2+}] = 7.88 \times 10^{-4} \text{ M}$	44
$[\text{TS}^-] = 1.02 \times 10^{-4} \text{ M}$. $[\text{Ca}^{2+}] = 3.29 \times 10^{-4} \text{ M}$	48
$[\text{TS}^-] = 1.08 \times 10^{-4} \text{ M}$. $[\text{Ca}^{2+}] = 2.99 \times 10^{-4} \text{ M}$	53
$[\text{TS}^-] = 1.10 \times 10^{-4} \text{ M}$. $[\text{Ca}^{2+}] = 1.22 \times 10^{-3} \text{ M}$	45
$[\text{TS}^-] = 1.12 \times 10^{-4} \text{ M}$. $[\text{Ca}^{2+}] = 6.11 \times 10^{-4} \text{ M}$	44
$[\text{TS}^-] = 1.26 \times 10^{-4} \text{ M}$. $[\text{Ca}^{2+}] = 6.09 \times 10^{-4} \text{ M}$	51
NaOS	
$[\text{OS}^-] = 5.04 \times 10^{-5} \text{ M}$. $[\text{Na}^+] = 1.96 \times 10^{-3} \text{ M}$	95
$[\text{OS}^-] = 5.16 \times 10^{-5} \text{ M}$. $[\text{Na}^+] = 3.50 \times 10^{-3} \text{ M}$	96

$[\text{OS}^-] = 5.99 \times 10^{-5} \text{ M}$, $[\text{Na}^+] = 6.26 \times 10^{-4} \text{ M}$	94
$[\text{OS}^-] = 6.97 \times 10^{-5} \text{ M}$, $[\text{Na}^+] = 5.74 \times 10^{-4} \text{ M}$	94
$[\text{OS}^-] = 7.54 \times 10^{-5} \text{ M}$, $[\text{Na}^+] = 1.17 \times 10^{-3} \text{ M}$	95
$[\text{OS}^-] = 9.36 \times 10^{-5} \text{ M}$, $[\text{Na}^+] = 2.61 \times 10^{-4} \text{ M}$	99
CaOS	
$[\text{OS}^-] = 1.87 \times 10^{-5} \text{ M}$, $[\text{Ca}^{2+}] = 3.54 \times 10^{-4} \text{ M}$	72
$[\text{OS}^-] = 2.00 \times 10^{-5} \text{ M}$, $[\text{Ca}^{2+}] = 3.46 \times 10^{-4} \text{ M}$	69
$[\text{OS}^-] = 2.42 \times 10^{-5} \text{ M}$, $[\text{Ca}^{2+}] = 9.98 \times 10^{-5} \text{ M}$	74
$[\text{OS}^-] = 2.87 \times 10^{-5} \text{ M}$, $[\text{Ca}^{2+}] = 1.70 \times 10^{-4} \text{ M}$	72
$[\text{OS}^-] = 2.93 \times 10^{-5} \text{ M}$, $[\text{Ca}^{2+}] = 8.86 \times 10^{-5} \text{ M}$	71
$[\text{OS}^-] = 3.16 \times 10^{-5} \text{ M}$, $[\text{Ca}^{2+}] = 1.17 \times 10^{-4} \text{ M}$	75
CaC ₈	
$[\text{C}_8^-] = 0.0068 \text{ M}$, $[\text{Ca}^{2+}] = 2.74 \times 10^{-3} \text{ M}$	93
$[\text{C}_8^-] = 0.0091 \text{ M}$, $[\text{Ca}^{2+}] = 4.64 \times 10^{-3} \text{ M}$	92
$[\text{C}_8^-] = 0.0103 \text{ M}$, $[\text{Ca}^{2+}] = 5.31 \times 10^{-3} \text{ M}$	94
$[\text{C}_8^-] = 0.0132 \text{ M}$, $[\text{Ca}^{2+}] = 4.86 \times 10^{-3} \text{ M}$	92
CaC ₁₂	
$[\text{C}_{12}^-] = 4.49 \times 10^{-5} \text{ M}$, $[\text{Ca}^{2+}] = 5.74 \times 10^{-4} \text{ M}$	85
$[\text{C}_{12}^-] = 4.79 \times 10^{-5} \text{ M}$, $[\text{Ca}^{2+}] = 3.49 \times 10^{-4} \text{ M}$	83
$[\text{C}_{12}^-] = 5.81 \times 10^{-5} \text{ M}$, $[\text{Ca}^{2+}] = 3.24 \times 10^{-4} \text{ M}$	85
$[\text{C}_{12}^-] = 1.04 \times 10^{-4} \text{ M}$, $[\text{Ca}^{2+}] = 2.44 \times 10^{-4} \text{ M}$	82

4.4 Effect of pH of Fatty Acid Solutions

The contact angles for saturated fatty acid solutions (C₁₂, C₁₆), with pH from 4.0 to 10.0, onto its own precipitate surface are shown in Figure 4.2. The dodecanoic acid has a contact angle 77° to 81°, whereas the contact angle of hexadecanoic acid varies from 82° to 84°. According to Drelich *et al.* (1994), the extent of dissociation of carboxylic groups depends on the pH of

the aqueous phase, and it can be expected that significant dissociation of carboxylic groups occurs in the solution under the alkaline conditions. The pK_a of sodium octanoate is 5.3 (Rodriguez *et al.*, 1998) and should depend little on the hydrophobe chain length of the surfactant. Therefore, the range of pH values studied here (4-10) corresponds to almost completely protonated (neutral) surfactant to almost completely anionic surfactant. Since the solid precipitate must be almost electrically neutral, there is one hydrogen (or hydronium) ion per surfactant anion in the crystalline solid. However, as pH varies, the ratio of ionized surfactant/neutral (protonated) surfactant in solution changes. Therefore, the fact that the value of θ_A had almost no pH dependence for the fatty acid in Figure 4.2 indicates that the protonated and unprotonated surfactants have approximately the same surface activity at the solid/liquid and liquid/vapor interfaces.

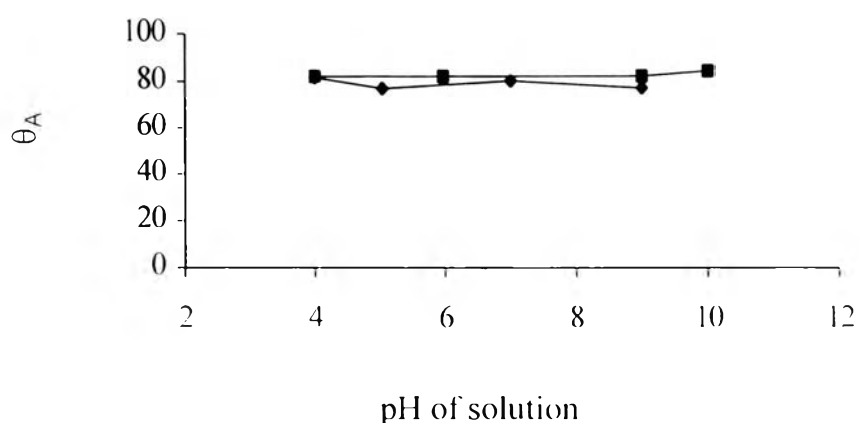


Figure 4.2 The advancing contact angle of (\blacklozenge) dodecanoic acid, (\blacksquare) hexadecanoic acid

4.5 Effect of Second Sub saturated Surfactant

The contact angles of saturated calcium dodecanoate solutions containing a second subsaturated surfactant (NaDS), are shown in Figure 4.3. Concentrations of 0.5, 1, 10, 50, 100 and 200 mM NaDS were used in these experiments. The results show that the contact angle decreases significantly with increasing NaDS concentration from 0 to 10 mM and remained constant after 10 mM. The NaDS is acting as a classical wetting agent reducing contact angles by presumably adsorbing onto the precipitated surfactant surface from solution and at the solution/air interface more efficiently than the precipitating surfactant alone.

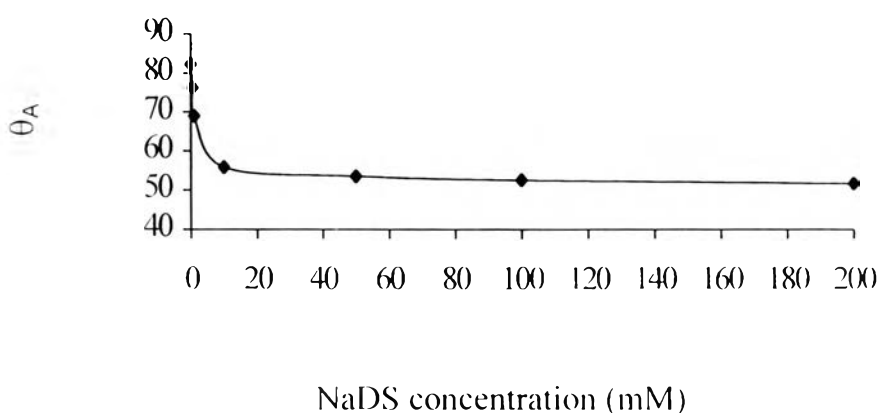


Figure 4.3 The advancing contact angle of saturated calcium dodecanoate solution with varying NaDS concentrations

Above the CMC, adsorption of the surfactant mixture at the solid/liquid and liquid/gas interfaces is approximately constant, so interfacial tension above the CMC is approximately constant. Therefore, it is not surprising that the value of θ_A becomes constant at higher NaDS concentrations. This

leveling off of surface tension above the CMC is often seen (Rosen, 1989). Therefore, it was postulated that for the mixed surfactant solution CMC is in the concentration range from 1 mM to 10 mM in Figure 4.3, above which the contact angle levels off. It is not possible to estimate the CMC because of the mixture of counterions present (calcium and sodium) with the mixture of surfactants (dodecanoate and dodecyl sulfate).

4.6 Feel/Appearance of Surfactants

The fatty acids and calcium salts of the fatty acids are greasy to the touch. The sodium salts of the fatty acids are greasy as well, but less than those of fatty acids and calcium salts of the fatty acids. Sodium and calcium salts of alkyl sulfates are slippery, but do not feel greasy. That is, the surface is slick and exhibits low friction when sliding a finger over it, but the layers of the crystals do not slide over each other easily, so it is not greasy.

Table 4.4 The average advancing contact angles of sodium and calcium salts of alkyl sulfates, fatty acids, sodium and calcium salts of fatty acids

Chemicals	Average θ_A (degree)		
	C ₁₂	C ₁₄	C ₁₈
Sodium alkyl sulfate	56	56	72
Calcium alkyl sulfate	46	47	96
Sodium soap	-	50	69
Calcium soap	82	83	92
Fatty acid	82	87	91

* data from literature (Luangpirom *et al.*, 2000)

The surface of the precipitate is more hydrophobic as the length of the hydrophobic group increases (Table 4.4). Possible explanations are reduced

adsorption of surfactant at the air/water and/or the solid/water interface due to decreased surfactant concentration in the water (due to lower solubility since solutions are saturated) as the hydrophobe size increases. Reduced surfactant adsorption could result in increased surface or interfacial tensions and the higher contact angle. 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 4.5, both the surfactant type (sulfate or carboxylate) and the counterion type have important effects on wetting. The highest contact angles were observed with the largest hydrophobic groups studied, consistent with large hydrophobes being used industrially in fatty acid antifoams. Greasiness is not necessarily related to hydrophobicity as illustrated by the high contact angle of the CaOS of 96°, a surfactant which is slippery, but not greasy. There have not had 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 greasy feel and appearance. 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 e.g., the sodium salt of an alkyl sulfate, while the surface exposed to a liquid droplet may be ordered.

Table 4.5 Feel/appearance of various surfactants

Surfactant	Feel/Appearance
Fatty acids	Greasy
Sodium salts of fatty acids	Greasy
Calcium salts of fatty acids	Greasy
Sodium salts of alkyl sulfates	Slippery
Calcium salts of alkyl sulfates	Slippery

Some of the soap scums here are hydrophobic, but the contact angle barely exceeds 90° . Also, other high molecular weight surfactants are also hydrophobic. Even if the dewetting mechanism of a soap's antifoam behavior is correct, then is there some special characteristic besides wetting which makes a fatty acid a particularly effective defoamer and antifoam? Future work will address this.

4.7 Kinetics of Wetting for Cycling Experiment

The advancing contact angles for HC_{16} with time for cycling experiments are shown in Figure 4.4. It was found that the advancing contact angles decrease slightly with time, but reach equilibrium after first minute for every cycle. The relationship between the receding contact angles and time for different drop volumes for HC_{16} is shown in Figure 4.5. The receding contact angles are constant when the drop volumes are $50 \mu\text{L} - 70 \mu\text{L}$, and the receding contact angles decrease substantially ($9-10^\circ$) with time for small drop volumes ($40 \mu\text{L}$).

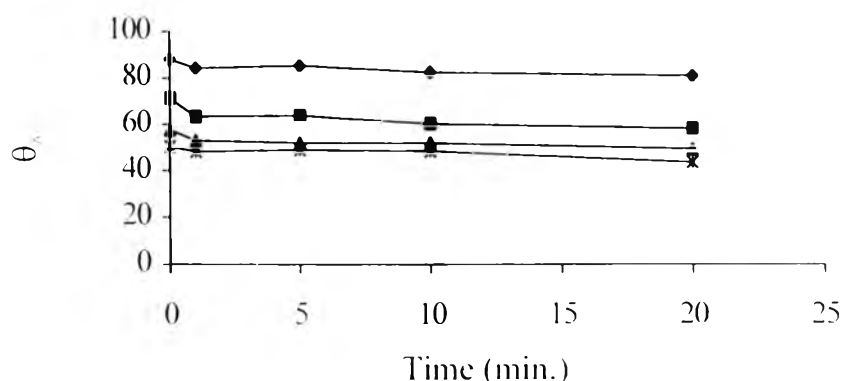


Figure 4.4 Advancing contact angle of hexadecanoic acid as a function of time for cyclic experiments. (\blacklozenge) 1st cycle, (\blacksquare) 2nd cycle, (\blacktriangle) 3rd cycle, ($*$) 4th cycle

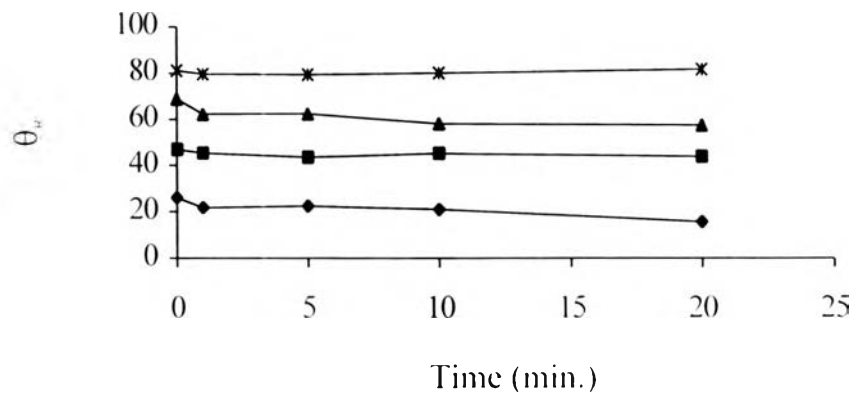


Figure 4.5 Receding contact angle of hexadecanoic acid as a function of time for different drop volumes. (♦) 40 μL . (■) 50 μL . (▲) 60 μL . (*) 70 μL .