



CHAPTER IV

RESULTS AND DISCUSSION

The objective of this study was to study microemulsion formation of motor oil with both single nonionic surfactant (alcohol ethoxylates) and mixed surfactant systems by obtaining phase diagrams of oil/water/surfactants system to illustrate different Winsor Type I–III–II–IV, the so-called fish diagram. In addition, the solubilization capacities are calculated in terms of the solubilization parameter, the IFT values between the two equilibrated phases were measured by the spinning drop tensiometer (Krüss, SITE 04).

In all experiments, surfactant, cosurfactant, and NaCl concentrations are expressed in weight percent (wt.%) per volume of the aqueous phase consisting of water, salt, cosurfactant and surfactant (not including oil).

4.1 Microemulsion Phase Diagram

The main purpose of this section was to construct the microemulsion phase diagrams (fish diagram) by plotting surfactant concentration versus cosurfactant concentration. The fish diagram is generally used to determine a minimum surfactant concentration required to form a Winsor Type III microemulsion which is known as the critical microemulsion concentration ($C_{\mu C}$) and solubilization capacity at point E (the transition point from Type III to Type IV microemulsion), revealing the minimum concentration of surfactant and cosurfactant added to totally mix oil and water into a single phase.

4.1.1 Effects of oil

The microemulsions of different oils were first studied by using the single nonionic surfactant system of AE3 without cosurfactant at 30°C and α (the mass fraction of oil to water plus oil) = 0.5. In this study, n-octane, motor oil and palm oil were used because they have different polarity with following order: n-octane < motor oil < palm oil. The volume of both oil phase and water phase did not change and no middle microemulsion phase was formed with all of the studied oils.

From the results, the hydrophilic-lipophilic balance (HLB) of these oils did not match that of AE3 while has high hydrophilicity. However, the water-in-oil (w/o) microemulsion phase (Winsor type II) could occur at high concentrations AE3 around 10 wt.% with only n-octane because n-octane has smaller molecule can penetrate the surfactant palisade layer of the micelles of AE3.

Next, the microemulsions of both motor oil and n-octane with AE3 and n-butanol as the cosurfactant were studied at 30°C and $\alpha = 0.5$. The only motor oil could be formed all oil-in-water (Winsor type I), middle (Winsor type III) and water-in-oil (Winsor type II) microemulsions and the fish diagram was constructed while the microemulsions of n-octane appeared only water-in-oil (Winsor type II).

4.1.2 Effects of EO Groups

The effect of EO group of AEs on microemulsions was investigated. AEs with three EO groups (AE3), five EO groups (AE5), seven EO groups (AE7), eight EO groups (AE8) and nine EO groups (AE9) and nonylphenol ethoxylate with nine EO groups (NP9) were used as surfactants in microemulsion formation in this studied. Surfactant which has higher EO group has higher hydrophilicity following in the order: AE3 < AE5 < AE7 < AE8 < AE9.

The preliminary results showed that all studied could not form a Winsor Type III microemulsion because their HLB do not match that of the motor oil.

Next, the microemulsion phase study of motor oil was performed using the single nonionic surfactant system with n-butanol as the cosurfactant at 30°C and $\alpha = 0.5$. Alcohol ethoxylates with three EO groups (AE3), seven EO groups (AE7) and nine EO groups (AE9) and nonylphenol ethoxylates with nine EO groups (NP9) were investigated in this study. The results showed that only AE3 with n-butanol could form a Winsor Type III microemulsion because it has the lowest hydrophilicity and the addition of cosurfactant makes the interfacial layer less hydrophilic, resulting in the motor oil dissolved in the interfacial layer. The higher the EO group of alcohol ethoxylates, the longer the hydrocarbon chain such as n-pentanol or n-hexanol may be used as the cosurfactant in microemulsion formation in order to make the interfacial layer less hydrophilic.

4.1.3 Effects of Temperature

The fish diagrams of AE3/n-butanol/motor oil/water were constructed at three different temperatures, 20, 30 and 40 °C and $\alpha = 0.5$, as shown in Figure 4.1. The fish head tilted slightly downward and the fish tail tilted slightly upward. The middle microemulsion phase region (Winsor Type III) is in the fish body, and the single phase (Winsor Type IV) is at the fish tail. The oil-in-water microemulsion phase region (Winsor Type I) and the water-in-oil microemulsion phase region (Winsor Type II) is located below and above the fish body, respectively. The surfactant concentration at the tip of the fish head is the critical microemulsion concentration or $C_{\mu C}$ which is the lowest surfactant concentration to form the Winsor Type III microemulsion (the middle phase). At the $C_{\mu C}$, the system exhibits the ultra-low interfacial tension (IFT). The temperature showed a significant effect on the microemulsion phase transformation and the $C_{\mu C}$ value which decreased with increasing temperature. The lowest value of $C_{\mu C}$ was achieved at 40 °C (see Table 4.1). Point E reveals the minimum concentrations of AE3 and n-butanol to obtain a single microemulsion phase (Winsor Type IV). Lower concentration of surfactant and alcohol at point E indicate a higher solubilization capacity of the system. With increasing temperature, the system reached the HLB value of the motor oil at lower surfactant and alcohol concentrations and at this point, the system can solubilize the equal maximum amount of oil and water. AE3 becomes less hydrophilic with increasing temperature and, hence, a lower amount of lipophilic n-butanol is required to form a microemulsion. It has been reported earlier that nonionic surfactants become lipophilic at the elevated temperature due to the dehydration of oxyethylene group.

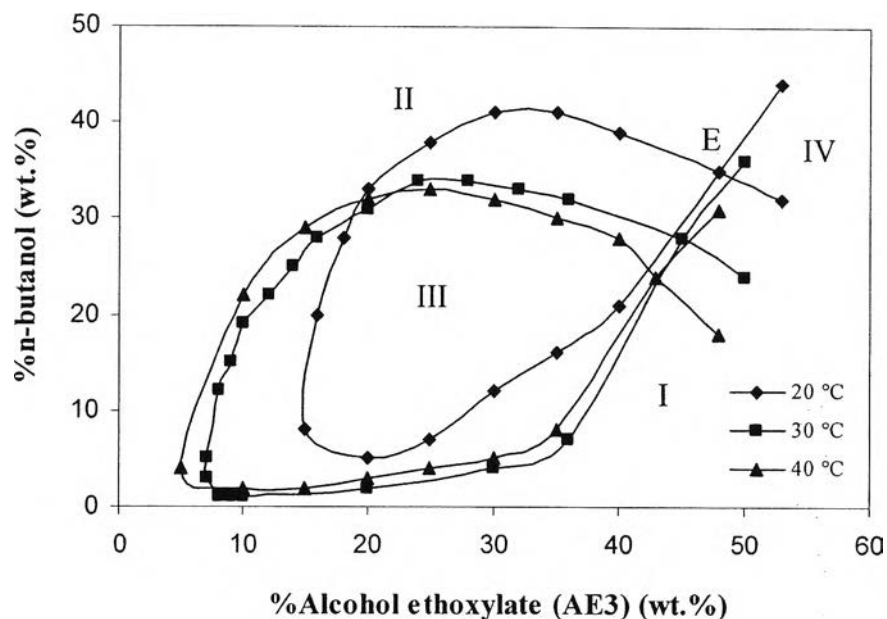


Figure 4.1 Phase behavior of AE3/n-butanol/motor oil/water with α (weight fraction of oil in oil and water mixture) = 0.5 at 20 (◆), 30 (■) and 40 °C (▲).

Table 4.1 $C_{\mu C}$ value and AE3 and n-butanol concentrations at point E for the system of AE3/n-butanol/motor oil/water with $\alpha = 0.5$ at different temperatures

Temperature (°C)	$C_{\mu C}$ (Total surfactant concentration, wt.%)	E (total surfactant conc., n-butanol conc.)
20	15	(48,35)
30	7	(45,28)
40	5	(43,24)

These mixed surfactant systems could provide middle microemulsions because n-butanol acts as a cosurfactant and cosolvent to facilitate the surfactant adsorption at oil/water interface. The role of a cosurfactant is to ensure the existence of the association structure and to destroy the liquid crystalline and/or gel structure which obviate the formation of microemulsion. Alcohol molecules arrange themselves in the hydrophilic-lipophilic layer with the OH group orient toward the aqueous domain so as to change the hydrophilicity, making the interfacial layer more lipophilic or less hydrophilic.

4.1.4 Effects of salinity

The fish diagram of the system of AE3/MES/n-butanol/motor oil/water at 30 °C with $\alpha = 0.5$ and δ (weight fraction of MES in AE3 and MES) = 0.02 as a function of NaCl concentration (0, 3, 5 and 7 wt.%) is shown in Figure 4.2. It was observed that no oil-in-water microemulsion phase region (Winsor Type I) appeared at all NaCl concentrations because there was a little amount of MES surfactant at a weight fraction of MES = 0.02 in the system and the dissociation of MES head group is suppressed from the presence of NaCl. It is evident from this figure that the $C_{\mu C}$ value decreases with increasing NaCl concentration from 0 to 3 wt.% but it increases with increasing NaCl concentration to 7 wt.% as shown in Figure 4.2 and Table 4.2. The point of maximum solubilization (point E) moves toward lower mixed surfactant and n-butanol concentrations with increasing NaCl concentration as shown in Figure 4.2 and Table 4.2. The increasing NaCl decreases the hydrophilicity of AE3 and suppresses the dissociation of MES head group, resulting in the MES molecules less hydrophilic, and hence a lower n-butanol concentration is required to establish the hydrophilic-lipophilic balance.

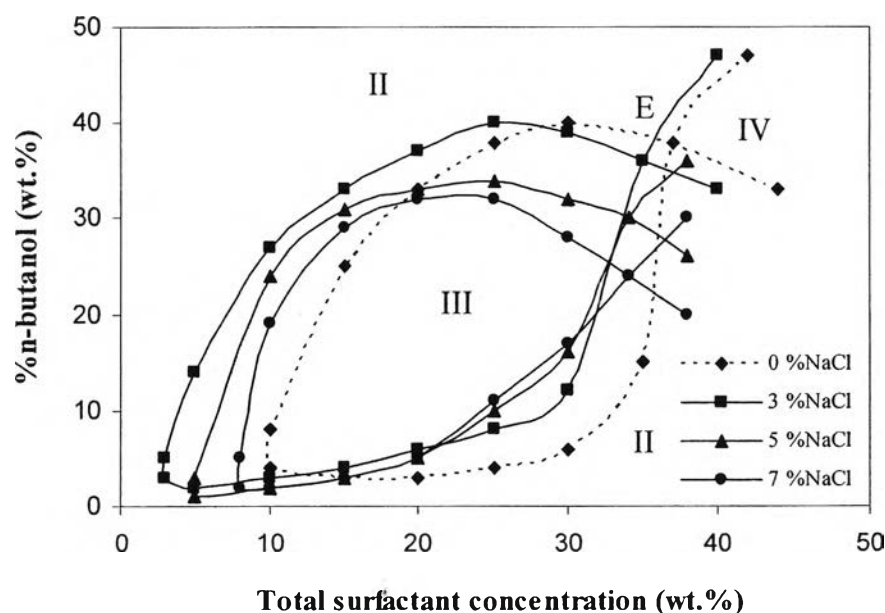


Figure 4.2 Phase behavior of the system of AE3/MES/n-butanol/NaCl/motor oil/water with $\alpha = 0.5$ and $\delta = 0.02$ at 30 °C and different NaCl concentrations.

Table 4.2 $C_{\mu C}$ value and AE3 and n-butanol concentrations at point E for the system of AE3/MES/n-butanol/motor oil/water with $\alpha = 0.5$ at 30 °C at different NaCl concentrations

NaCl (wt.%)	$C_{\mu C}$ (Total surfactant concentration, wt.%)	E (total surfactant conc., n-butanol conc.)
0	10	(37,38)
3	3	(35,36)
5	5	(34,30)
7	8	(34,24)

4.1.5 Comparison of phase diagram between single and mixed systems

The phase behaviors of the single nonionic surfactant and mixed surfactant systems are shown in Figure 4.3. For the mixed surfactant system, the addition of MES was found experimentally to facilitate the formation of single phase microemulsion (Winsor Type IV) at a lower mixed surfactant concentration but a higher n-butanol concentration with a slightly higher $C_{\mu C}$ value. The addition of MES increases the solubilization of the mixed micelles in oil medium due to the reduction of the electrical repulsion but n-butanol must be represented in a high amount to balance in the hydrophilic-lipophilic interfacial layer.

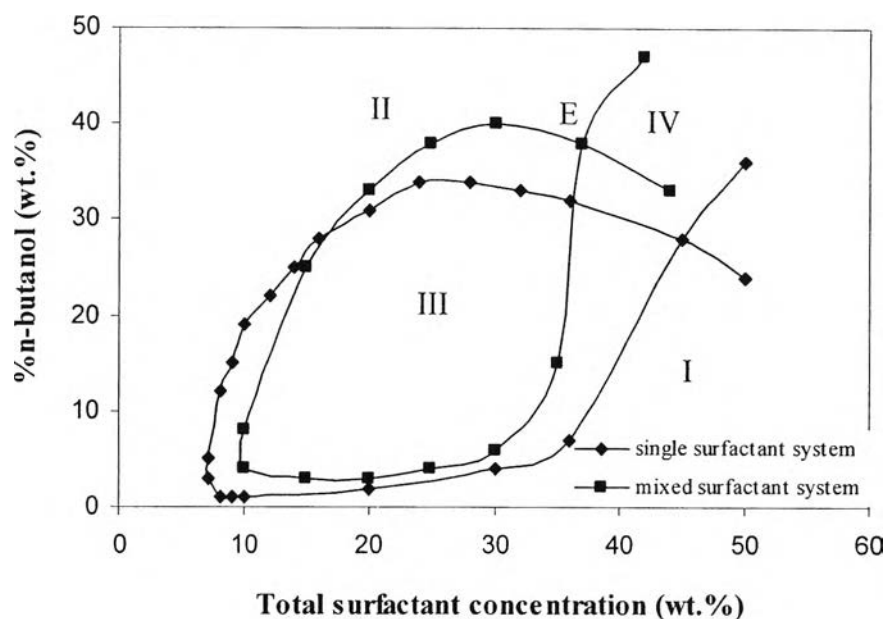


Figure 4.3 Phase behaviors of the pure AE3 and mixed surfactant system (AE3/(MES)/n-butanol/motor oil/water) with $\alpha = 0.5$ and $\delta = 0.02$ at 30 °C for single surfactant system (◆) and mixed surfactant system(■).

Table 4.3 $C_{\mu C}$ value and AE3 and n-butanol concentrations at point E for the AE3/(MES)/n-butanol/motor oil/water system with $\alpha = 0.5$ and $\delta = 0.02$ at 30 °C of single and mixed surfactant systems

System	$C_{\mu C}$ (Total surfactant concentration, wt.%/vol)	E (total surfactant conc., n-butanol conc.)
Single surfactant system	7	(45,28)
Mixed surfactant system	10	(37,38)

4.2 Solubilization Parameter (SP) Results

The solubilization capacities were calculated in terms of the solubilization parameter, which is the volume of either oil or water dissolved per weight of total surfactants.

4.2.1 Effects of temperature

Solubilization parameter (SP) is defined as the volume of oil solubilized (SP_o) or of water solubilized (SP_w) per weight of total surfactants in the microemulsion phase. Figure 4.4 illustrates the phase behavior of motor oil in terms of the solubilization parameters of water and oil (SP_w and SP_o, respectively) for the AE3/n-butanol/motor oil/water system. The transition of microemulsion phase shifted from a water-in-oil (Winsor Type II), middle (Winsor Type III), to oil-in-water (Winsor Type I) microemulsion phase with increasing AE3 concentration. The middle microemulsion phase region is larger with increasing temperature in the range of 20 to 40 °C. The SP_w slightly increased and reached constant, the SP_o was very high in the water-in-oil (Winsor Type II) microemulsion phase and dramatically dropped in the middle (Winsor Type III) microemulsion phase then slightly increased to reach a constant with increasing AE3 concentration. From the results, it can be concluded that the temperature facilitates the solubilization of oil helping the formation of middle (Winsor type III) microemulsion phase in the studied temperature range.

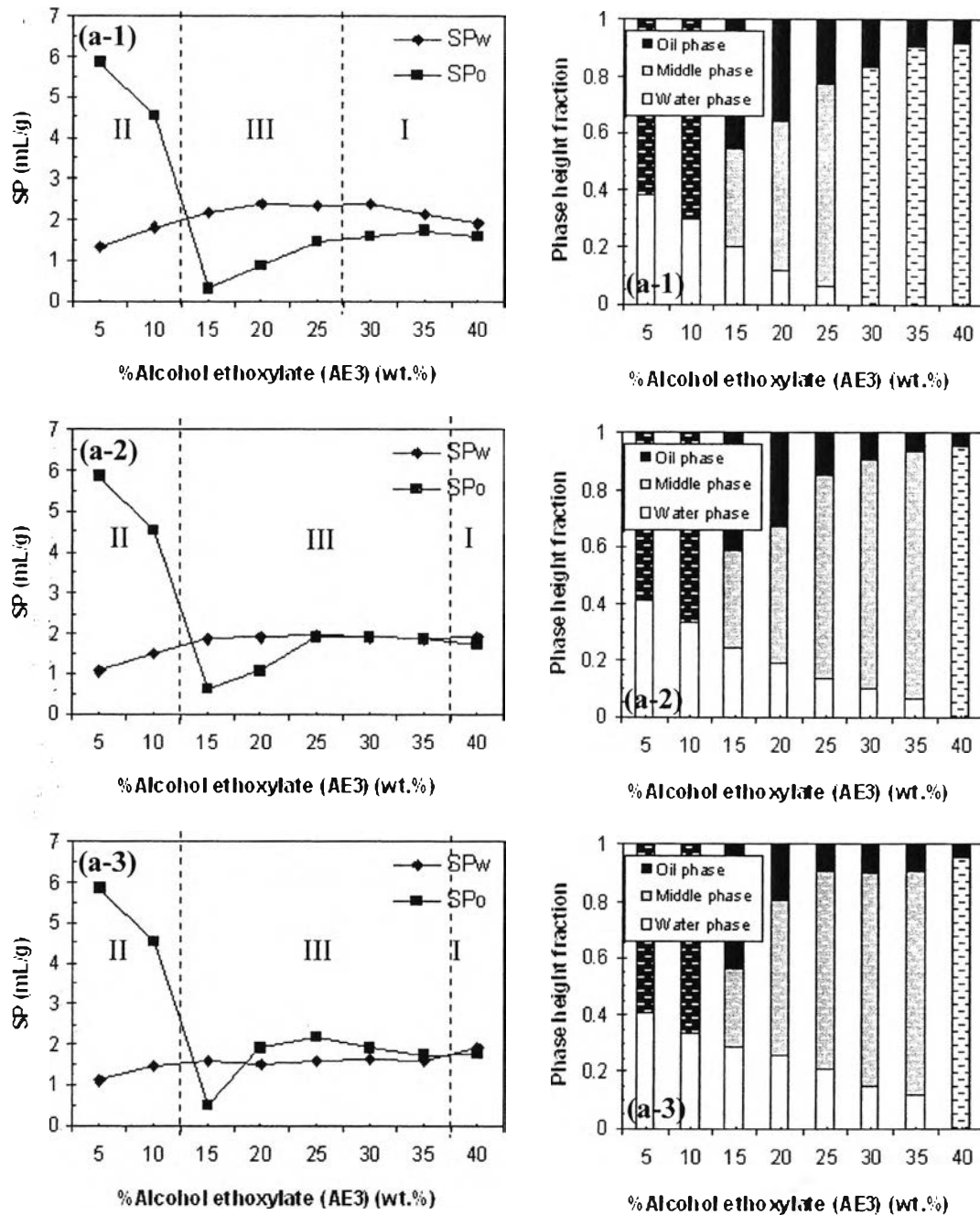


Figure 4.4 Solubilization parameters (SP) and phase height fraction as a function of AE3 concentration and temperature of the AE3/n-butanol/motor oil/water system with $\alpha = 0.5$: (a-1) 20 °C, (a-2) 30 °C and (a-3) 40 °C.

4.2.2 Effects of salinity

To investigate the effect of salinity on microemulsion formation and solubilization parameters of the mixed surfactant system of AE3/MES/n-butanol/motor oil/water, the experiments were conducted at four different NaCl concentrations, 0, 3, 5 and 7 wt.%, $\alpha = 0.5$, $\delta = 0.02$ and 30 °C. From Figure 4.5, the water-in-oil (Winsor Type II) microemulsion phase shifted to the middle (Winsor Type III) microemulsion phase with increasing mixed surfactant concentration. The SP_w was found to be approximately constant while the SP_o was very high in the water-in-oil (Winsor Type II) microemulsion region and dramatically dropped when the AE3 concentration further increased. In the middle (Winsor type III) microemulsion region, an increased AE3 concentration resulted in increasing SP_o . The result can be explained in that the addition of NaCl leads to increasing hydrophobicity of the system. As a consequence, the SP_o and the phase height middle phase (Winsor Type III) microemulsion increases with increasing NaCl concentration.

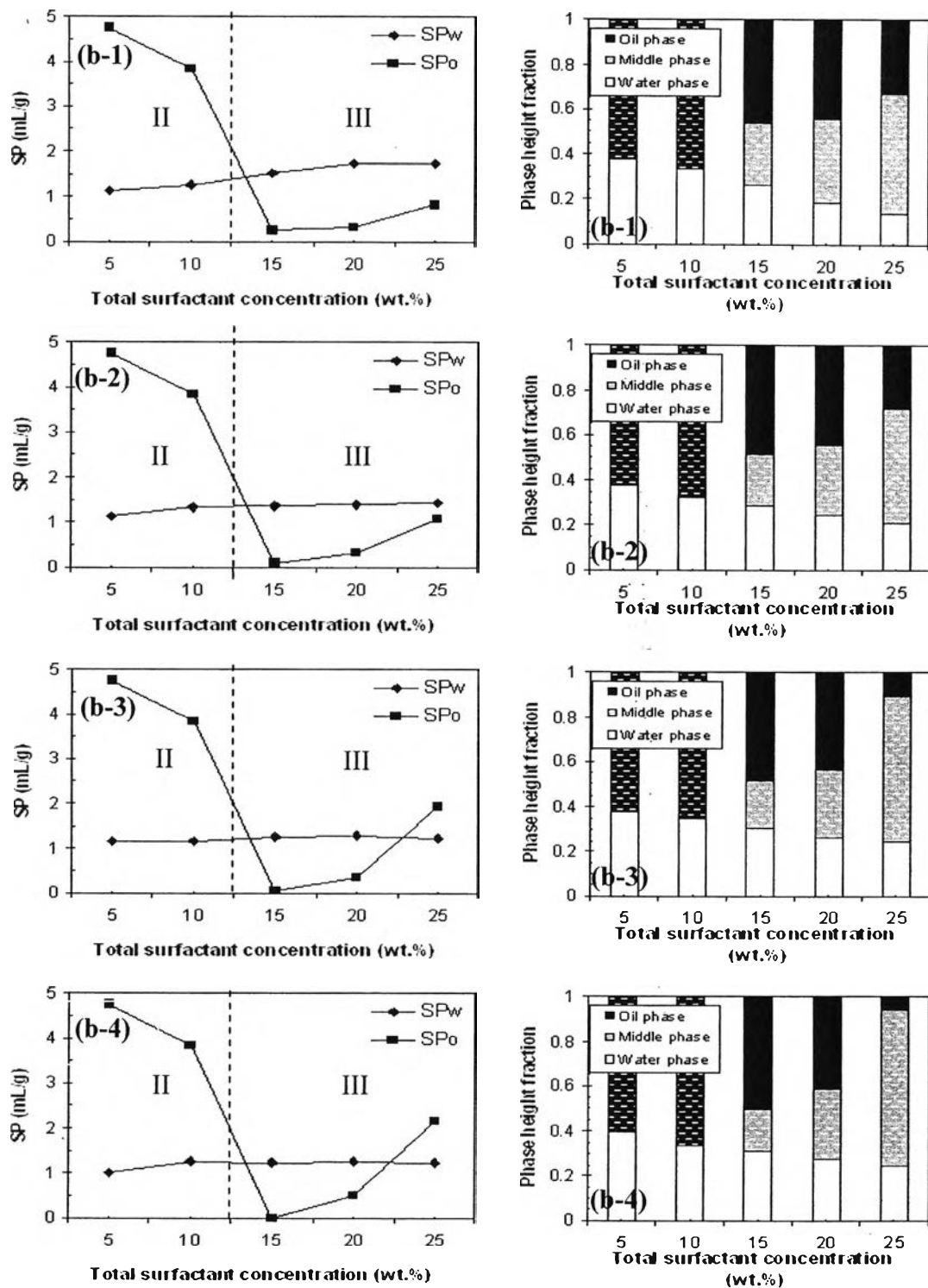


Figure 4.5 Solubilization parameters (SP) and phase height fraction as a function of AE3 concentration and salinity of the AE3/MES/n-butanol/motor oil/water system with $\alpha = 0.5$, and $\delta = 0.02$ at 30 °C : (b-1) 0%NaCl, (b-2) 3%NaCl, (b-3) 5%NaCl and (b-4) 7%NaCl.

4.3 Equilibrium Interfacial Tension (IFT) Results

Hydrophilic and lipophilic linkers are molecules which can decrease the rigidity and increase the thickness of the interfacial layer between the oil and water phases which can result in more rapid microemulsion formation and lower oil/water IFT in microemulsion systems. In this study, only the interfacial tension of microemulsion-water interface (γ_{mw}) was measured, interfacial tension measurement for microemulsion-oil interface (γ_{mo}) was not carried out because of the solution's high viscosity.

4.3.1 Effects of temperature on IFT

The equilibrium IFT of the oil and surfactant solution as a function of AE3 concentration at different temperatures of AE3/n-butanol/motor oil/water system with $\alpha = 0.5$ is shown in Figure 4.6. With increasing AE3 concentrations, IFT decreased first, and reached the lowest IFT at the optimum AE3 concentration of 15 wt.% for both two studied temperature of 30 and 40 °C. The lowest IFT was found to locate in the Winsor Type III microemulsion region which were 0.0186 mN/m at 30°C, and 0.0438 mN/m at 40°C when the AE3 concentration further increased beyond the optimum AE3 concentration, the IFT slightly increased. The result can be explained in that the surfactant adsorption at the oil/water interface decreased with increasing temperature from 30 to 40 °C which are below its cloud point.

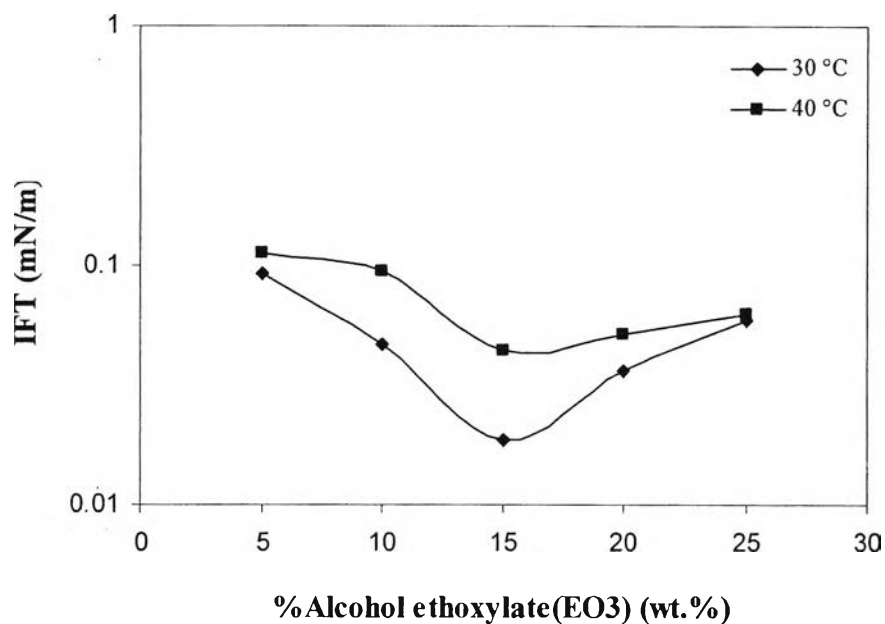


Figure 4.6 The interfacial tension between the oil and aqueous phase as a function of AE3 concentration of the AE3/n-butanol/motor oil/water system with $\alpha = 0.5$ at 30 (◆), and 40 °C (■).

4.3.2 Effects of salinity on IFT

The interfacial tension between the oil and aqueous phase of AE3/MES/n-butanol/motor oil/water system with $\alpha = 0.5$, $\delta = 0.02$, 30 °C at different NaCl concentrations is shown in Figure 4.7. For any given NaCl concentration, the IFT decreased, and reached the lowest IFT at an optimum total surfactant concentration. Beyond the optimum total surfactant concentration, the IFT increased with increasing total surfactant concentrations. For any given total surfactant concentration, the IFT decreased with increasing salinity from 0 to 3 %NaCl and beyond 3%NaCl, the IFT further increased with increasing salinity. The optimum total surfactant concentration at the lowest IFT shifted to a higher value when the NaCl concentration was increased (15, 18, and 21 %wt/vol at 0, 3, and 5%NaCl, respectively) excepting 7%NaCl. The amount of surfactants partitioning on the interface between oil and water phase is responsible for the reduction of the IFT. The addition of salt into an ionic surfactant can shield the charges of surfactant head groups to destroy hydrated shells around the ions and enhance the hydrophobic

ability of the surfactant, which causes the movement of surfactant molecules into the oil phase and breaks both the water-interfacial and the oil-interfacial adsorption equilibrium resulting in reduction of the surfactant molecules at the interfaces; as a result, the IFT is higher when NaCl is added at a very high concentration. Therefore, there must be an optimum salinity.

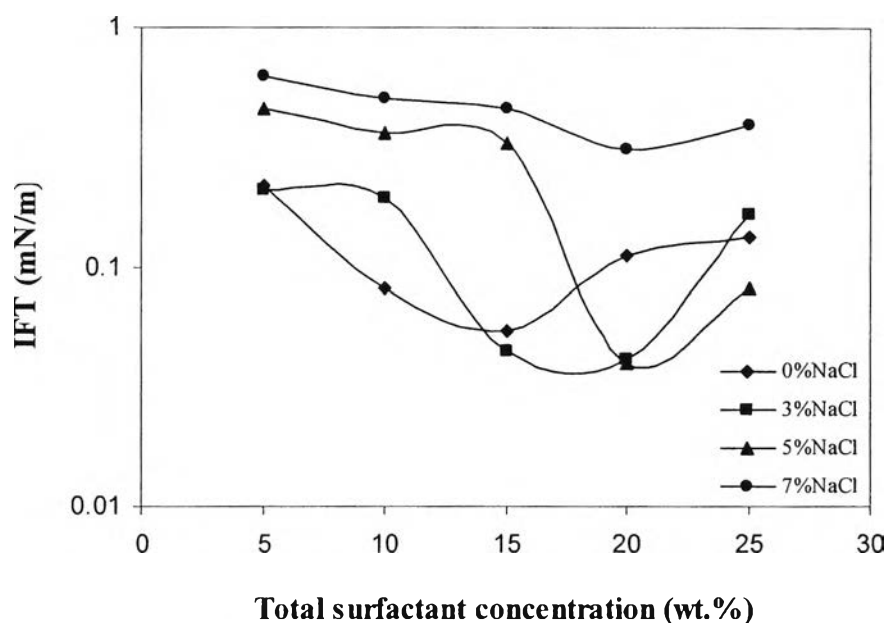


Figure 4.7 The interfacial tension between the oil and aqueous phase as a function of AE3 concentration of the AE3/MES/n-butanol/motor oil/water system with $\alpha = 0.5$, $\delta = 0.02$ at 30 °C for 0%NaCl (◆), 3%NaCl (■), 5%NaCl (▲) and 7%NaCl (●).

4.3.3 Comparison of IFT between single and mixed system

The IFT as a function of total surfactant concentration of both system of single nonionic surfactant (AE3) and mixed surfactant system (AE3/MES) at $\delta = 0.02$ and 30 °C is shown in Figure 4.8. The results show that the single nonionic surfactant system could reduce the IFT to 0.0280 mN/m, while the mixed surfactant system could reduce it to 0.0550 mN/m, indicating that the single nonionic surfactant system is better packing at the interface and has a higher interfacial activity as compared to the mixed surfactant system. However, for the mixed surfactant system,

an addition of NaCl at around 3 to 5 % was able to reduce the IFT as low as that of the pure AE3 system.

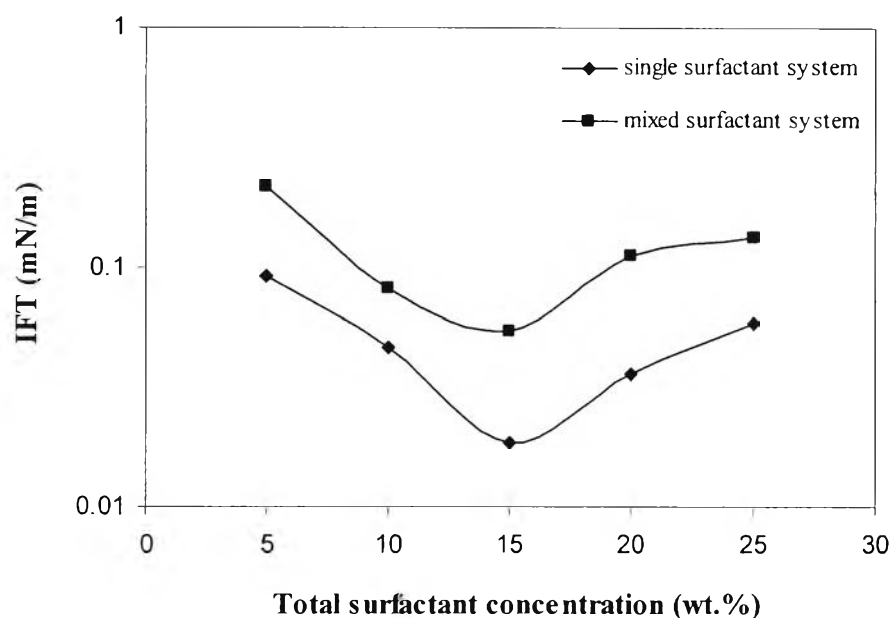


Figure 4.8 IFT as a function of total surfactant concentration of both system at $\alpha = 0.5$, $\delta = 0.02$ and $30\text{ }^{\circ}\text{C}$ for single surfactant system (AE3/n-butanol/motor oil/water) (◆), and mixed surfactant system (AE3/MES/n-butanol/motor oil/water) (■).

4.4 Critical micelle concentration (CMC)

The critical micelle concentration (CMC), one of the basic parameters of surfactants, is a lowest concentration at which a surfactant solution begins to form micelles. Surface tensions of different surfactant solutions at different concentrations were measured and plotted versus logarithmic concentrations. The point at which the surface tension levels off as surfactant concentration is increased is taken as the CMC. The surface tension of the surfactant at the CMC, γ_{CMC} , indicates the ability of surfactant to lower surface tension. Figure 4.9 shows the surface tension isotherm of the mixed surfactant system (AE3/MES) with a weight fraction of MES 0.02 at $30\text{ }^{\circ}\text{C}$, it can be seen that the CMC is 0.01 wt.% and γ_{CMC} is 25.27 mN/m. The CMC of the AE3/MES mixed surfactant system is close to those of both single AE3 and single MES surfactant systems, as shown in Figure 4.10 and Figure 4.11, respectively. The formation of micelles represents an important interfacial activity

because they eventually lead to formation of microemulsion and in turn results in the reduction in the IFT.

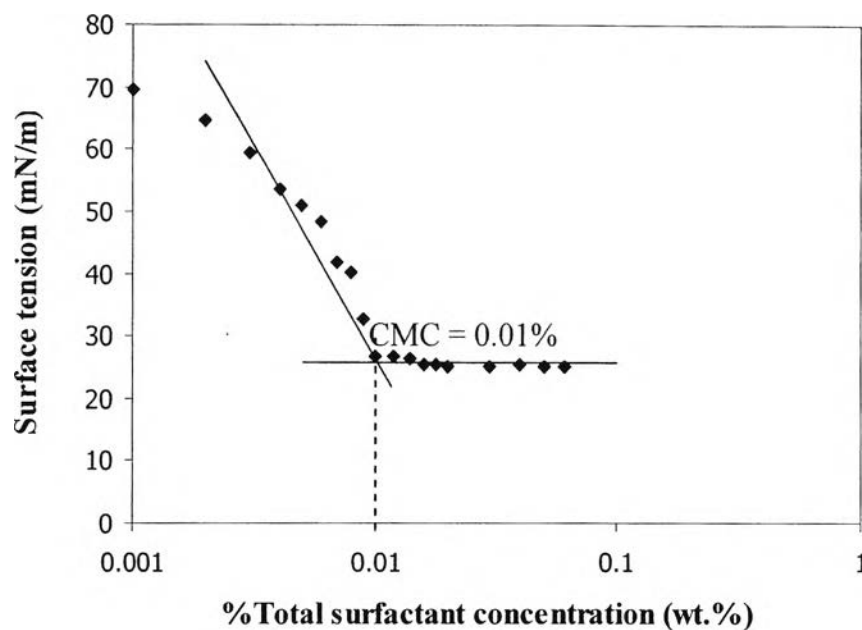


Figure 4.9 Surface tension isotherm of the mixed AE3/MES system at $\delta = 0.02$ and $30\text{ }^{\circ}\text{C}$.

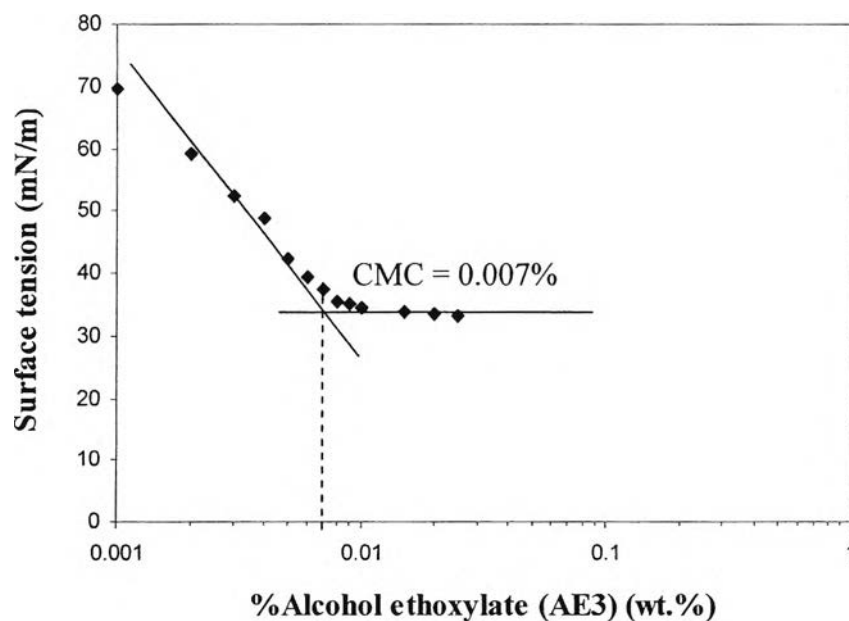


Figure 4.10 Surface tension isotherm of the single AE3 system at $30\text{ }^{\circ}\text{C}$.

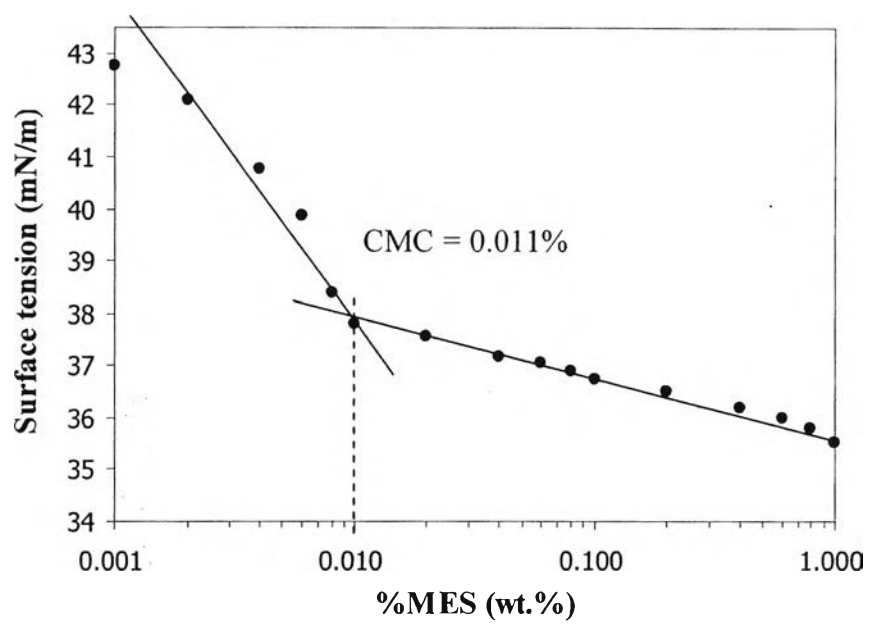


Figure 4.11 Surface tension isotherm of the single MES system at 30 °C.