CHAPTER IV
RESULTS AND DISCUSSION

The aim of this work was to investigate the microemulsion formation of motor oil with mixed of alcohol ethoxylate and the lipophilic linker at various temperatures. The microemulsion of surfactant/hydrophilic surfactant/lipophlic linker/motor oil/water system to form different Winsor types (I, II and III) microemulsion were obtained, know as fish diagram. In order to find the suitable condition for specific application the effect of hydrophilic surfactant and temperature were studied. Moreover, critical micelle concentration of added hydrophilic surfactant and lipophilic linker into the AE3 was also investigated. In all experiments, the surfactant, hydrophilic surfactant and lipophilic linker were presented in weight percent per volume of the aqueous solution (%w/v). The volumetric of water to oil equals to 1.

4.1 Microemulsion Phase Diagram

The main purpose of this section is to plot the microemulsion phase diagram (fish diagram) of this system by plotting as the concentration of mixed surfactants between the surfactant and the hydrophilic surfactant versus the concentration of the lipophilic linker at various hydrophilic surfactants and temperatures.

The fish diagram is generally used to determine a minimum surfactant concentration required to form a Winsor Type III microemulsion which was known as the critical microemulsion concentration (CμC) and solubilization capacity were calculated in terms of the solubilization paramter.

In these research, alcohol ethoxylate with three EO groups (AE3), a nonionic surfactant, was used as a main surfactant in microemulsion formation because motor oil, used as a model of oil, has very low hydrophilicity, so to form microemulsion with motor oil had to use a lipophilic surfactant as the alcolhol ethoxylate with the small number of EO groups. But AE3 cannot form microemulsion by itself, so Span 80 was added into the system as a lipophilic linker helped a AE3 to form Winsor Type III microemulsion due to presenting in oil phase and increasing the interaction between tail of AE3 and motor oil. In other word, the Winsor type III cannot occur without added Span 80.

4.1.1 Effect of Hydrophilic Surfactant on Fish Diagram

To investigate the effect of hydrophilic surfactant on fish diagram, the microemulsion formation of AE3/Span 80/motor oil/water system was studied by adding AE7, AE9 and MES as the hydrophilic surfactant at 20 °C, 30 °C, 40 °C and 50 °C. The results represent in Figure 4.1 to 4.4 and table 4.1.Oil-in-Water microemulsion region (a Winsor Type I microemulsion), Water-in-Oil microemulsion region (a Winsor Type II microemulsion) and the middle phase microemulsion region (a Winsor Type III microemulsion) appeared in the phase diagrams regions. The head of the fish is downward and the middle phase microemulsion (a Winsor Type III microemulsion) is in the body of the fish. In the body lay above the fish is Water-in-Oil microemulsion region (a Winsor Type II microemulsion) and below is Oil-in-water microemulsion region (a Winsor Type I microemulsion). The single phase microemulsion (a Winsor Type IV microemulsion) did not present in the phase diagram because of liquid crystal regions occurred. At the critical microemulsion concentration (CμC) or head of the fish is the lowest surfactant concentration required to form the middle phase (a Winsor Type III microemulsion).

Figure 4.1 illustrated the fish diagram of AE3/Span80/motor oil/water system at 30°C. The microemulsion regions that occurred in this system was only a Winsor Type II and Type III microemulsion regions without a Winsor Type I microemulsion region because AE3 and Span 80 were lipophilic surfactants that prefer to solubilize in oil phase more than water phase. So the transition of the system started at a Winsor Type II microemulsion and increasing the concentration of the AE3 and Span 80 the microemulsion would transform to a Winsor Type III microemulsion. But also increasing the concentration of AE3 and Span 80 a Winsor Type I microemulsion did not present in the system.

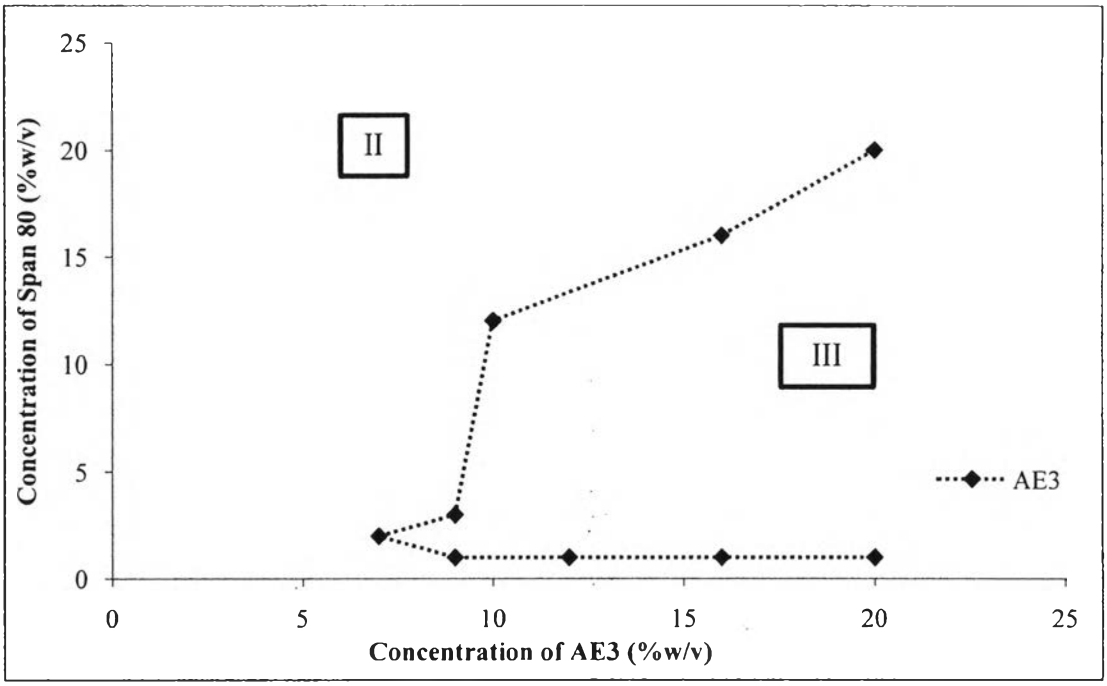

Figure 4.1 Fish diagram of AE3/Span80/motor oil/water system at 30 °C.

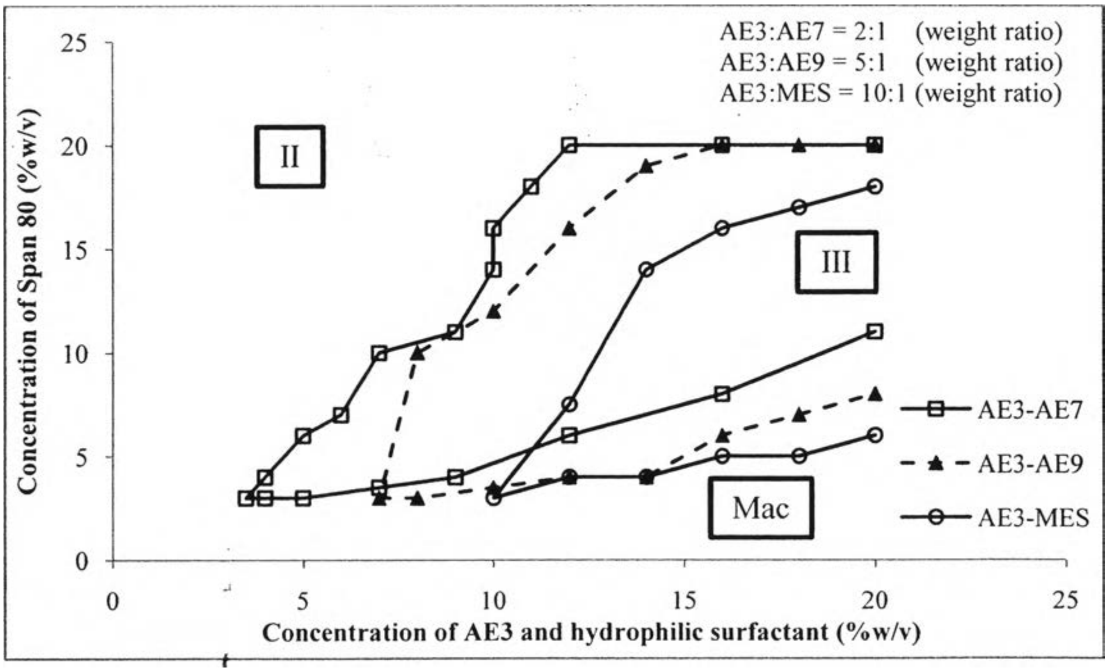

Figure 4.2 Fish diagram of AE3/hydrophilic surfactant/Span 80/motor oil/water system at 30 °C.

Figure 4.2 showed the effect of the hydrophilic surfactant on fish diagram of AE3/ Span 80/motor oil/ water system at 30°C. Hydrophilic surfactants were added in the system were alcohol ethoxylate with seven and nine ethoxylate groups (AE7 and AE9) and methyl ester sulfonate (MES). The result showed that a Winsor Type I occurred in the microemulsion region because the hydrophilic surfactants added in the system would increase a hydrophilicity of the system; therefore, the interaction between water and surfactants were improved. In contrast at the low-concentration of Span80 and high concentration of mixed AEs, macroemulsion is presented because motor oil has very high hydrophobicity that was very hard to form microemulsiom with water.

Moreover, the hydrophobicity of the system was decreased by added hydrophilic surfactant and total surfactant concentration was not get the microemulsion concentration, so the oil drop will solubilize in water phase that was covered by the surfactants in the macroemulsion phase.

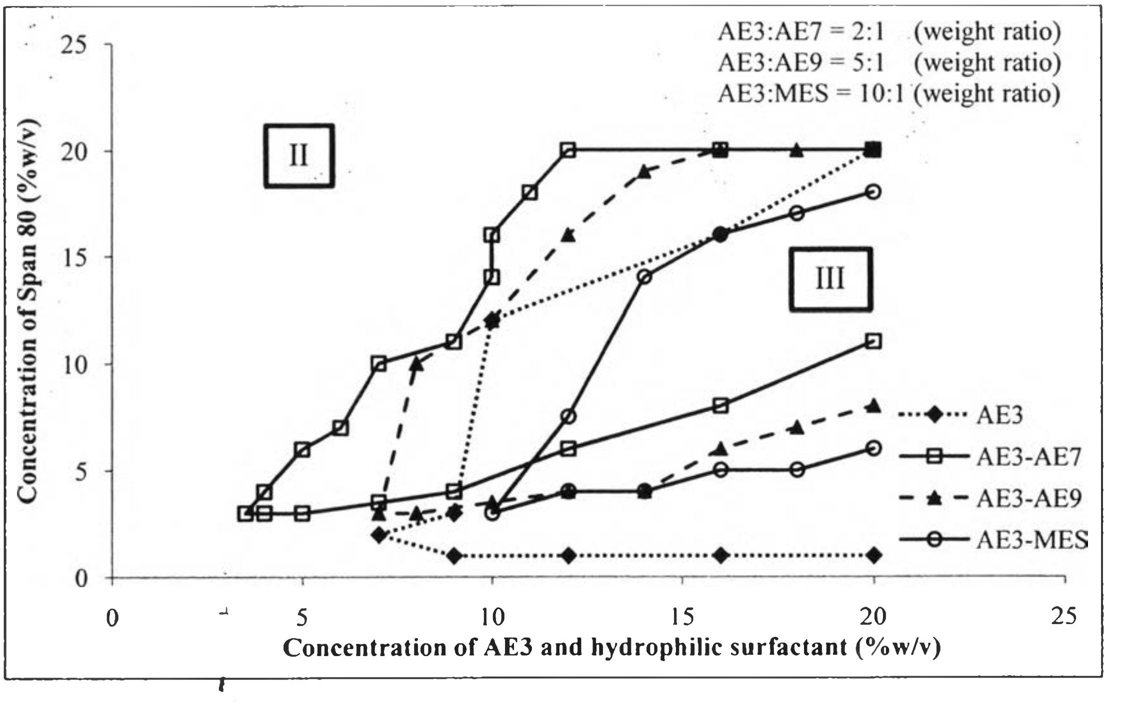

Figure 4.3 The effect of various hydrophilic surfactants on phase diagram (fish diagram) of AE3/Span80/motor oil/water at 30 °C.

Figure 4.3 illustrated the effect of hydrophilic surfactants on CμC of the fish diagram of AE3/Span80/motor oil/water at 30°C. The weight ratio of AE3:AE7, AE3:AE9 and AE3:MES were 2:1, 5:1 and 10:1, respectively. Those ratios were collected from our preliminary results that were not shown here. The result shows that the addition of AE7 as a hydrophilic surfactant provides the most significant effect on the reduction in the CμC because the system would have the optimum hydrophobic-lipophilic balance (HLB). The system with Span 80 has a very low HLB so that the interaction between surfactants and water is decreased. When the AE7 was added, the interaction of the surfactants and water is increased, causing the decreased in the CμC of the system. On the other hand, the CμC value of the system with AE9 addition was not lower than that without added AE9 since the addition of a too high HLB surfactant will decrease the interaction between surfactant and oil, therefore the concentration of alcohol ethoxylate at the first point of forming microemulsion of the system was not improved. The addition of MES into the system was found to increase the CμC of the system. This is because MES is an anionic surfactant which the repulsion forces between the head of the surfactant has the significant effect on the adsorption of the surfactant on the water-oil interface. Furthermore, the HLB of the MES is high but a number of carbons on the tail of MES are 16 to 18 carbons that higher than a number of carbons on tail of the AEs which increasing number of carbon in the tail will increasing hydrophobic that have more effect than hydrophilic effect at the head of the surfactant. Therefore, the system of AE3/AE7/Span 80/motor oil/water was selected for further investigation. The result in the other temperatures showed the same resulted as 30 °C and illustrated in Figure 4.4 to Figure 4.6.

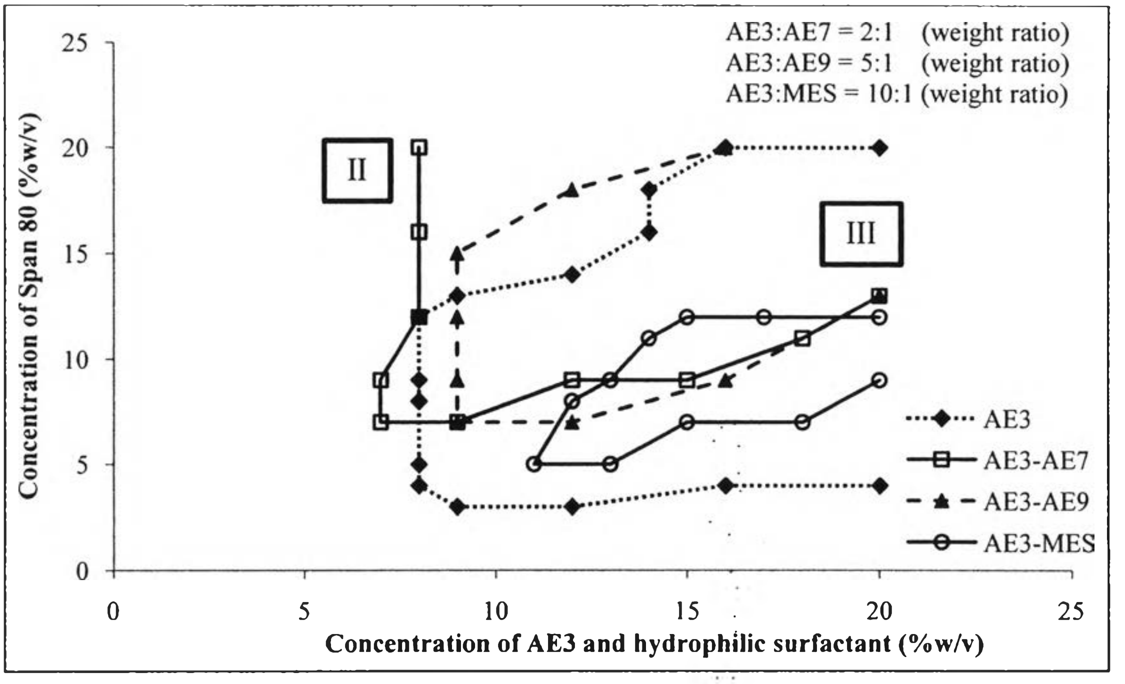

Figure 4.4 The effect of various hydrophilic surfactants on phase diagram (fish diagram) of AE3/Span80/motor oil/water at 20 °C.

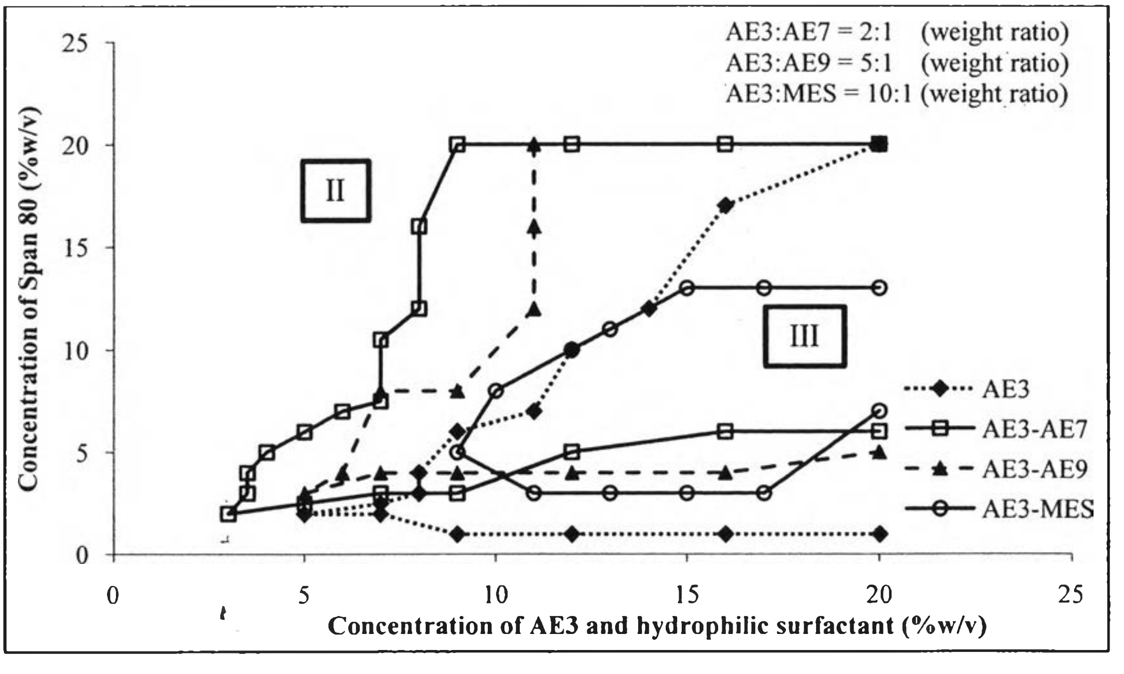

Figure 4.5 The effect of various hydrophilic surfactants on phase diagram (fish diagram) of AE3/Span80/motor oil/water at 40 °C.

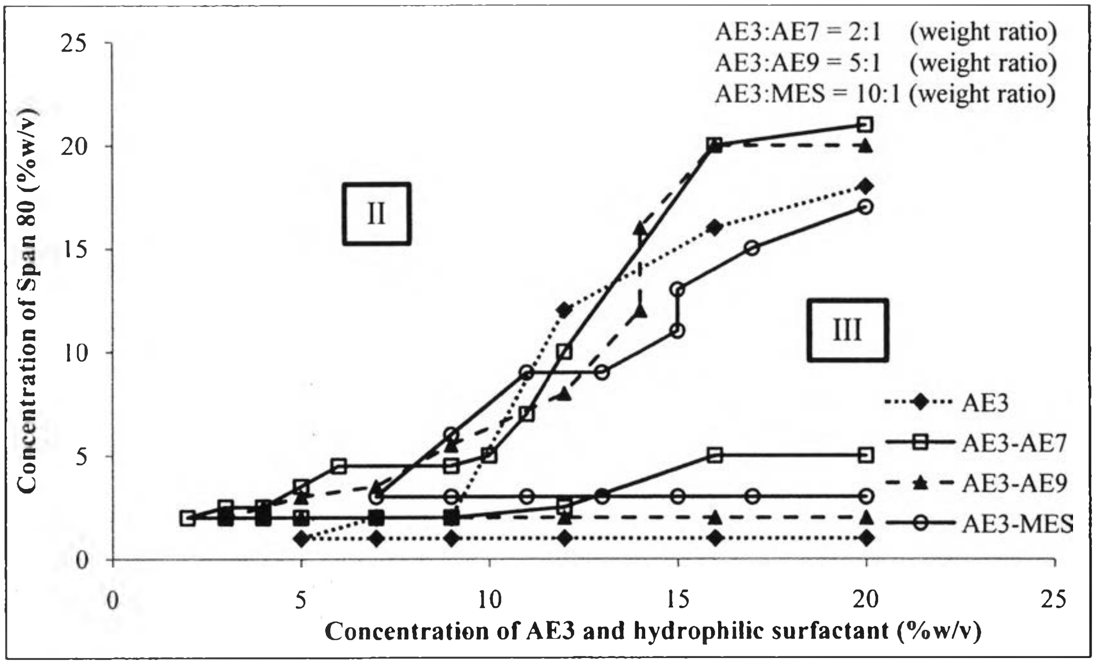

Figure 4.6 The effect of various hydrophilic surfactants on phase diagram (fish diagram) of AE3/Span80/motor oil/water at 50 °C.

Table 4.1 CμC values of AE3/Span80/motor oil/water systems at various hydrophilic surfactants

Surfactant	Linker	Temperature (°C)	Hydrophilic surfactant	CμC (%w/v)
AE3	Span 80	20	N/A	8
			AE7	7
			AE9	9
			MES	11
AE3	Span 80	30	N/A	7
			AE7	5
			AE9	7
			MES	10
AE3	Span 80	40	N/A	5
			AE7	3.5
			AE9	5
			MES	9
AE3	Span 80	50	N/A	5
			AE7	2
			AE9	3
			MES	7

4.1.2 Effect of Temperature on Fish Diagram

In order to study the effect of temperature on the fish diagram, the microemulsion formation of surfactant (AE3)/hydrophilic surfactant (AE7, AE9 and MES)/lipophilic linker (Span80) /motor oil/water system were investigated at 20 °C, 30 °C,40 °C and 50 °C. the result represent in Figure 4.7 to 4.10 and table 4.2

Figure 4.7 illustrated the fish diagram of AE3/Span80/motor oil/water system at different temperature. The head of the fish is downward. The middle phase microemulsion region (a Winsor type III microemulsion) is in the body of the fish. The body lay below the fish is Oil-in-Water microemulsion region (a Winsor type I).

The temperature showed a significant effect on the critical microemulsion concentration (CμC). The CμC decreased with increasing temperature. The lowest of CμC was achieved at 50°C. The result can be explained in that the system reached optimum HLB at lower concentration of alcohol ethoxylate due to the dehydration of EO groups, hence, AE3 became more hydrophobic at the high temperature.

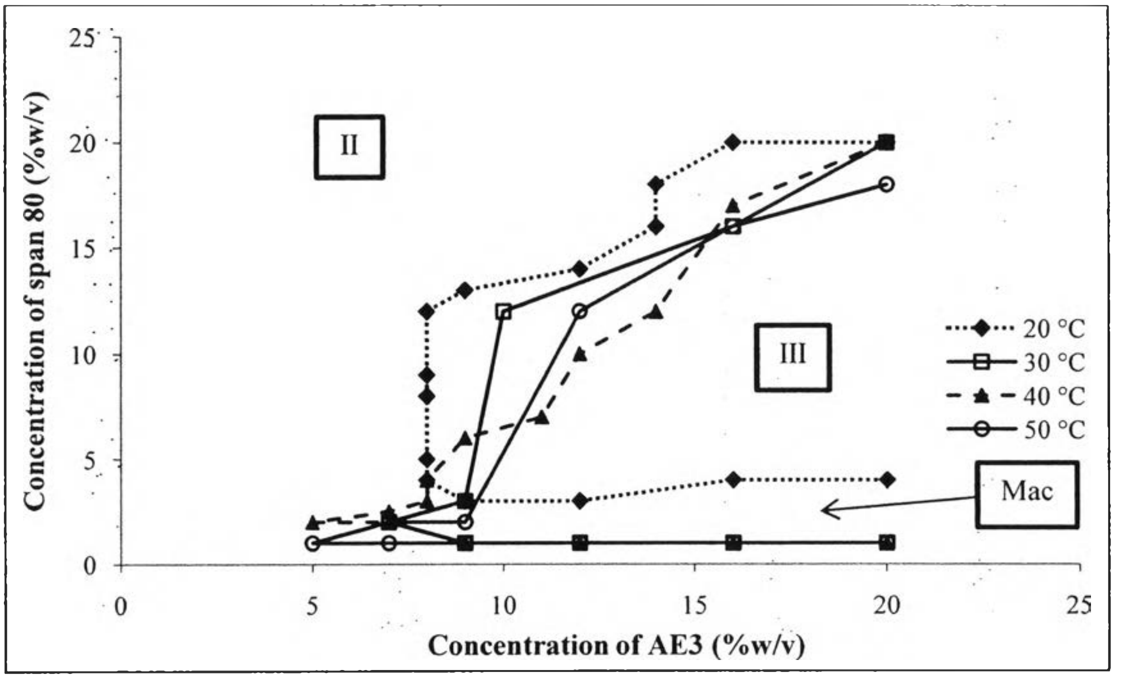

Figure 4.7 Fish diagram of AE3/Span 80/motor oil/water system at different temperature.

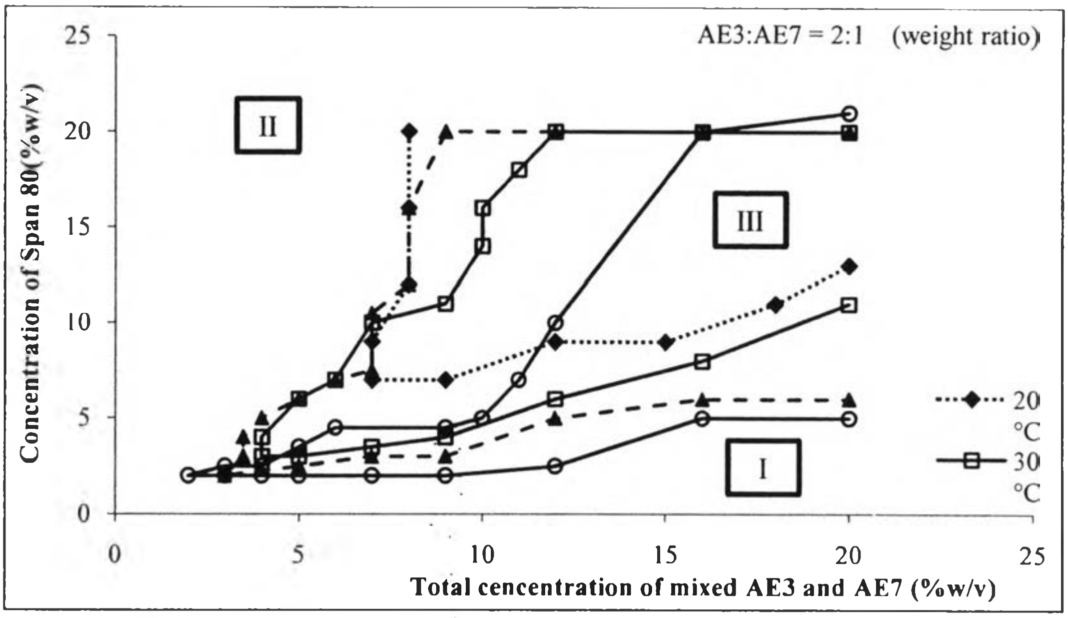

Figure 4.8 Fish diagram of AE3/AE7/Span 80/motor oil/water system at different temperature.

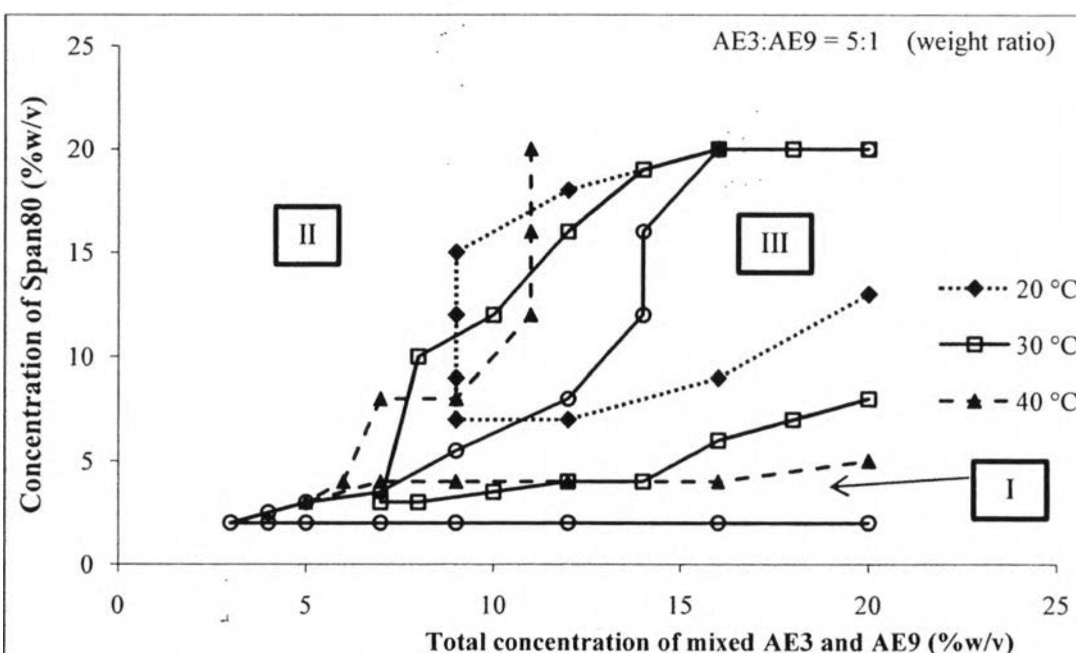

Figure 4.9 Fish diagram of AE3/AE9/Span 80/motor oil/water system at different temperature.

Figure 4.8 and 4.9 illustrated the fish diagram of AE3/AE7/Span80/motor oil/water system and AE3/AE9/Span80/motor oil/water system, respectively. The result show that Winsor Type I can be formed as the same reason that discussed in the effect of hydrophilic surfactant on fish diagram section. Temperature has the significant effect on decreasing CμC. However, a macroemulsion was formed at the low temperature (20°C and 30°C), a macroemulsion would disappear at the high temperature (40°C and 50°C). The result can be explained by the hydrogen bonds were break when the temperature increased; therefore the strength of hydrogen bonds was reduced at higher temperature. In other words, AEs become more hydrophibic at higher temperature which had more similar polarity with motor oil. So, the system reached hydrophilic-lipophilic balance at lower surfactant and lipophilic linker concentrations and the capacity to solubilize equal amount of oil and water increased in temperature.

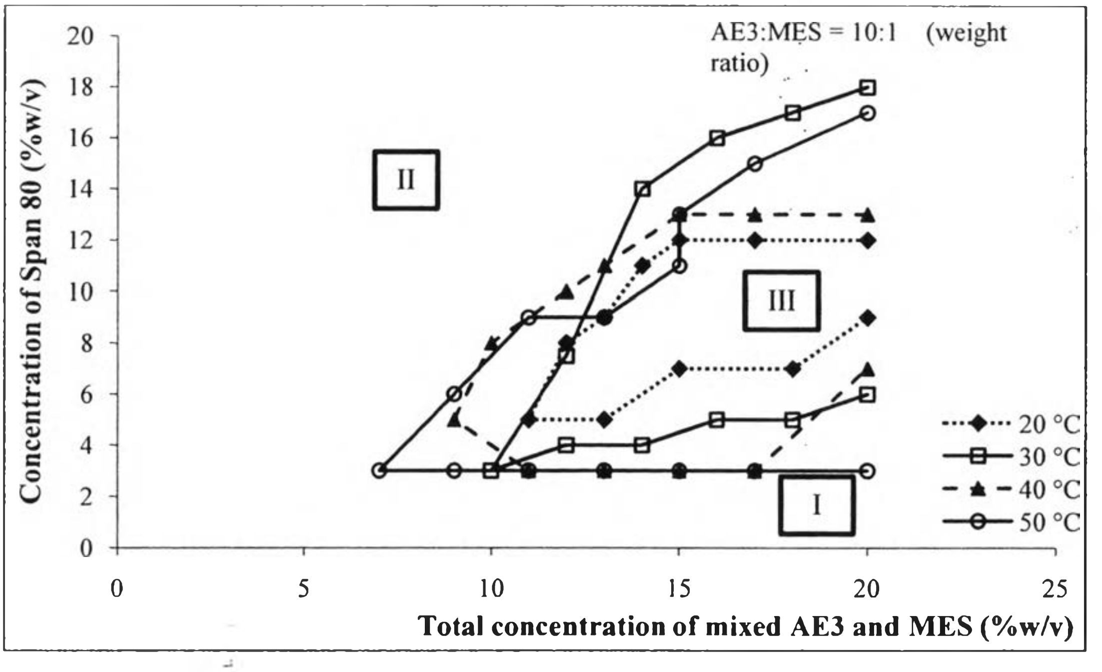

Figure 4.10 Fish diagram of AE3/MES/Span 80/motor oil/water system at different temperature.

Figure 4.10 illustrated the fish diagram of AE3/MES/Span80/motor oil/water system. The result showed that the CμC with increasing the temperature slightly decrease when compare with the other systems because MES was an anionic surfactant that temperature has less effect on its head group. For improving this system, adding NaCl in the system will decrease the repulsion force between the head of MES and increase the adsorption of MES at the interface.

Table 4.2 CμC values of AE3/Span80/motor oil/water systems at various temperatures

Surfactant	Linker	Hydrophilic surfactants	Temperature (°C)	CμC (%w/v)
AE3	Span 80	N/A	20	8
		N/A	30	7
		N/A	40	5
		N/A	50	5
AE3	Span 80	AE7	20	7
		AE7	30	5
		AE7	40	3.5
		AE7	50	2
AE3	Span 80	AE9	20	9
		AE9	30	7
		AE9	40	5
		AE9	50	3
AE3	Span 80	MES	20	11
		MES	30	10
		MES	40	9
		MES	50	7

4.2 Solubilization Parameter (SP)

After equilibrium, the height of each liquid phase was measured using a cathetometer. 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 Effect of Hydrophilic Surfactant on SP

Solubilization Parameter (SP) of the surfactant system consisting of AE3/hydrophilic surfactant/lipophilic linker/motor oil/water system were examined with three hydrophilic surfactants (AE3, AE7 and MES) at fixed the lipophilic linker (Span 80) concentration at 7%w/v. The SP is defined as the volume of oil solubilized (SPo) or water solubilized (SPw) per weight of total surfactant in tne microeowmulsion phase (TanTakit, P. et., 2009)

Figure 4.11 to Figure 4.14 illustrated the effect of hydrophilic surfactants on the phase behavior of motor oil in term of SPo and SPw in different temperatures. The transition of microemulison phase shifted from a Winsor type II microemulsion to a Winsor Type III microemulsion with increasing concentration of AE3 and hydrophilic surfactant. The SPw slightly increased with increasing AEs concentration while the SPo was high in the Winsor Type II microemulsion and dramatically dropped in the Winsor Type III microemulsion region. Among the studied of hydrophilic surfactants, AE7 was the most efficient to enhance the Winsor Type III microemulsion formation because it provided the largest middle phase region at the lowest concentration. Moreover, at the low temperature (20 and 30 °C) in the systems with AE7 or AE9, macroemulsion occurred at low concentrations since both surfactants are hydrophilic surfactants that can increase the hydrophilicity of the system and increase the solubilization of oil in water phase but at low concentrations the amount of the surfactants is not enough to adsorption at the oil and water interface, so the oil can combine each other to form a bigger drop and stay in the water phase with the surfactants which appeared turbid, known as macroemulsion. Furthermore, at the concentrations of mixed AEs, the macroemulsion also occurred due to the limitation of the oil solubilization in water phase.

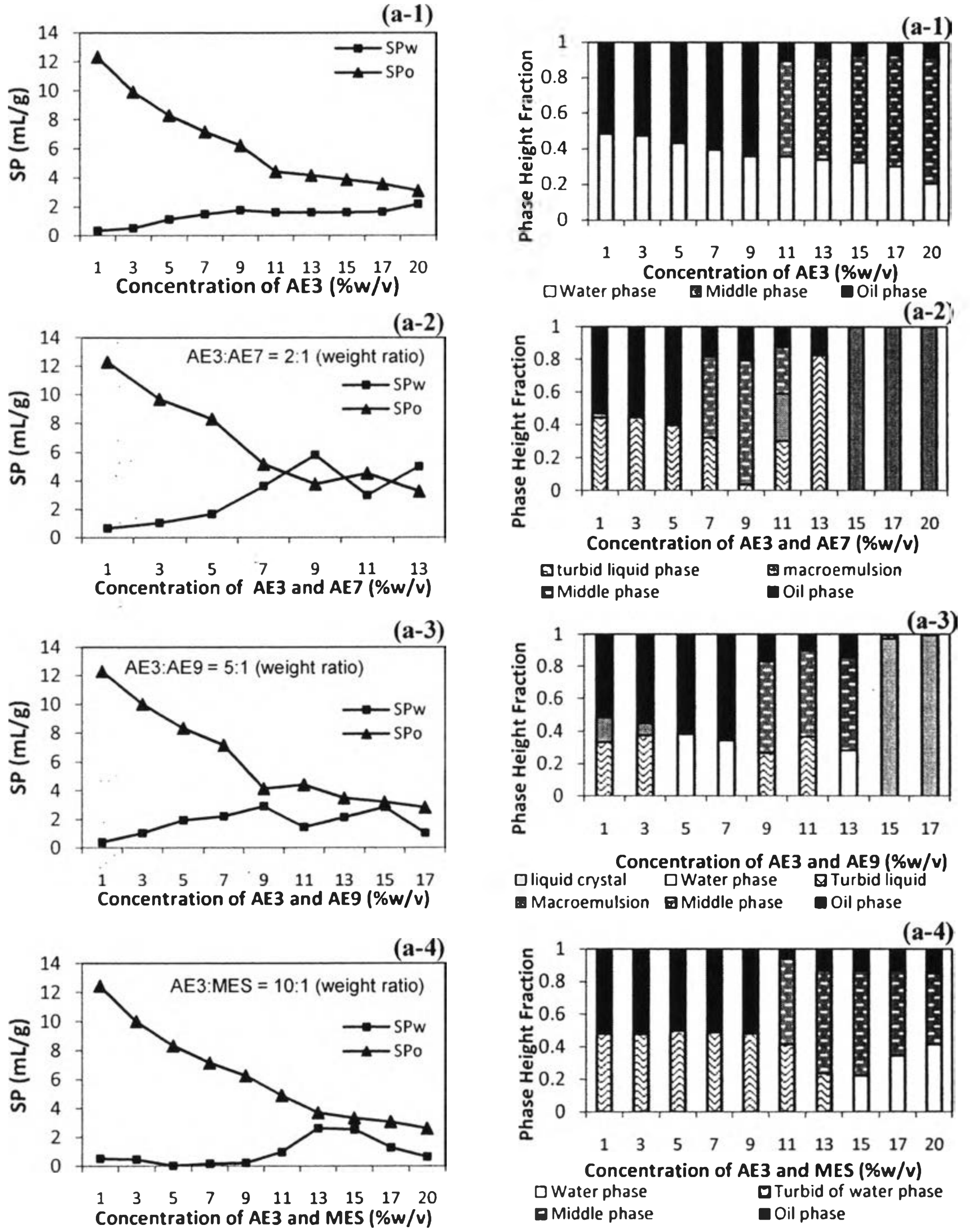

Figure 4.11 Solubilization Parameters (SP) and phase height fraction as a function of mixed surfactants concentration comprising AE3/hydrophilic surfactants/Span 80/motor oil/water at 20 °C (a-1) pure AE3, (a-2) AE3 with AE7, (a-3) AE3 with AE9 and (a-4) AE3 with MES.

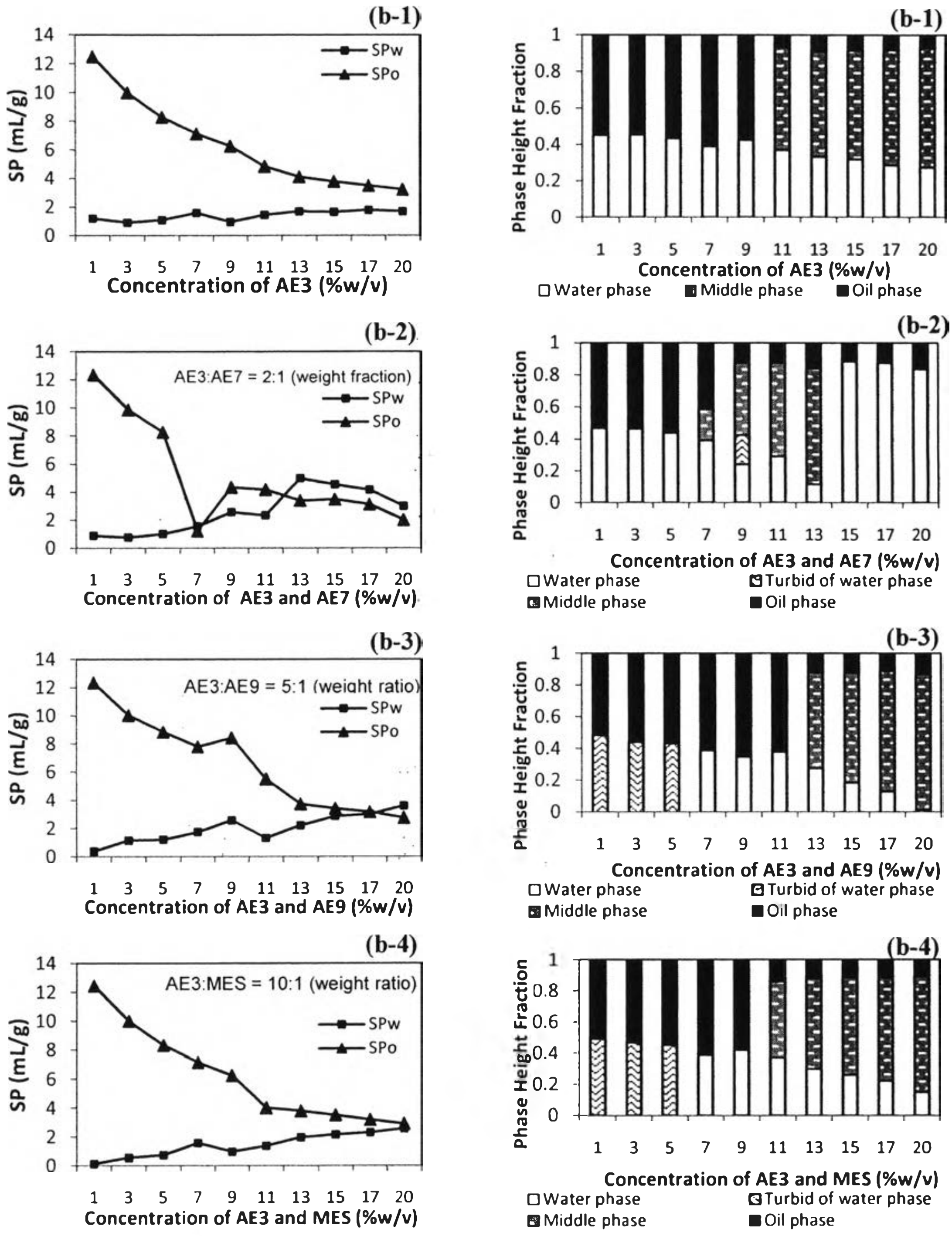

Figure 4.12 Solubilization Parameters (SP) and phase height fraction as a function of mixed surfactants concentration comprising AE3/hydrophilic surfactants/Span 80/motor oil/water at 30 °C (b-1) pure AE3, (b-2) AE3 with AE7, (b-3) AE3 with AE9 and (b-4) AE3 with MES.

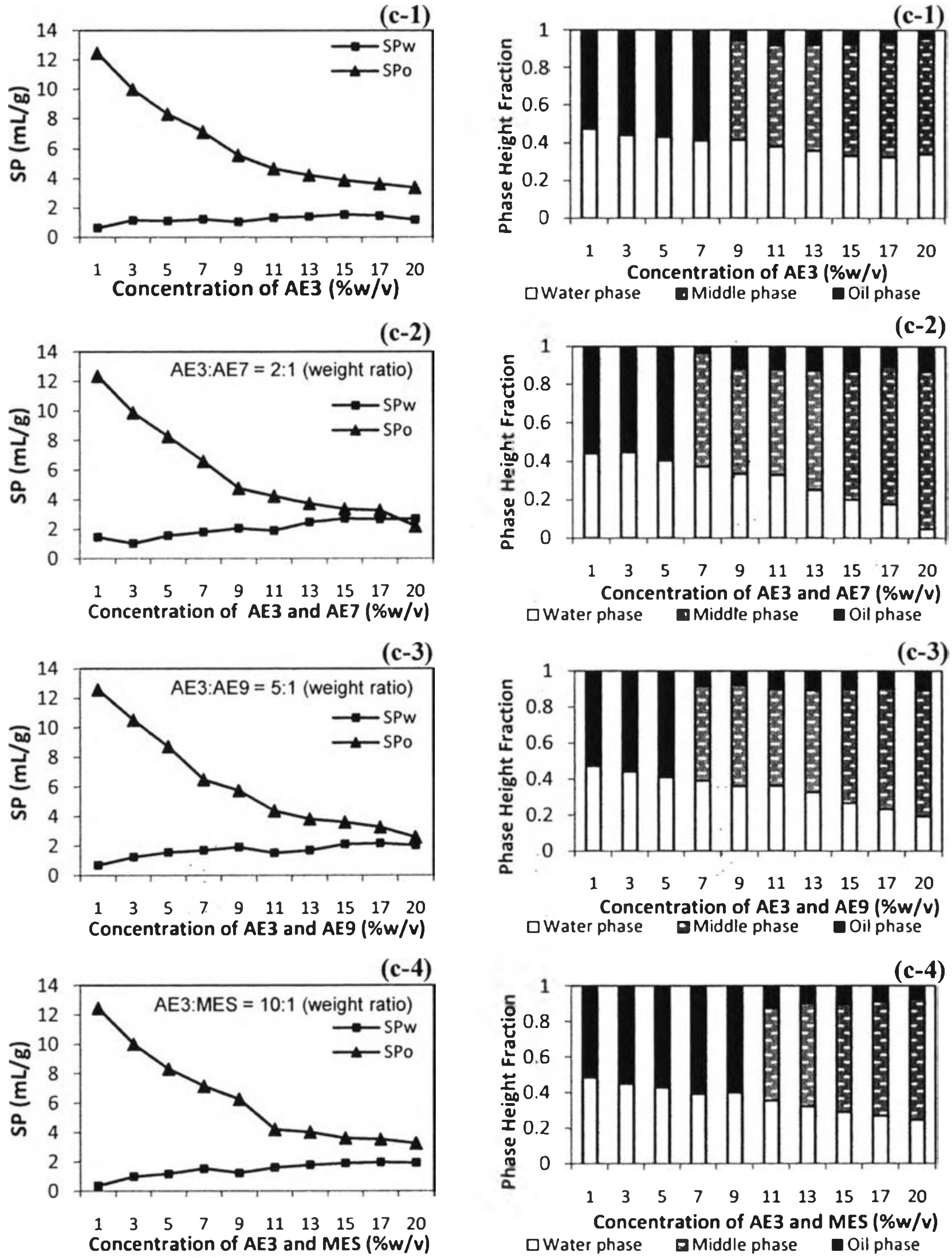

Figure 4.13 Solubilization Parameters (SP) and phase height fraction as a function of mixed surfactants concentration comprising AE3/hydrophilic surfactants/Span 80/motor oil/water at 40 °C (c-1) pure AE3, (c-2) AE3 with AE7, (c-3) AE3 with AE9 and (c-4) AE3 with MES.

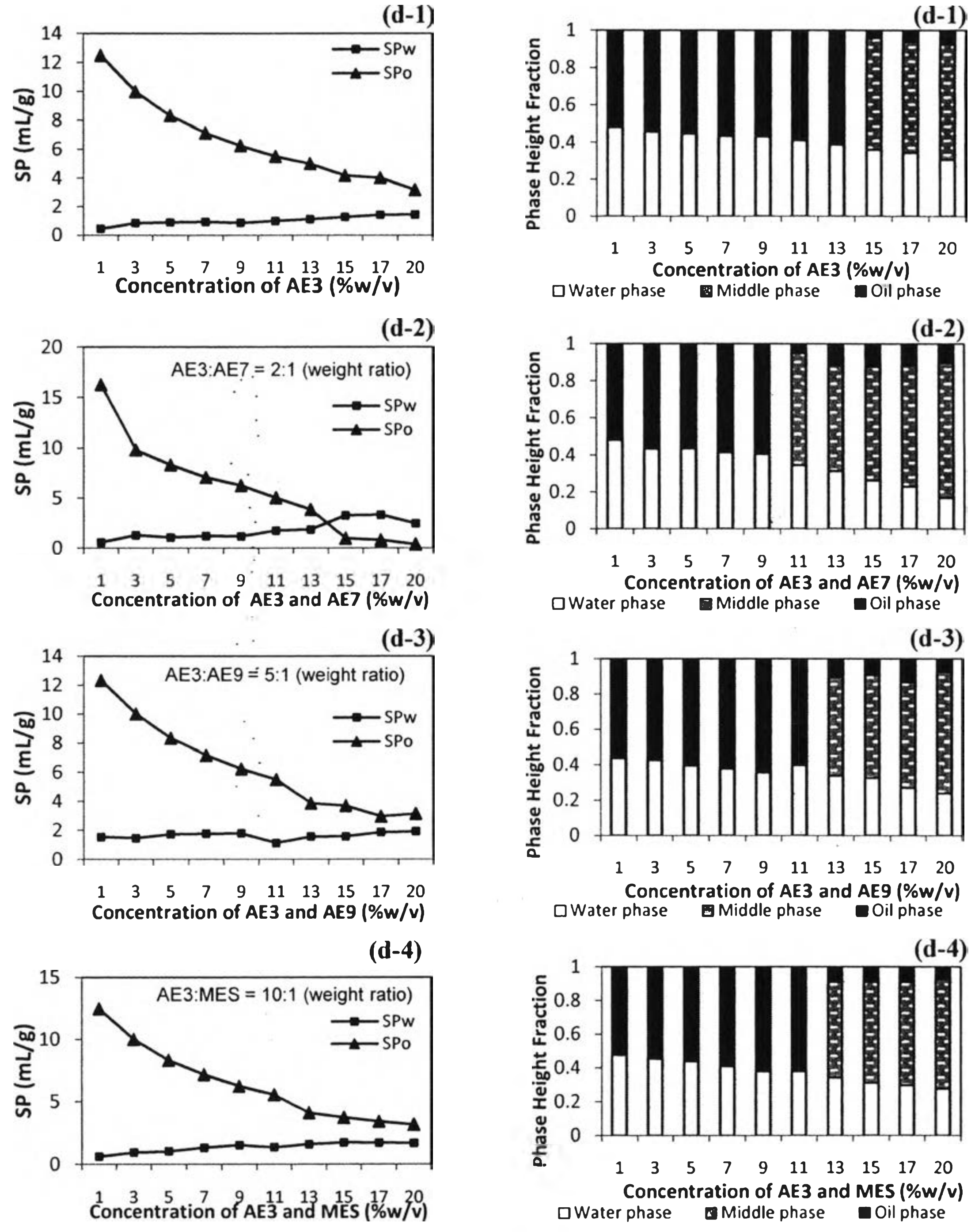

Figure 4.14 Solubilization Parameters (SP) and phase height fraction as a function of mixed surfactants concentration comprising AE3/hydrophilic surfactants/Span 80/motor oil/water at 50 °C (d-1) pure AE3, (d-2) AE3 with AE7, (d-3) AE3 with AE9 and (d-4) AE3 with MES.

4.2.2 Effect of Temperature on SP

In order to study the effect of temperature on SP were examined at four different temperature (20°C, 30°C, 40°C and 50°C) for constant of liphophilic linker (Span 80) concentration at 7%w/v as same as previous studied.

Figure 4.15 to Figure 4.18 indicated the phase behavior of motor oil in terms of SPw and SPo and the phase height fraction of water, middle and oil phase. The Winsor type II microemulsion moved to the Winsor type III microemulsion when increasing the concentration of mixed alcohol ethoxylates. At the 40°C, the volume fraction of the middle phase was larger than the other temperatures. Moreover, mostly for the low temperature (20°C and 30°C), the macroemulsion are appeared at the high concentration of AEs and low concentration of Span 80 or at the high concentration of Span80 and low concentration of AE3 but it will disappeared at the high temperature. In the case of AE3 which is hydrophobic surfactant, the SPw slightly increased and then remain constant with increasing AE concentration while the SPo was high in the W/O microemulsion region and dramatically dropped in the middle phase region. While adding AE7, AE9 and MES which are hydrophilic surfactant into the system, the SPw at the low temperature (20°C and 30°C) were increasing with increasing the cocnetration of AEs while the SPo was high in the W/O microemulsion region and dramatically dropped in the middle phase region. In addition, for AE7 system at the low temperature the Winsor Type I microemulsion the value of SPo became lower than SPw. At the highest temperature (50°C), the SPo was decreased when compare with the low temperature. From the results, the result can be concluded that temperature facilitates the solubilization of oil, helping the formation of a Winsor Type III microemulsion.

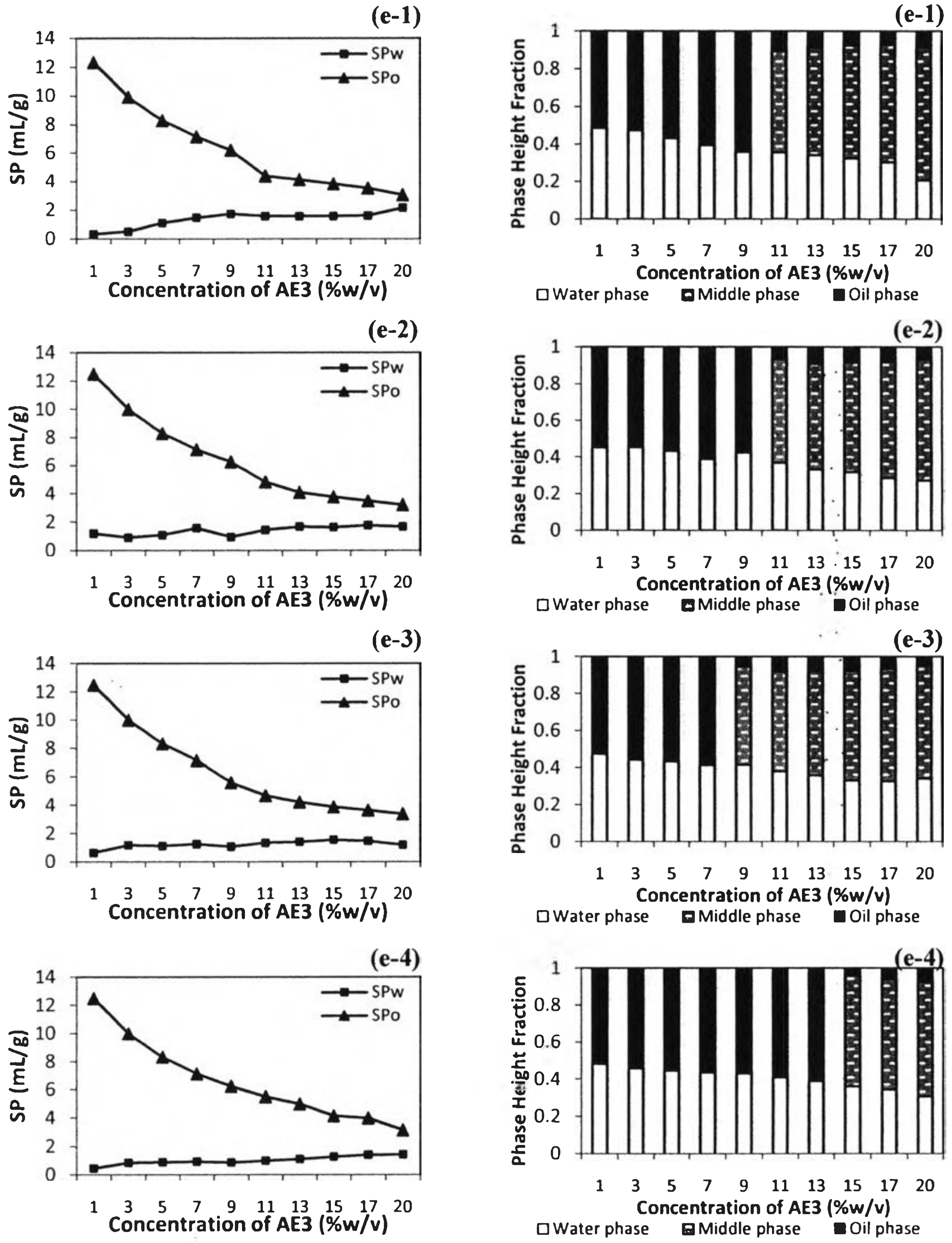

Figure 4.15 Solubilization Parameters (SP) and phase height fraction as a function of AE3 concentration comprising AE3/Span 80/motor oil/water: (e-1) at 20 °C, (e-2) at 30 °C, (e-3) at 40 °C, and (e-4) at 50 °C.

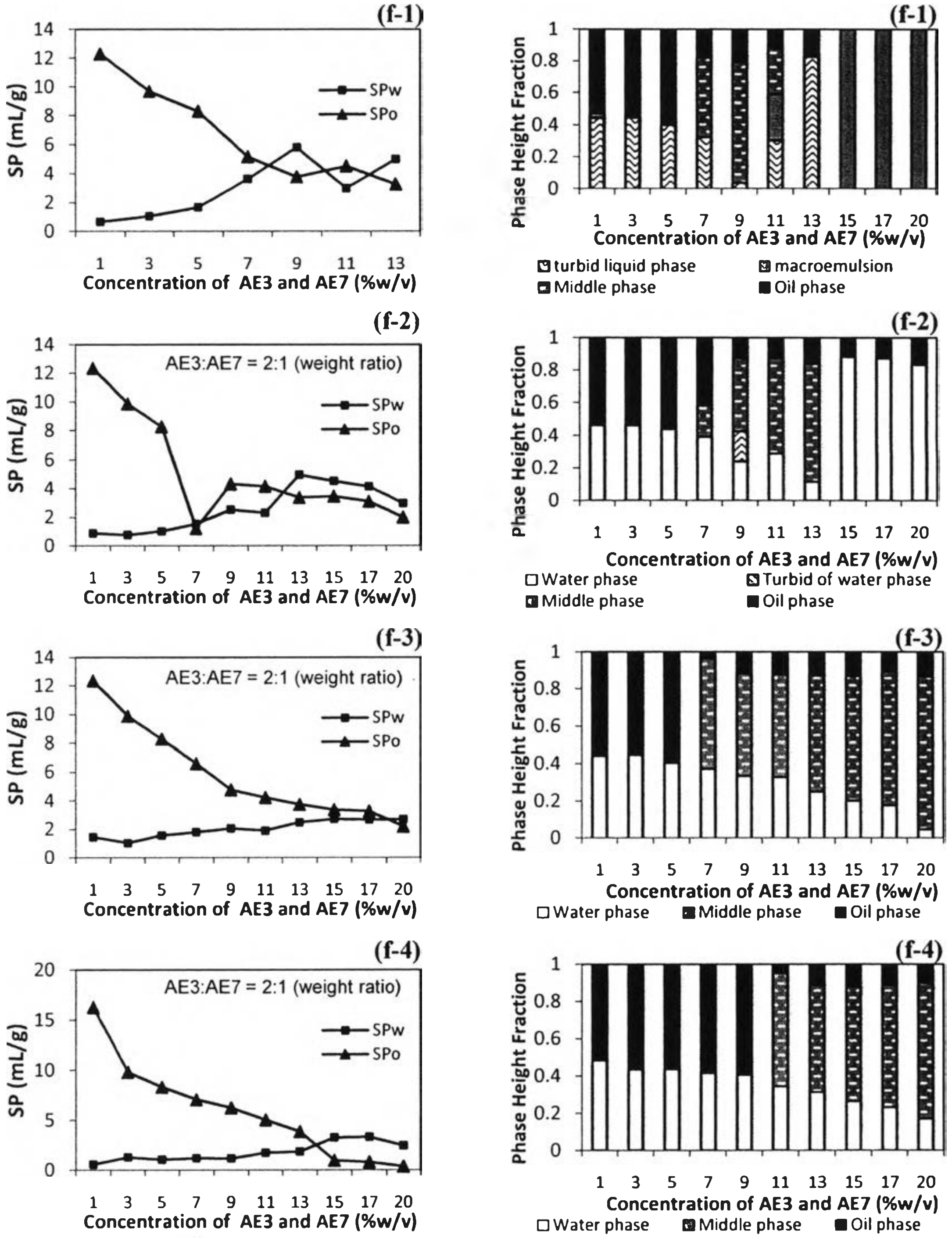

Figure 4.16 Solubilization Parameters (SP) and phase height fraction as a function of mixed surfactants of AE3 and AE7 concentration comprising AE3/AE7/Span 80/motor oil/water: (f-1) at 20 °C, (f-2) at 30 °C, (f-3) at 40 °C, and (f-4) at 50 °C.

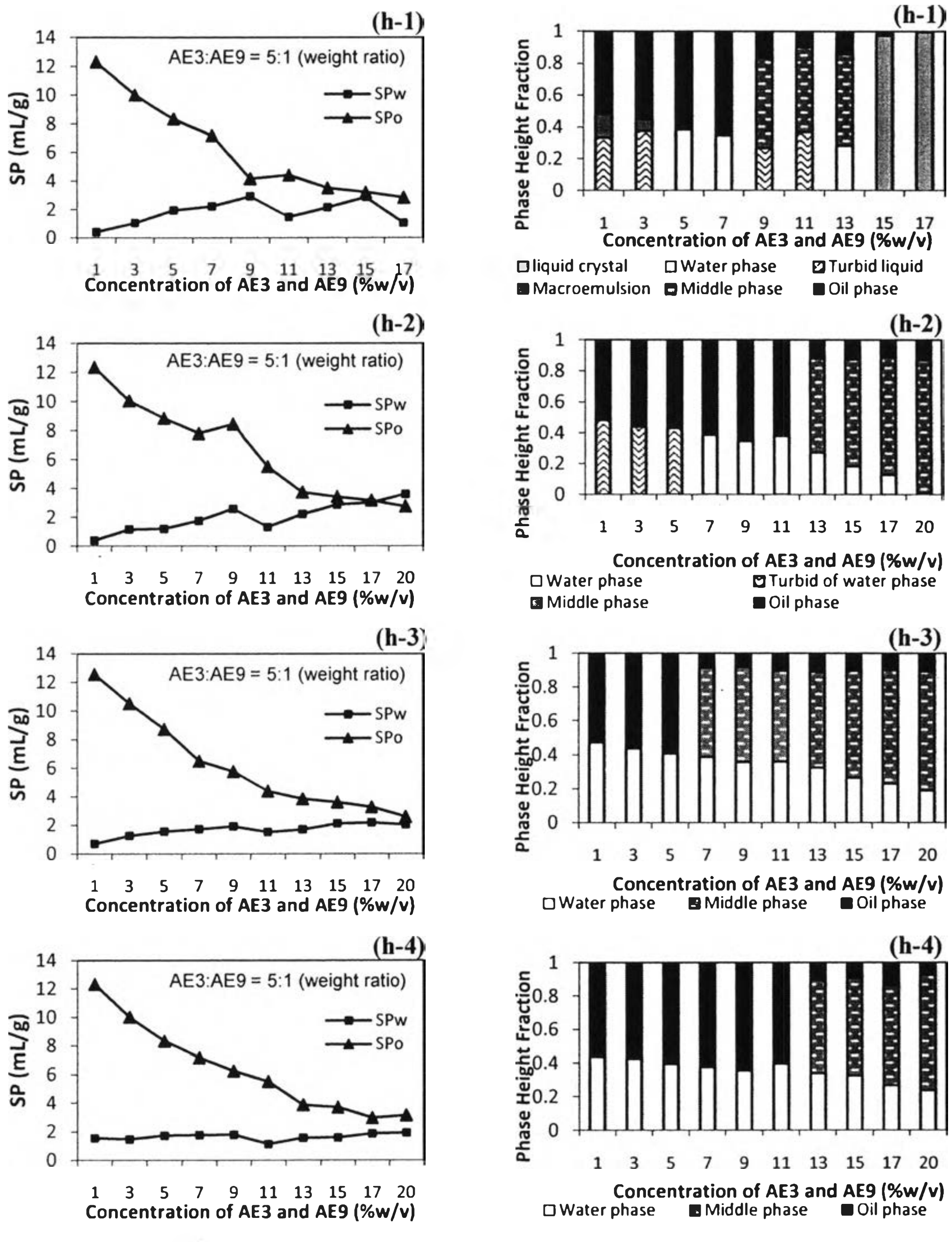

Figure 4.17 Solubilization Parameters (SP) and phase height fraction as a function of mixed surfactants of AE3 and AE9 concentration comprising AE3/AE9/Span 80/motor oil/water: (h-1) at 20 °C, (h-2) at 30 °C, (h-3) at 40 °C, and (h-4) at 50 °C.

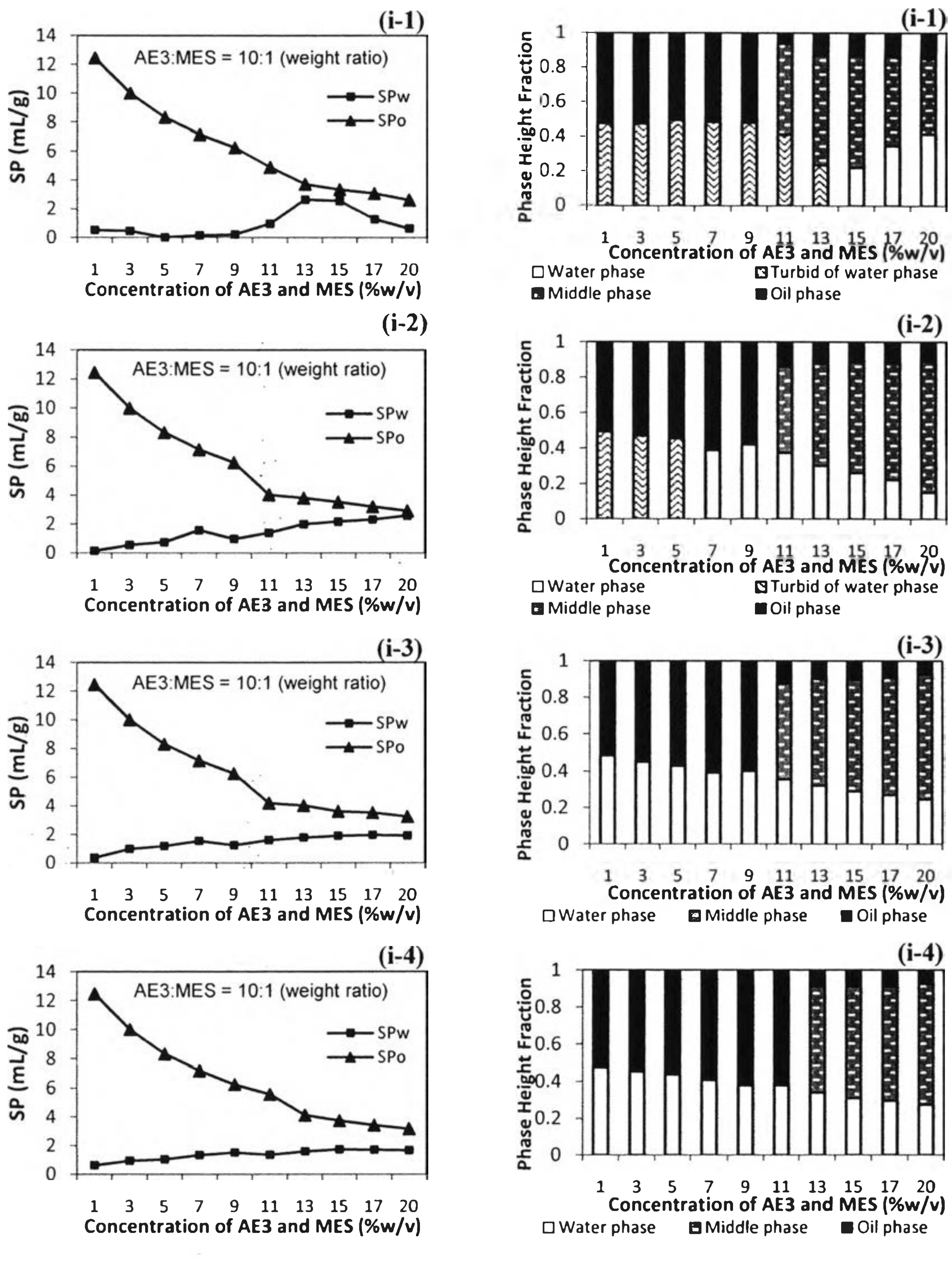

Figure 4.18 Solubilization Parameters (SP) and phase height fraction as a function of mixed surfactants of AE3 and MES concentration comprising AE3/MES/Span 80/motor oil/water: (i-1) at 20 °C, (i-2) at 30 °C, (i-3) at 40 °C, and (i-4) at 50 °C.

4.3 Critical Micelle Concentration (CMC)

The critical micelle concentration (CMC), one of the main properties for surfactants, is the concentration at which surfactant molecule in solutions start to form micelle. Surface tensions of the surfactant solution at different concentrations were measured and plotted versus logarithmic concentrations. The point at which the surface tension levels off when surfactant concentration is increased is taken as the CMC. The surface tension of the surfactant at CMC, γ_{CMC}, indicates the ability of surfactant's lowering surface tensions, and accordingly CMC indicates the efficiency.

The CMC of mixed surfactants between AE3, hydrophilic surfactants (AE7, AE9 and MES) and lipophilic linker (Span 80) systems are shown in Figure 4.18, 4.19 and 4.20, respectively. The approximately CMC values of those three systems are 0.0022, 0.004, and 0.005% wt/vol, respectively. The CMC of systems are slightly increased with increasing EO content of hydrophilic surfactants. An increase in the EO content will increase water solubility by increasing the interaction between EO and water molecule resulting in an increase the amount of energy required to dehydrate the molecule during its form micelle. The formation of micelles represents an important interfacial activity because they eventually lead to formation of microemulsion and in turn to reduction in IFT.

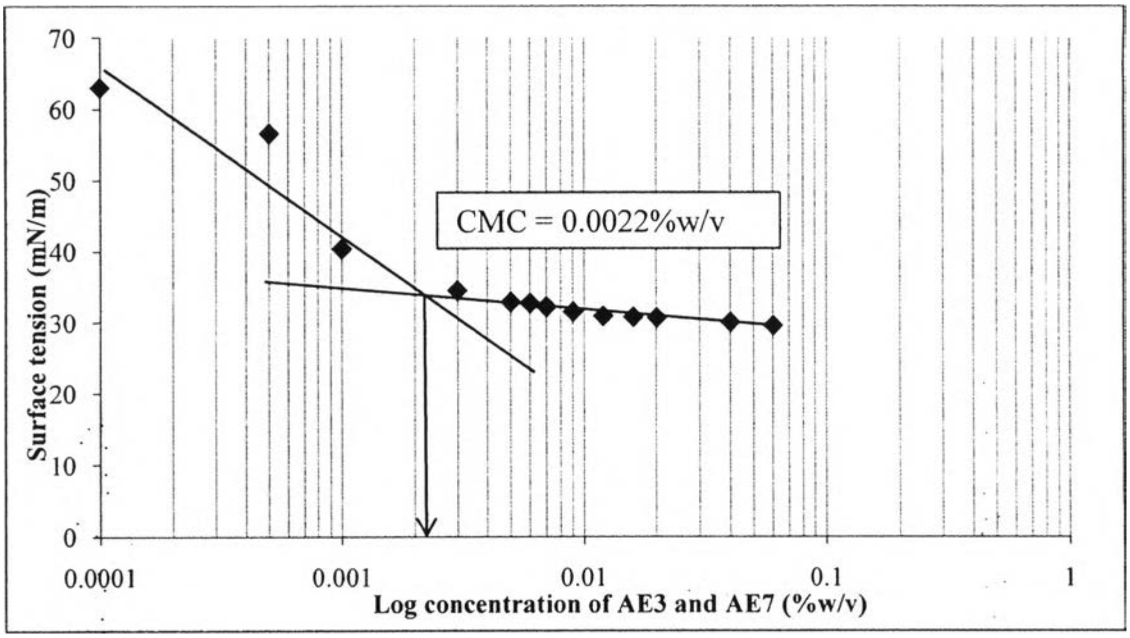

Figure 4.19 Critical micelle concentration (CMC) of mixed surfactants of AE3, AE7 and Span 80 system at 30 °C.

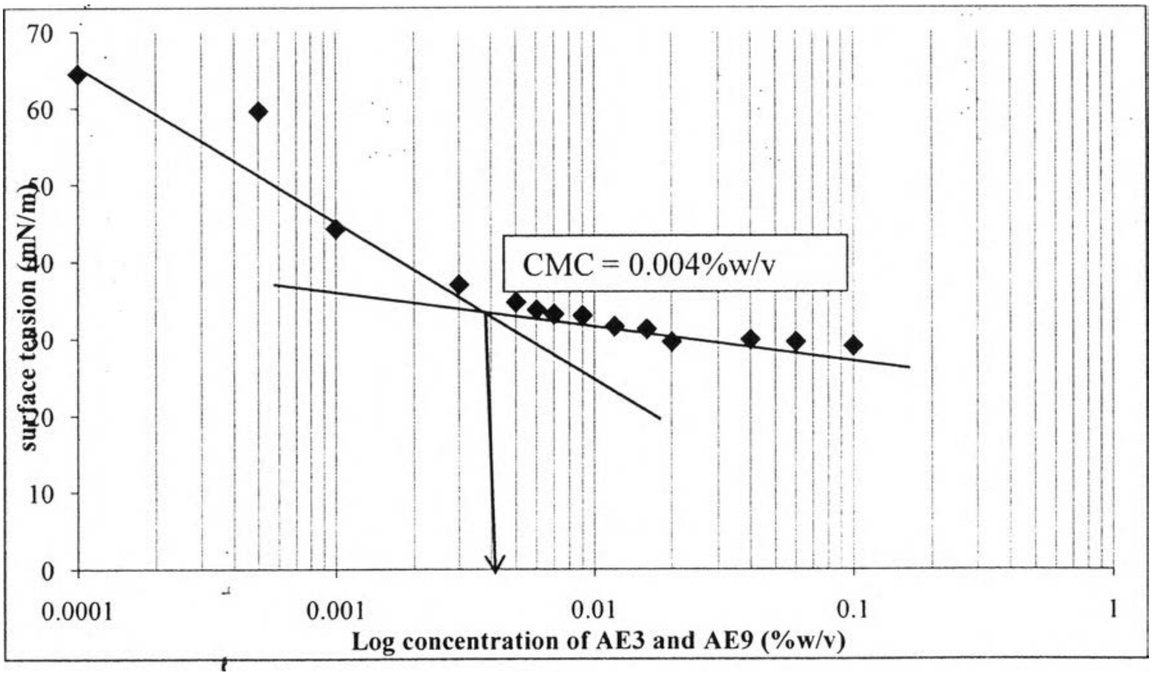

Figure 4.20 Critical micelle concentration (CMC) of mixed surfactants of AE3, AE9 and Span 80 system at 30 °C.

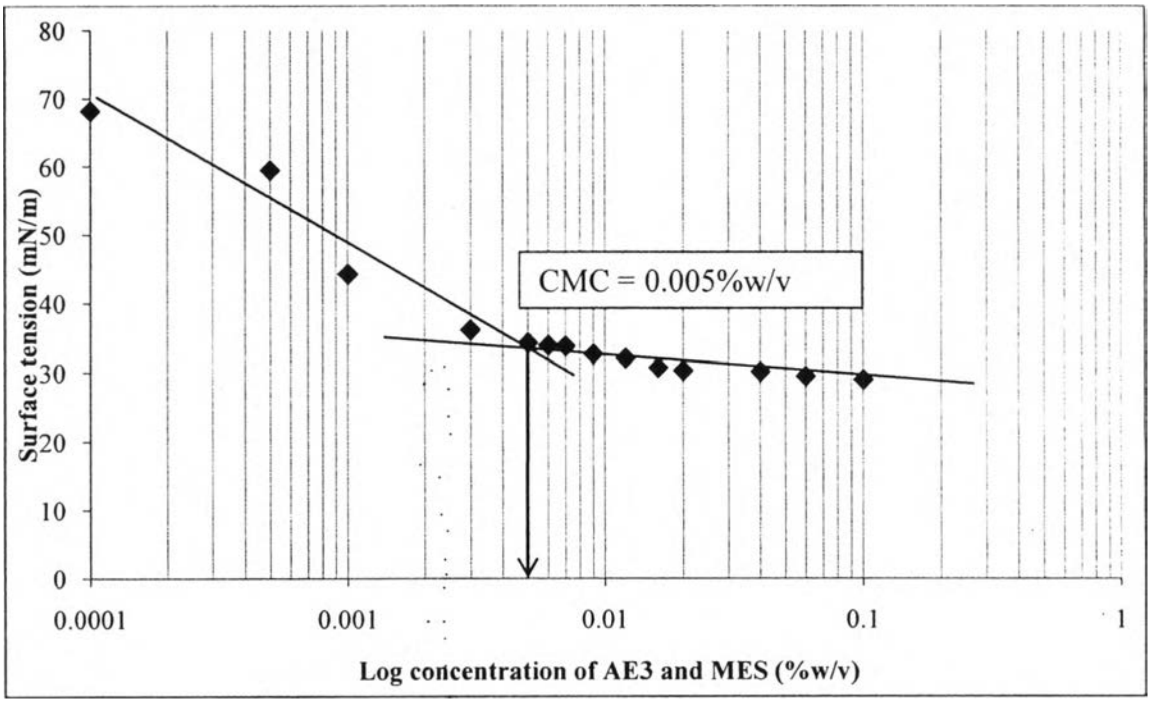

Figure 4.21 Critical micelle concentration (CMC) of mixed surfactants of AE3, MES and Span 80 system at 30 °C.