CHAPTER IV
RESULTS AND DISCUSSION

4.1 Precipitation of Anionic and Cationic Surfactant Mixtures

4.1.1 Precipitation Phase Boundaries

Since mixing of anionic and cationic surfactants tends to form precipitate, the knowledge of precipitation phase boundary is necessary for surfactant selection in practical applications. The precipitation phase boundaries of SDS (single-chain anionic surfactant, C12) with three different cationic surfactants, which are DPCl (similar single-chain surfactant, C12), CTAB (longer single-chain surfactant, C16), and DTDACl (di C18-chain surfactant), in the absence of electrolyte and oil systems were investigated.

The precipitation phase boundaries of these three systems: SDS-DPCl, SDS-CTAB, and SDS-DTDACl are shown in Figure 4.1. These diagrams exhibit the similar results to the work of Stellner *et al.* (1988). At equilibrium, surfactant precipitation will occur if anionic surfactant activity (roughly proportional to its monomer concentration) and cationic surfactant activity (roughly proportional to its monomer concentration) equals to the solubility product of the anionic-cationic salt (Scamehoen and Harwell, 1993). For SDS-DPCl and SDS-CTAB, the straight-line with negative slope represents monomer-precipitate boundary of each system. At low concentration of both anionic and cationic surfactants, where no micelles are present, the cationic surfactant (DPCl or CTAB) concentration to form precipitate decreases as the SDS concentration increases. The monomer-precipitate boundary of both SDS-DPCl and SDS-CTAB shows the similar behavior while the monomer-precipitate boundary of SDS-DTDACl is different. The monomer-precipitate equilibrium of for SDS-DTDACl was occurred at almost constant DTDACl concentration. It is possible to explain that the structure of surfactant is the reason of this effect because both DPCl and CTAB are the single tail C12 and C16, whereas, the DTDACl is a double tails C18 cationic surfactant and insoluble in water.

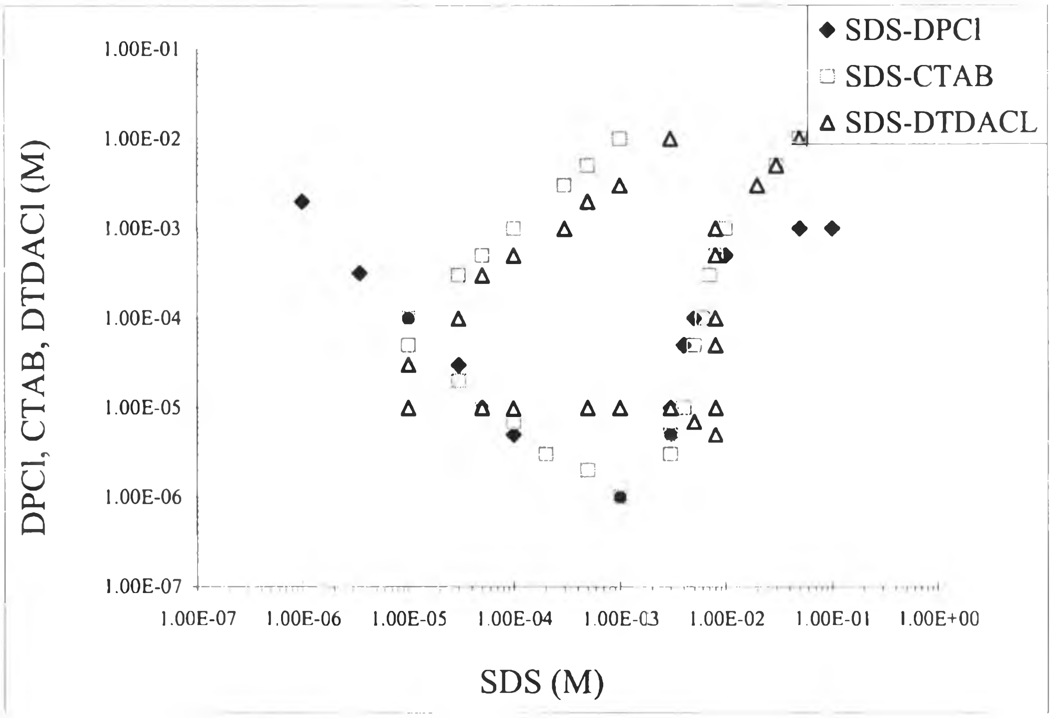

Figure 4.1 Precipitation Phase Boundaries of no added salt systems: SDS-DPCl, SDS-CTAB, and SDS- DTDACl.

The two sharp breaks along the monomer-precipitate equilibrium line correspond to the points where the cationic and anionic micelles begin to form in the solution. From these points, the precipitation boundary extends as two branches, cationic-rich and anionic-rich. These two break points can be implied as a mixed CMC in both anionic- and cationic-rich regions. Table 4.1 shows the comparison between the CMC of each pure surfactant and the approximate CMC of each mixed surfactants system. As expected, in the anionic-cationic surfactant system, the mixed CMC is lower than using single pure surfactant.

However, for SDS-DPCl, the cationic-rich branch cannot be determined in the precipitation boundary. At low SDS concentration, the precipitates still remained in the solution as DPCl concentration is increasing. This is probably due to the strong electrostatic attractive force between the head groups and highly compatible of the tail groups.

Table 4.1 Comparison between the CMC of each pure surfactant and the approximate CMC of each mixed surfactants system.

System	Condition	CMC of pure surfactant[a]		CMC of mixed system	
		SDS alone	Cationic surfactant alone	In anionic-rich	In cationic-rich
SDS-DPCl	no salt	8.2×10^{-3}	1.7×10^{-2}	3.0×10^{-3}	b
SDS-CTAB	no salt	8.2×10^{-3}	9.2×10^{-4}	3.0×10^{-3}	1.0×10^{-4}
SDS-DTDACl	no salt	8.2×10^{-3}	c	8.0×10^{-3}	1.0×10^{-5}
SDS-DPCl[d]	0.15 M NaCl	7.7×10^{-4}	4.0×10^{-3}	4.0×10^{-4}	2.8×10^{-3}

a--Data obtain from Rosen (1989)
b--Can not be defined
c--Not analyzed
d--Data obtain from Doan (2002)

The effect of hydrophobic group on the precipitation study is also considered. From Figure 4.1, exploiting the same tail length in a mixture of an anionic and a cationic surfactant, SDS-DPCl system, the precipitates occurred in wide range concentration. Whereas, using asymmetric tails, SDS-CTAB and SDS-DTDACl system, reduced the tendency to precipitate. This is consistent with the suggestion by Ranghavan *et al.* (2002) that is the precipitation can be avoided if the surfactants contain one long and one short alkyl tail. In addition, Patist *et al.* (1997) reported that, as the difference in chain lengths of mixed surfactants is greater, the spacing between the adjacent surfactant molecules is larger. However, the precipitation phase boundaries of all these systems exhibited the similar results in anionic-rich branches. Therefore, the addition of different cationic surfactant structure in anionic rich has very little effect. Adjusting the tail structure of surfactants is a useful way in controlling the phase behavior of mixed surfactants systems.

4.1.2 Effect of Electrolyte

To study the effect of electrolyte on the precipitation phase diagram, the precipitation phase diagrams of SDS-DPCl without NaCl and with 0.15 M NaCl are plotted together as shown in Figure 4.2. The data of the precipitation phase diagram of SDS-DPCl with 0.15 M NaCl was obtained from Doan (2002). As expected, the precipitation phase diagram of SDS-DPCl without NaCl is broader than the system with 0.15 M of NaCl. However, the solubility products or the straight line with the negative slope of these two systems are similar.

As observed in Figure 4.2, the cationic-rich mixed micelles begin to form at lower anionic surfactant concentration in the added electrolyte system, precipitation requires higher oppositely charged surfactant concentrations to occur (precipitation is inhibited). Since adding small amount of salt can avoid the precipitation and enhance the microemulsion formation, the microemulsion study is further investigated in the presence of 0.15 M NaCl.

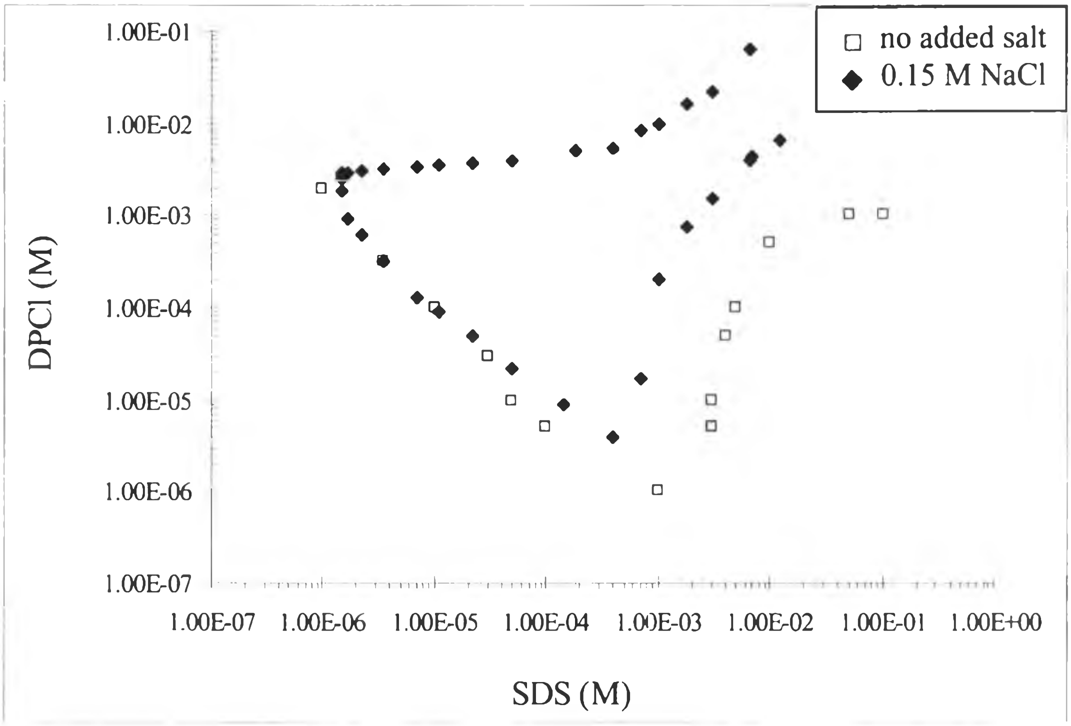

Figure 4.2 Comparison between precipitation phase diagrams of SDS-DPCL with no added salt and 0.15 M NaCl.

4.2 Effect of Cationic Surfactant Structures in Microemulsion Formation by Mixed Surfactants.

The main anionic surfactant used in this section was a single-tail anionic sodium dodecyl sulfate (SDS). In each system, the SDS was mixed with the other cationic surfactant. Four cationic surfactants with different tail structures were selected. They were dodecyl trimethyl ammonium bromide (DTAB), cetyltrimethyl ammonium bromide (CTAB), didodecyl dimethyl ammonium bromide (DDAB), and ditallow dimethyl ammonium chloride (DTDACl). The DTAB is a single tail C_{12} and CTAB is a longer single tail cationic surfactant (C_{16}). The DDAB is a twin tail C_{12} surfactant compared to the single tail of DTAB. The DTDACl is a twin tail C_{18} surfactant. The interfacial tension, solubilization, and phase transition were investigated as a function of the cationic surfactant mole fraction. The mole fraction of a cationic surfactant in a mixture, Y_1 is given by the concentration ratio of cationic surfactant, $C_1/(C_1+C_2)$, where the label 1 and 2 refer to the cationic and anionic surfactant, respectively. In this section, all systems were carried out at 0.05 M total surfactant concentration and 0.15 M NaCl, and were stabilized in equal volume of water and hexane at 25°C.

4.2.1 Microemulsion Phase Behavior of SDS-DTAB System

In this system, SDS and DTAB were selected because they have the same tail length, C12. As shown in Figure 4.3, the interfacial tension (IFT) of both anionic- and cationic-rich decreased as the oppositely charged surfactant is added into the system. This is probably due to the increasing in the electrostatic interaction between surfactants. In anionic-rich, as increased the mole fraction of cationic surfactant ratio (Y) equals to 0, 0.2, 0.3, and 0.4, the IFT values were 1.91, 1.72, 0.27, and 0.18 mN/m, respectively. In cationic-rich region, the IFT values from Y equals to 1.0, 0.9, 0.8, and 0.7 were 2.48, 1.92, 0.84, and 0.38 mN/m, respectively. In this case, the oil phase is the light phase or upper phase and the aqueous solution is the heavy phase or lower phase. The precipitates occurred particularly in the heavy phase and near the equimolar ratio (Y= 0.5 and 0.6) in SDS-DTAB system. If the precipitate or turbid solution forms in the heavy phase of samples, the IFT could not be measured by the spinning drop method. The lowest IFT of mixed SDS-DTAB system is 0.18 mN/m, whereas the IFT values of pure SDS and DTAB are 1.9 and 4.2 mN/m, respectively. As a result, the lowest IFT in surfactant mixture is much lower than the IFT values of both single surfactants. Since low liquid-liquid interfacial tension is important in promoting emulsification, in the removal of oil and soil in detergents, in enhanced oil recovery (Rosen, 1993), and in enhanced subsurface remediation (Sabatini *et al.*, 2000), reduction of interfacial tension is one of the most commonly measured properties of surfactants in solution. For example, in the subsurface remediation case, the oil- water interfacial tension is what traps oil in porous media. By greatly reducing the interfacial tension, the trapped oil phase can be mobilized.

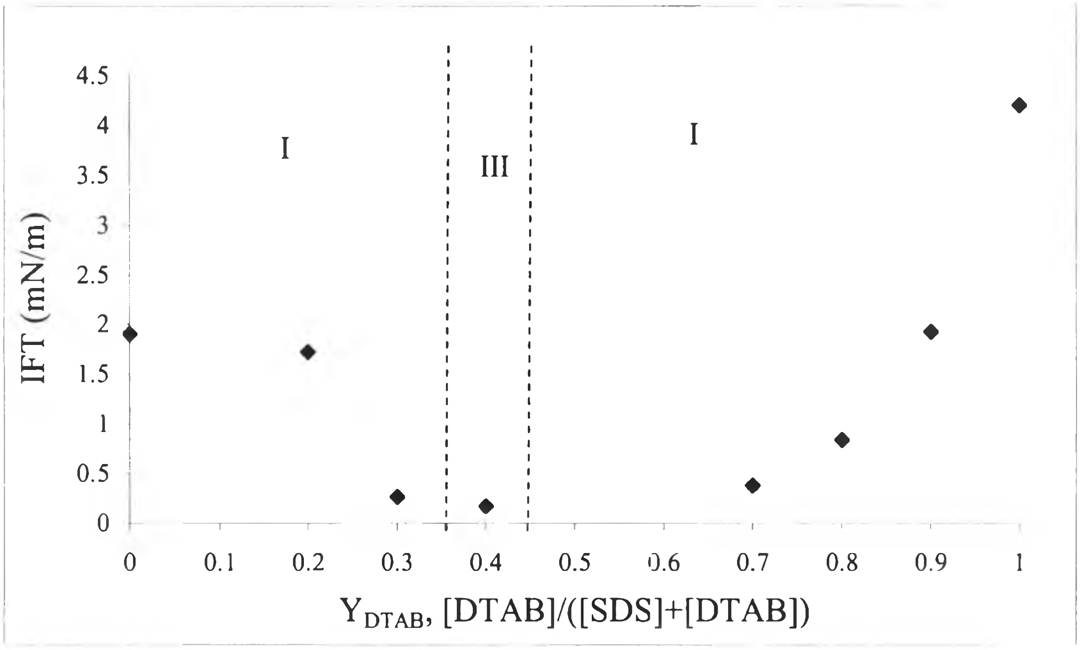

Figure 4.3 The interfacial tension between excess phase and microemulsion phase of SDS-DTAB system as a function of cationic surfactant fraction.

The transition of system was from Type I to Type III to Type I along this scan and the liquid crystals appeared during the transition from Type III to Type I. Surprisingly, the middle phase microemulsion can form at Y value of 0.4. Whereas, in the aqueous solution of SDS-DTAB mixture, the solid precipitates and/or turbid solution present at the surfactant concentration approach to the equimolar mixture because of the strong attractive interactions between the oppositely charge head groups and also the hydrophobic tails. This shows that the oil molecules can partition into the mixture of anionic-cationic surfactant, and then the middle phase microemulsion is formed instead of the solid structures. The solubilization parameters of oil and water at Y = 0.4 were 11.09 and 6.43 ml/g, respectively.

Doan (2002) determined the microemulsion phase behavior of SDS-DPCl (dodecyl pyridinium chloride) at total surfactant concentration 0.02 M. This mixture also composes of the same tail length, C12 anionic-cationic surfactant. However, the phase transition changes from Type I to Type II to Type I across the cationic surfactant fraction scan and the liquid crystal phases appeared rather than the middle phase microemulsion. Although, the SDS-DPCl mixture has the same tails as the SDS-DTAB mixture, the SDS-DPCl did not show the same phase transition as SDS-DTAB mixture. This is probably due to the effects of different cationic surfactant head groups and the total surfactant concentration.

4.2.2 Microemulsion Phase Behavior of SDS-CTAB System

In the first hypothesis, the formulation of different tail anionic-cationic surfactants is expected that it could enhance the middle phase microemulsion formation without alcohol addition. Therefore, the cetyltrimethyl ammonium bromide or CTAB was chosen as a cationic surfactant because its tail length is longer than SDS (single-tail C16 for CTAB versus single-tail C12 for SDS). As shown in Figure 4.4, the middle phase microemulsions were shown at low fraction of cationic surfactant, Y = 0.2 and 0.3. Figure 4.5 shows the solubilization parameters of oil were 5.43 and 13.18 ml/g at Y= 0.2 and 0.3, respectively. And at those cationic surfactant ratios, the water solubilization parameters were 25.66 and 15.19 ml/g. Obviously, the solubilization parameters of oil and water were approximately equal at Y = 0.3. It could be implied that the optimum concentration nearly occurs at this cationic surfactant ratio. Further increased cationic surfactant ratio from Y = 0.4 to 0.6, the precipitate and/or milky solution occurred in the heavy phase of this system. In cationic-rich region, the IFT values decreased as the mole fraction of CTAB decreased from Y= 1.0 to 0.7. The IFT values at Y 1.0, 0.9, 0.8, and 0.7 were 2.48, 1.15, 0.99, and 0.78 mN/m, respectively. Figure 4.5 shows the transition from Type I to Type III to Type I for increasing mole fraction of CTAB (Y). The system transform from Type III to Type I in this scan, structured liquid crystal phases appeared rather than Type II. As known that the microemulsion system changes from a Type I to Type III to Type II microemulsion along the salinity increases. In the same way, for an anionic-cationic surfactant system, one surfactant acts as a counter ion for the other surfactant. In other word, as the cationic surfactant concentration increases in the anionic surfactant dominated system, more cationic surfactants adsorb between the anionic head groups. This phenomenon occurs by reducing the electrostatic repulsion between the surfactant head groups, as sodium reduces charge repulsion when sodium chloride is added to obtain the phase transition. Therefore, the system is expected to change from a Type I to Type III to Type II microemulsion as the cationic molar fraction increases (as Y increases from 0).

Conversely, for a cationic-rich surfactant mixture, the anionic surfactant acts as the counter ion, and as the anionic surfactant fraction increases the system is again expected to transition from a Type I to Type III to Type II system.

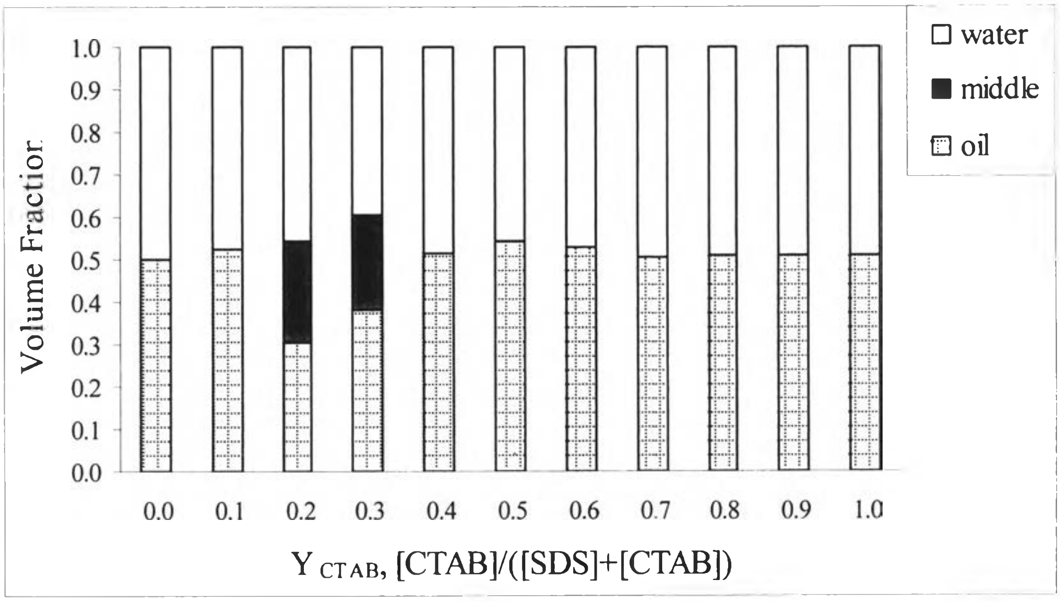

Figure 4.4 Volume fractions of SDS-CTAB system as a function of cationic surfactant fraction.

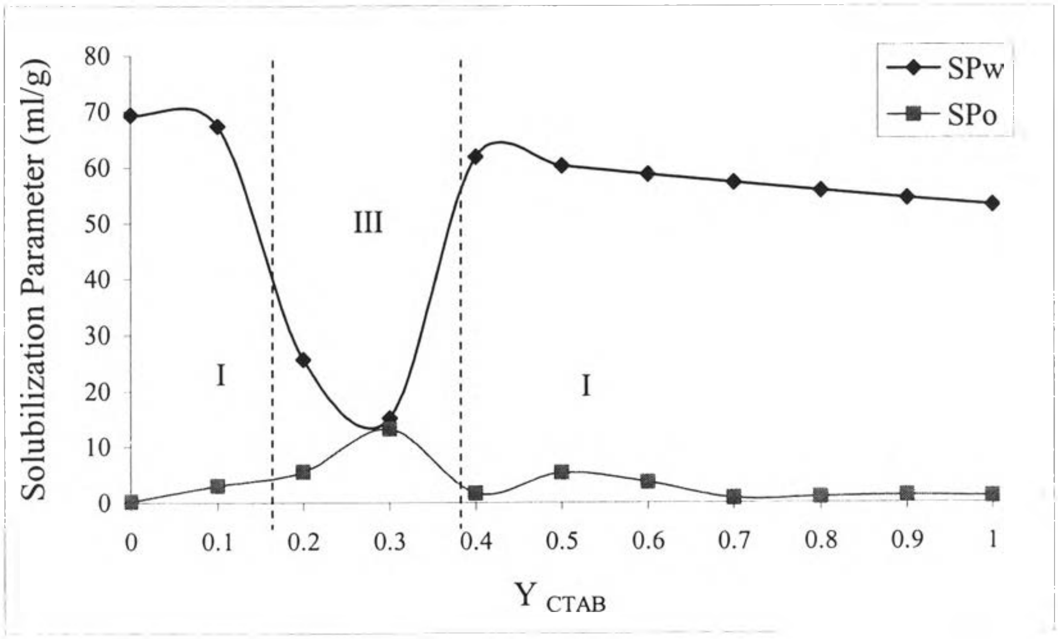

Figure 4.5 Oil and water solubilization parameters of SDS-CTAB system as a function of cationic surfactant fraction.

In the mixtures of SDS with DTAB or CTAB, these are the mixture of single- tail anionic and single-tail cationic surfactant, the IFT values decrease when added the oppositely charge surfactants into the system. In the other word, the IFT decreases in anionic-rich as upon addition DTAB or CTAB from Y = 0 up to near Y=0.5, and as the SDS fraction increases in cationic-rich, the IFT also decreases. Moreover, the precipitates or liquid crystals still appeared at the concentration close to the equimolar mixture in both systems, SDS-DTAB and SDS-CTAB. However, the formulating of both SDS-DTAB and SDS-CTAB system exhibited the alcohol-free middle phase microemulsion by adding small amount of cationic surfactant into anionic-rich phase. In particular, a middle phase microemulsion in SDS-CTAB system was obtained in the wider range of cationic surfactant fraction due to increasing tail length of cationic surfactant from C12 to C16. The phase transitions of both SDS-DTAB and SDS-CTAB along the cationic surfactant fraction scan are changed from Type I to Type III to Type I. As a result, the mixture of SDS-DTAB and SDS-CTAB show a greater synergism than using SDS, DTAB, or CTAB alone.

4.2.3 Microemulsion Phase Behavior of SDS-DDAB System

The asymmetric tails or branched chains in anionic-cationic surfactant mixture might also eliminate the need of alcohol addition. Since the surfactant heads and tails interactions could be reduced in the mixture of anionic and cationic surfactants with branching. The oil molecules might be partition between surfactants tails and the middle phase microemulsion could be formed easily. Thus, the didodecyldimethyl ammonium bromide or DDAB was selected because it is a double C12-chain cationic surfactant. Figure 4.6 shows the IFT values of SDS-DDAB system. In anionic-rich region, the IFT results of SDS-DDAB system show the same trend as using both single-tail anionic and cationic surfactant. The IFT decreased as increasing the ratio of cationic surfactant to anionic surfactant. The IFT values at Y= 0, 0.1, and 0.2 were 1.91, 0.51, and 0.4, respectively. Whereas, in cationic-rich region, the IFT results of SDS-DDAB system show the opposite trend when compared with the SDS-DTAB and SDS-CTAB system. The IFT decreases in cationic surfactant rich region. The IFT values at Y= 0.6, 0.7, 0.8, 0.9, and 1.0 were

3.99, 3.18, 1.72, 0.84, and 0.36 mN/m, respectively. The precipitate and/or turbid solution formed in the heavy phase and the gel also occurred in the light phase of this system at Y = 0.3-0.5. Consequently, the IFT cannot be defined at these cationic surfactant ratios.

As many other double-tail cationic surfactants, DDAB is highly insoluble in water because it has very high hydrophobic group. Therefore, a Type II microemulsion was formed when using DDAB alone. A Winsor Type I microemulsion performed at other cationic surfactant ratios. The middle phase microemulsion did not occur in this system. Moreover, the precipitates and gel were not formed in a wide range of concentration. This is probably due to the solubilization of DDAB and SDS. Since the DDAB is water-insoluble and the SDS is water-soluble, the electrostatic interactions between oppositely charged head groups might not be observed. As a result, when each surfactant in mixed anionic-cationic surfactant system is not preferred to solubilize in the same phase, the synergism behavior of mixed anionic-cationic surfactant could not be observed even it is a mixture of anionic and branched cationic surfactant.

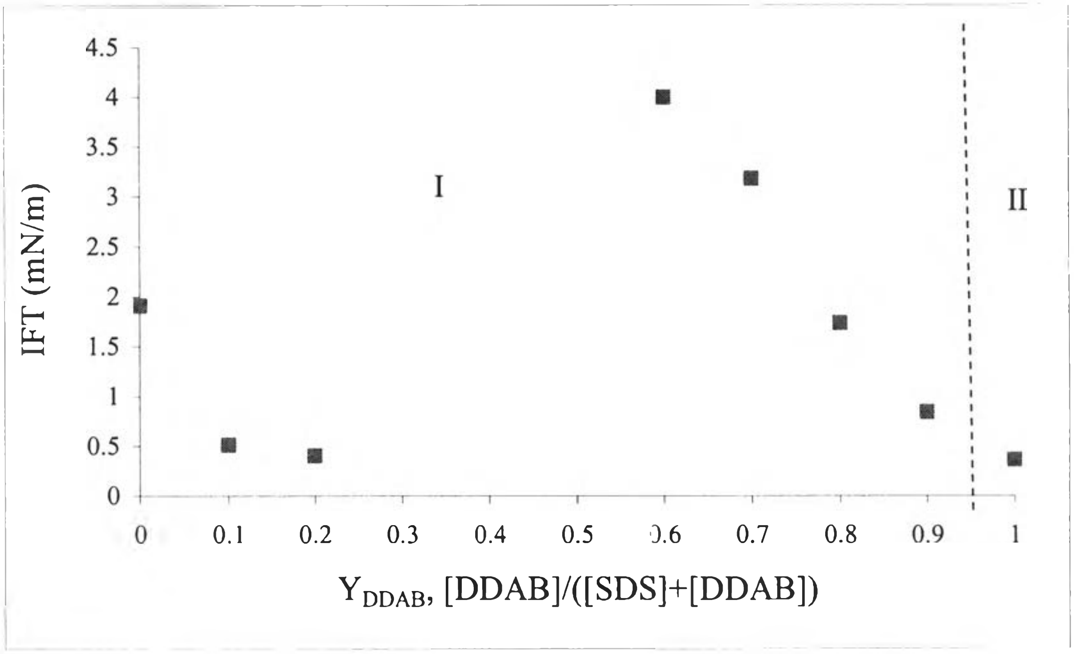

Figure 4.6 The interfacial tension between excess phase and microemulsion phase of SDS-DDAB system as a function of cationic surfactant fraction.

4.2.4 Microemulsion Phase Behavior of SDS- DTDACl System

Since mixing a double C12- chain cationic surfactant (DDAB) with a single tail C12 anionic surfactant (SDS) did not achieve the alcohol-free anionic-cationic surfactant middle phase microemulsion formation, the ditallow dimethyl ammonium chloride (DTDACl), which has twin-C18 tails, was used instead of DDAB because its longer branched tails might allow middle phase microemulsion formation. By visual observation, the precipitates occurred at low concentration of DTDACl (Y=0 to 0.3) and the middle phase microemulsions were formed at Y = 0.9 and 1.0--high DTDACl concentration and DTDACl alone. The water solubilization parameters at those fraction, were 1.72 and 1.82 ml/g, respectively. And the solubilization parameters of oil were 11.17 and 9.62 ml/g, respectively. For the IFT measurement, the IFT at Y = 0.4 and 0.5 cannot be detected by the spinning drop tensiometer because the oil droplet did not come out even though used very high number of revolutions was used. It can be implied that the IFT between oil and aqueous solution is very high. As DTDACl ratio increases in cationic-rich, the IFT values decrease as shown in Figure 4.7. The IFT values at Y=0.6, 0.7, 0.8, 0.9 and 1.0 were 1.04, 0.71, 0.42 0.39, and 0.35 mN/m, respectively.

Using a double-chain cationic surfactant with a single-tail anionic surfactant in SDS-DDAB and SDS-DTDACl system, give the similar results of interfacial tension in cationic-rich region. Increasing the double-alkyl chains length of cationic surfactant can enhance the ability to form the middle phase microemulsion. However, the better performance is shown at high cationic surfactant ratio. Thus, the addition of an anionic surfactant into the solution of double-chain cationic surfactant did not exhibit the synergism of anionic-cationic surfactant mixture. The DTDACl is very long double tails surfactant so it is a water-insoluble. Moreover, it is also an oil-insoluble in this system because the oil phase is hexane. Since the hydrophobicity of DTDACl is very high, it might not be appropriate with hexane. Therefore, DTDACl would be preferred to aggregate at the interface between oil and water phase, and then the middle phase microemulsion forms.

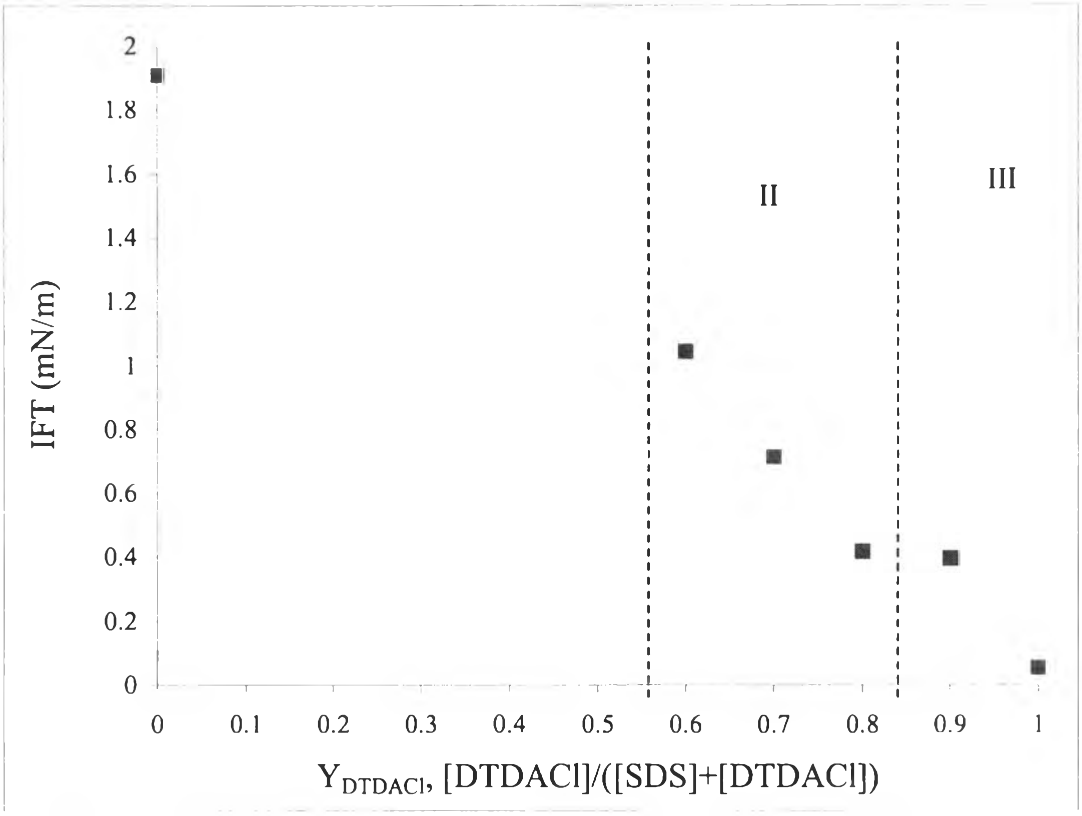

Figure 4.7 The interfacial tension between excess phase and microemulsion phase of SDS-DTDACl system as a function of cationic surfactant fraction.

4.3 Effect of Anionic Surfactant Structures in Microemulsion Formation by Mixed Surfactants

In this section, the main cationic surfactant used was a single-tail cationic Dodecyl trimethyl bromide (DTAB); other anionic surfactants were sodium di (2-ethylhexyl) sulfosuccinate or Aerosol OT, sodium dihexyl sulfosuccinate or Aerosol MA, and sodium diamyl sulfosuccinate or Aerosol AY, sodiumhexadecyl diphynyloxide disulfonate or Dowfax8390. All systems were carried out at the same condition as in the section 4.2.

4.3.1 Microemulsion Phase Behavior of DTAB-AOT System

To achieve the purpose of this work. the effect of using different hydrophobic structure of anionic surfactant was also investigated. In this section, dodecyl trimethyl ammonium bromide or DTAB was used as a cationic surfactant, which was mixed with various anionic surfactants. The series of Aerosol surfactants, Aerosol AY, Aerosol MA, and Aerosol OT, were selected as an anionic surfactant in the mixed system. The sodium di (2-ethylhexyl) sulfosuccinate or Aerosol OT is a unique type of surfactant molecule that has a double C6-chain anionic surfactant with a branched ethyl groups in each chain. Because of its molecular shape, it is particularly well suited to forming reverse micelles. The IFT values were increased by adding DTAB into the AOT-rich solution. As seen from Figure 4.8, the IFT from Y values of 0, 0.1, 0.2, 0.3, and 0.4 were 0.43, 0.64, 1.22, 1.69, and 3.28 mN/m, respectively. The IFT values were decreased at Y = 0.5, 0.6, and 0.7 to 2.1, 0.56, and 0.03 mN/m, respectively. The IFT values were increased again as increased the DTAB fraction to 0.8, 0.9, and 1.0. The IFT values at these points were 0.40, 0.99, and 2.48 mN/m, respectively. Although an IFT of using the AOT alone has a low value, 0.43 mN/m, it is a factor of fourteen higher than the lowest IFT in mixed DTAB-AOT, 0.03 mN/m.

Since AOT is very hydrophobic surfactant, it tends to form reverse micelle or a Type II microemulsion. The results show that using the AOT alone, Type II was formed. The phase transition along increasing the DTAB fraction, a Type II changes to Type I to Type II to Type I. Even if the middle phase microemulsion did not form, the precipitates or liquid crystals were diminished in all range of concentration in the DTAB-AOT mixture.

4.3.2 Microemulsion Phase Behavior of DTAB-AMA System

Since the middle phase microemulsion did not appear in AOT-DTAB mixture, the AOT was replaced by the Aerosol MA. The sodium dihexyl sulfosuccinate or Aerosol MA is a di C6-chain anionic surfactant without the ethyl branched as in the AOT. The results in Figure 4.9 show that the IFT values decreased as the oppositely charged surfactant is increased in both AMA- and DTAB- rich solution. However, the IFT values in both sides increased at the DTAB fraction approach to the equimolarity. The strong interaction between the proper AMA and DTAB amount is possible the reason in increasing the IFT at the equimolar ratio. The minimum IFT values on both anionic- and cationic-rich regions were 0.12 and 0.09 mN/m at Y = 0.3 and 0.7, respectively. The phase transition of DTAB-AMA is from Type I to Type II to Type I. Although, the mixture of DTAB-AMA did not allow the middle phase microemulsion formation, this formulation can avoid the precipitation.

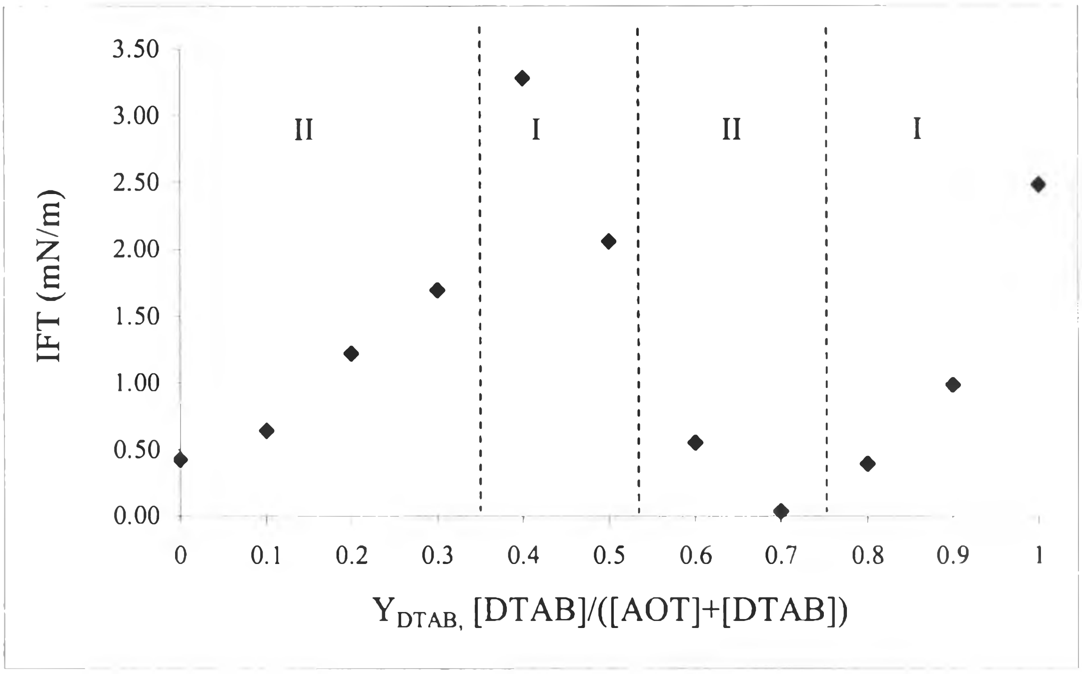

Figure 4.8 The interfacial tension between excess phase and microemulsion phase of DTAB-AOT system as a function of cationic surfactant fraction.

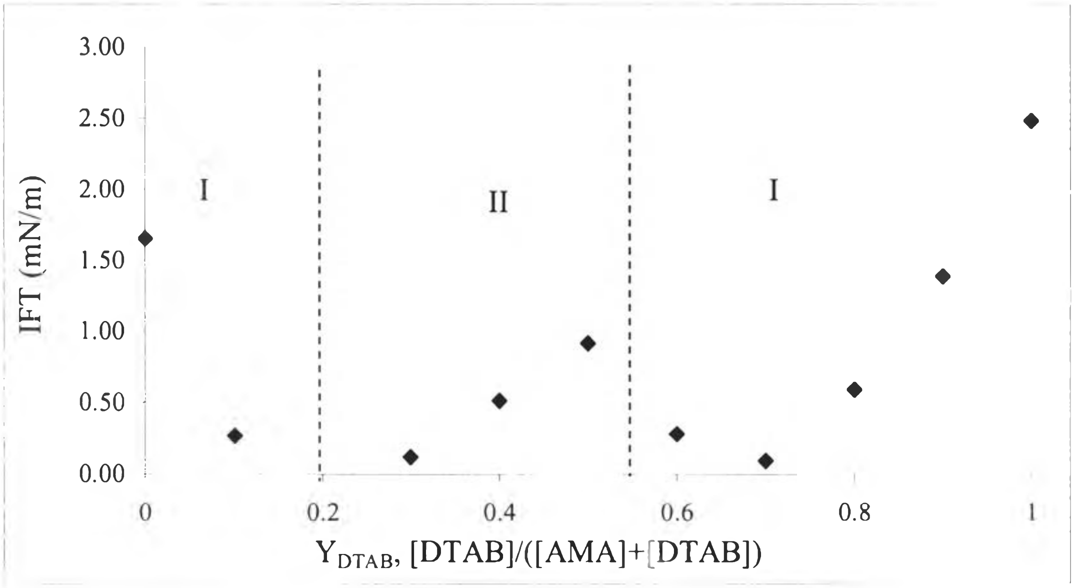

Figure 4.9 The interfacial tension between excess phase and microemulsion phase of DTAB-AMA system as a function of cationic surfactant fraction.

4.3.3 Microemulsion Phase Behavior of DTAB-AAY System

Since the middle phase microemulsion did not occur in AMA-DTAB mixture, the AMA was replaced by the Aerosol AY. The sodium diamyl sulfosuccinate or Aerosol AY has shorter double-tails than the AMA that might allow the middle phase microemulsion formation.

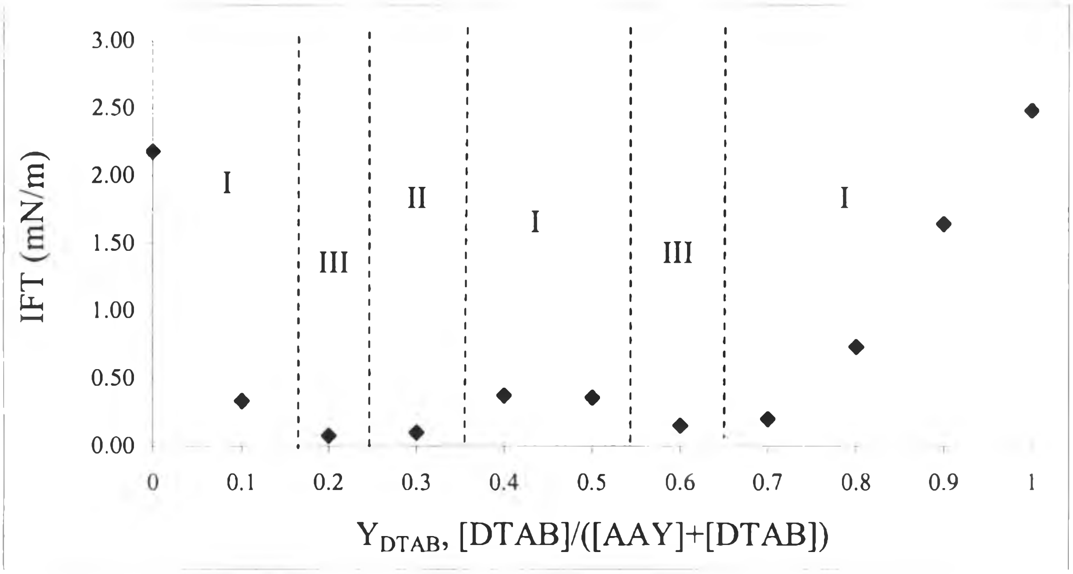

Figure 4.10 The interfacial tension between excess phase and microemulsion phase of DTAB-AAY system as function of cationic surfactant fraction.

Figure 4.10 shows the similar tendency of IFT in DTAB-AAY and DTAB-AMA system that the IFT values decreased as the oppositely charged surfactant is added in both anionic- and cationic- rich solution. The middle phase microemulsions were particularly observed at Y = 0.2 and 0.6 in DTAB-AAY mixture. The IFT values at these points were 0.08 and 0.15 mN/m, respectively. The water solubilization parameters at those fraction, were 12.92 and 7.27 ml/g, respectively. And the solubilization parameters of oil were 4.29 and 21.22 ml/g, respectively. The transition along this scan changes from Type I to Type III to Type II to Type I to Type III and to Type I.

4.3.4 Microemulsion Phase Behavior of DTAB-Dowfax8390 System

As expected in the second hypothesis, if the divalent anionic surfactant and monovalent cationic surfactant were used, the middle phase microemulsion might be formed at the mixture 2:1 cationic/anionic surfactant. Therefore, the sodium hexadecyl diphenyloxide sidulfonate or Dowfax8390 was employed because it is a twin head (divalent) anionic surfactant with single C16-tail. The IFT results of DTAB-Dowfax8390 system were shown in Figure 4.11. The lowest IFT values was observed at near 2:1 cationic/anionic surfactant mixture. In particular, the middle phase microemulsion was observed at Y values of 0.7, which is roughly to two cationic surfactants per one anionic surfactant. Because the divalent anionic surfactant has two head groups, it requires twice amount of oppositely charged surfactant – cationic surfactant – for highly matching.

As seen in Figure 4.11, in anionic- rich region, adding low concentration of DTAB (Y=0.1) into the system, the IFT increased rapidly and then decreased if the DTAB fraction is increased. The addition of Dowfax8390 into the cationic-rich region can reduce the IFT values. In anionic-rich region, only a Type I microemulsion was observed because Dowfax8390 is very hydrophilic. The phase transition changes from a Winsor Type I to Type III to Type I.

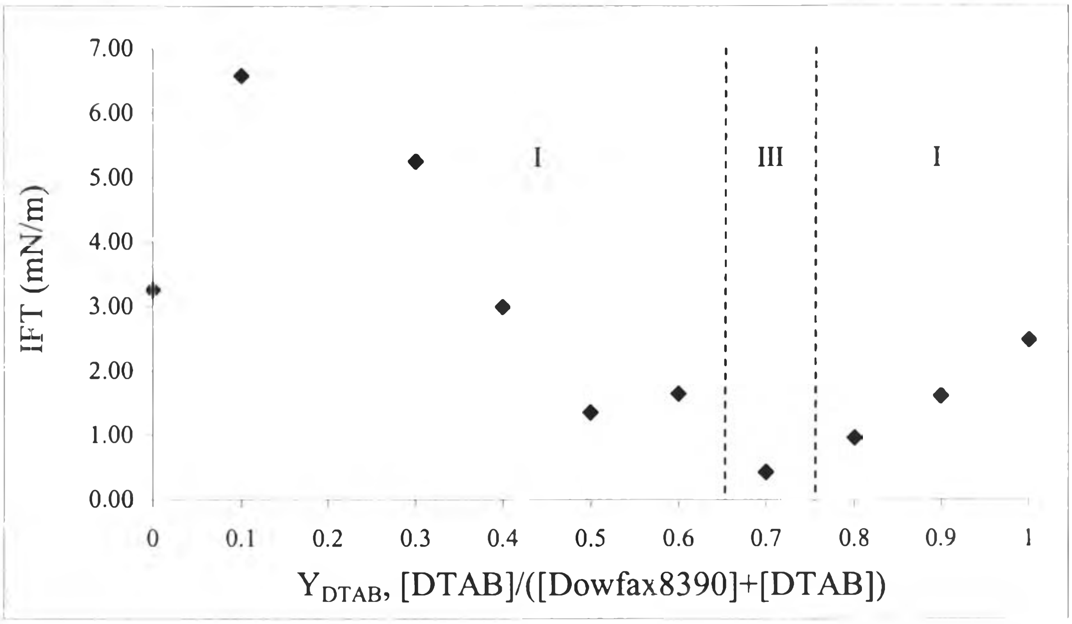

Figure 4.11 The interfacial tension between excess phase and microemulsion phase of DTAB-Dowfax8390 system as function of cationic surfactant fraction.

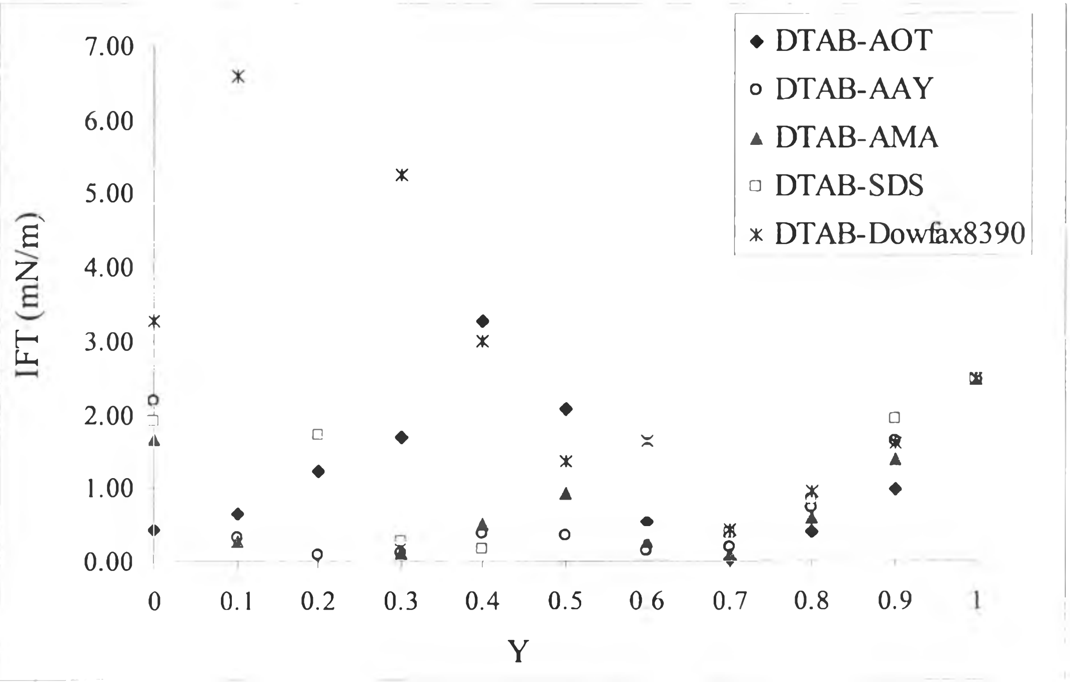

Figure 4.12 Comparison the IFT values of each system for DTAB with various anionic surfactants, AOT, AAY, AMA, SDS, and Dowfax8390.

Figure 4.12 is the comparison between the IFT values of each system for DTAB with various anionic surfactants, AOT, AMA, AAY, SDS, and Dowfax8390. The results show that the IFT in cationic-rich of all systems decreases from Y maximum (Y=1.0) as the fraction of anionic surfactant is increased. All systems show the similar values of IFT, therefore, the structure of anionic surfactants in a cationic-rich region does not affect the system. Whereas, adding only a small amount of anionic surfactant into the system, the IFT values of each mixture are quite different.

4.4 Effect of Hydrophobicity of Oils on Microemulsion Formation by Anionic-Cationic Surfactant Mixture

To investigate the hypothesis that as the oil EACN increases, the ratio of anionic to cationic surfactant mixture for the middle phase microemulsion formation will approach 1:1 for monovalent cationic/anionic surfactants. The microemulsion formation of mixtures of DTAB-AAY was carried out in three different hydrophobicity oils. Three oil representatives are TCE, hexane, and hexadecane, which are arranged in order of EACN values. Surfactant mixture of DTAB-AAY was selected to be investigated in this case, since it has a good potential to form the middle phase micromeulsion in hexane and has low interfacial tension in a wide range of cationic surfactant ratio.

Figure 4.13 shows the effect of hydrophobicity of oils on DTAB-AAY systems for varying cationic surfactant mole ratio at 0.05 M total surfactant concentration. The minimum IFT values on both anionic- and cationic-rich regions for TCE were 0.19 and 0.30 mN/m at $Y = 0$ and 0.7, respectively. The minimum IFT values for middle phase microemulsion systems with hexane were 0.08 and 0.15 mN/m at $Y = 0.2$ and 0.6, respectively and the minimum IFT values for hexadecane were 0.34 and 0.32 mN/m at $Y = 0.4$ and 0.6, respectively. As a result, the Y value to achieve the minimum IFT moves toward the equimolar ratio as the oil EACN increases (TCE<hexane<hexadecane). Therefore, these results are consistent with the previous study (Doan, 2002).

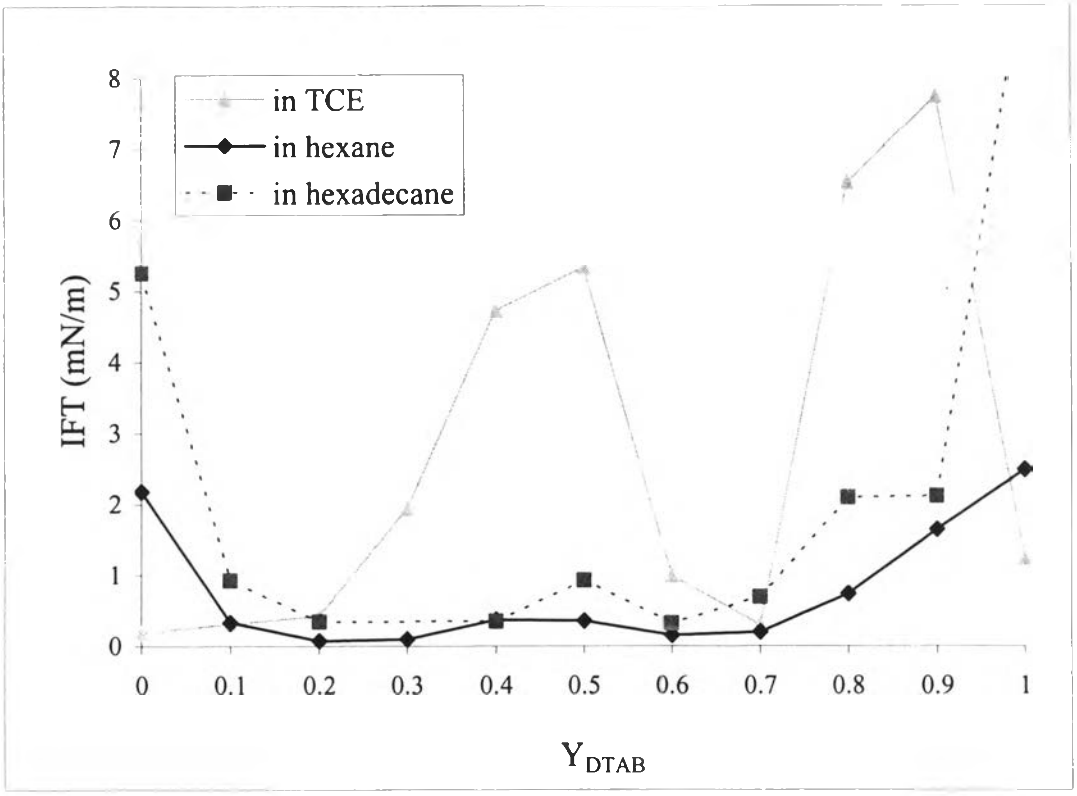

Figure 4.13 Effect of hydrophobicity of oils on DTAB-AAY systems.