CHAPTER IV
RESULTS AND DISCUSSION

The purpose of this work was to investigate the microemulsion formation of motor oil with AEs having different EO groups under the presence of cosurfactant with different chain lengths at various temperatures. The microemulsion formation of surfactant/cosurfactant/motor oil/water systems to form different Winsor Types (I, II, III, IV) microemulsion were obtained, known as fish diagrams. In order to enable to choose the suitable conditions for a specific application, the effects of number of EO groups of AEs, cosurfactant chain length, and temperature on microemulsion formation and solubilization capacity were studied. In addition, cloud point temperature of added alcohols into AEs was also investigated. In all experiments, the surfactant, and cosurfactant concentrations were expressed in weight percent per volume of the aqueous solution (%w/v).

4.1 Microemulsion Formation Experiment and Fish Diagram

The main purpose of this section was to classify the types of microemulsions by plotting fish diagrams of cosurfactant concentration versus surfactant concentration at various temperatures, alcohols, and AEs.

The fish diagrams are generally used to determine a minimum surfactant concentration required to form Winsor Type III microemulsion which is known as the critical microemulsion concentration (CμC). Moreover, the intersection between the three microemulsion regions (Winsor Types I, II, and III) or point E is the minimum concentrations of surfactant and cosurfactant are required to form a single microemulsion phase (Winsor Type IV microemulsion) (Yang, X.D *et al.*, 2007). The smaller the values at point E, the larger the solubilization capacity of the system.

4.1.1 The Effect of Temperature on Fish Diagram

In order to study the effect of temperature on the fish diagram, the microemulsion formation of AEs/alcohol (*n*-butanol, *n*-hexanol, and *n*-octanol)/ motor oil/water system was investigated at 20 °C, 30 °C, 40 °C, and 50 °C. The results represent in Figure 4.1 to Figure 4.10 and Table 4.1.

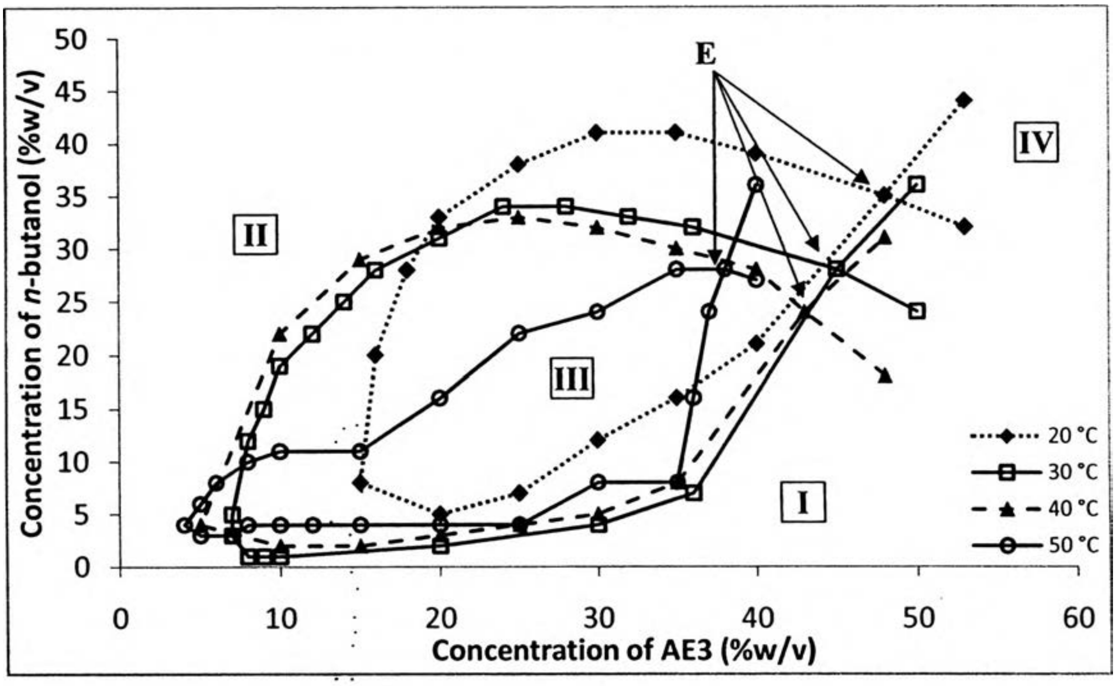

Figure 4.1 Fish diagram of AE3/*n*-butanol/motor oil/water system at different temperatures.

Figure 4.1 illustrated the fish diagrams of AE3/*n*-butanol/motor oil/water system at different temperatures. The fish head is pointing downward and the fish tail is pointing upward. The middle microemulsion region (Winsor Type III microemulsion) is in the body of the fish, the single microemulsion region (Winsor Type IV microemulsion) is located at fish tail. The body lay above is Water-in-Oil microemulsion region (Winsor Type II microemulsion) and below is Oil-in-Water microemulsion region (Winsor Type I microemulsion). At the critical microemulsion concentration (CμC) or head of the fish is the lowest surfactant concentration required to form the middle phase (Winsor Type III microemulsion).

The temperature showed a significant effect on both the CμC and the composition at point E. The CμC decreased with increasing temperature. The lowest value of CμC was achieved at 50 °C (shown in Table 4.1). Therefore, the system reached hydrophilic-lipophilic balance (HLB) at lower surfactant concentration.

Nevertheless, the concentration of AE3 at point E also decreased with increasing temperature, suggesting that an increase in temperature can reduce the quantity of AE3 to form Winsor Type IV microemulsion due to the dehydration of EO groups; hence, AE3 became more hydrophobic at higher temperatures.

By using *n*-butanol as cosurfactant, Winsor Type III microemulsion can be formed with only AE3. More detail will be further discussed in section 4.1.3.

The fish diagrams of AE3 and AE5/*n*-hexanol/motor oil/water systems were illustrated in Figures 4.2 and 4.3, respectively. The fish diagrams of both AE3 and AE5 with *n*-hexanol systems behaved like the fish diagrams of AE3 with *n*-butanol as the previous discussion. The lowest CμC values of AE3 and AE5 by using *n*-hexanol as cosurfactant were achieved at 50 °C (3.0 %w/vAE3 and 2.5 %w/vAE5, respectively). Moreover, the lowest concentrations of both AE3 and AE5 at point E were also achieved at 50 °C.

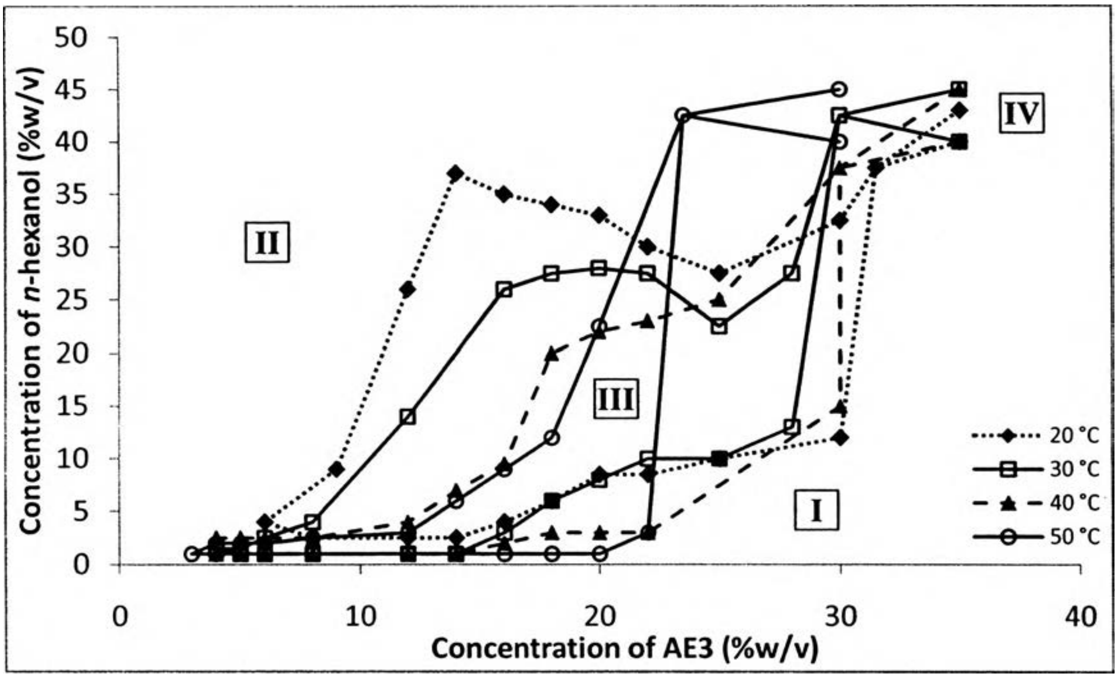

Figure 4.2 Fish diagram of AE3/*n*-hexanol/motor oil/water system at different temperatures.

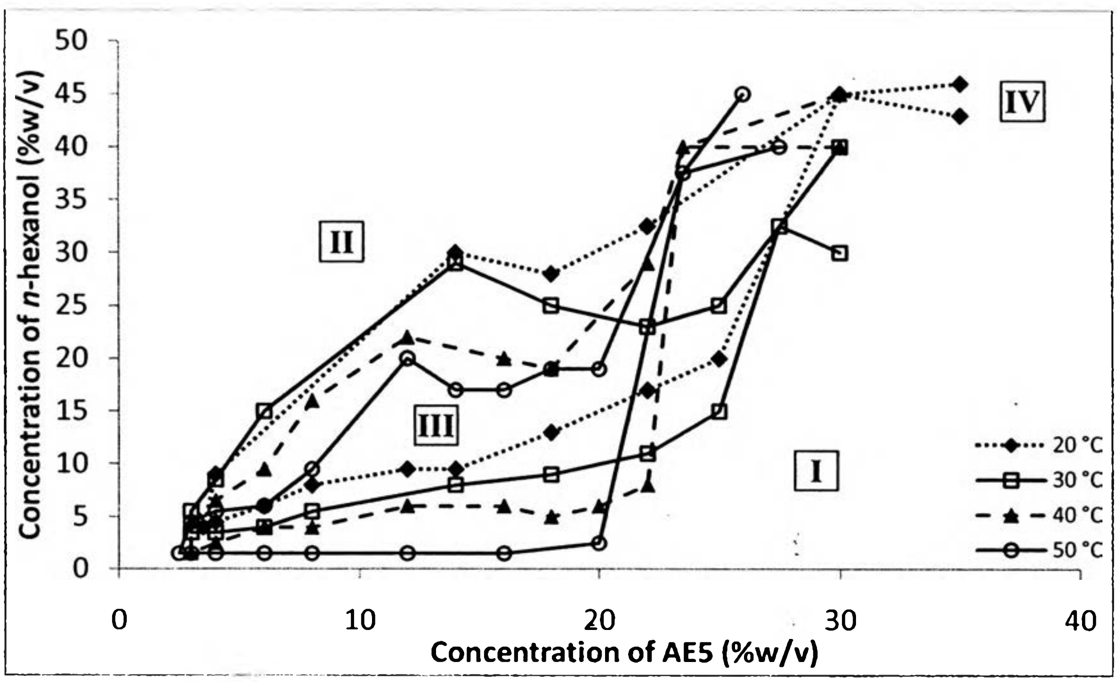

Figure 4.3 Fish diagram of AE5/*n*-hexanol/motor oil/water system at different temperatures.

Figure 4.4 illustrated the fish diagram of AE7/*n*-hexanol/motor oil/water system at different temperatures. The results show that at low temperatures (20 °C, and 30°C), Winsor Type IV microemulsion cannot be formed. In other words, only Winsor Types I, II, and III can be formed at 20 °C, and 30°C. With increasing temperature (40 °C, and 50°C), not only Winsor Type IV microemulsion can be formed, but CμC was also reduced. Similarly with the previous results, the CμC values and composition at point E were reported in Table 4.1. Hence, an increasing in temperatures affects the fish diagrams in terms of Winsor Type IV microemulsion formation and solubilization capacity of the system which reported as point E.

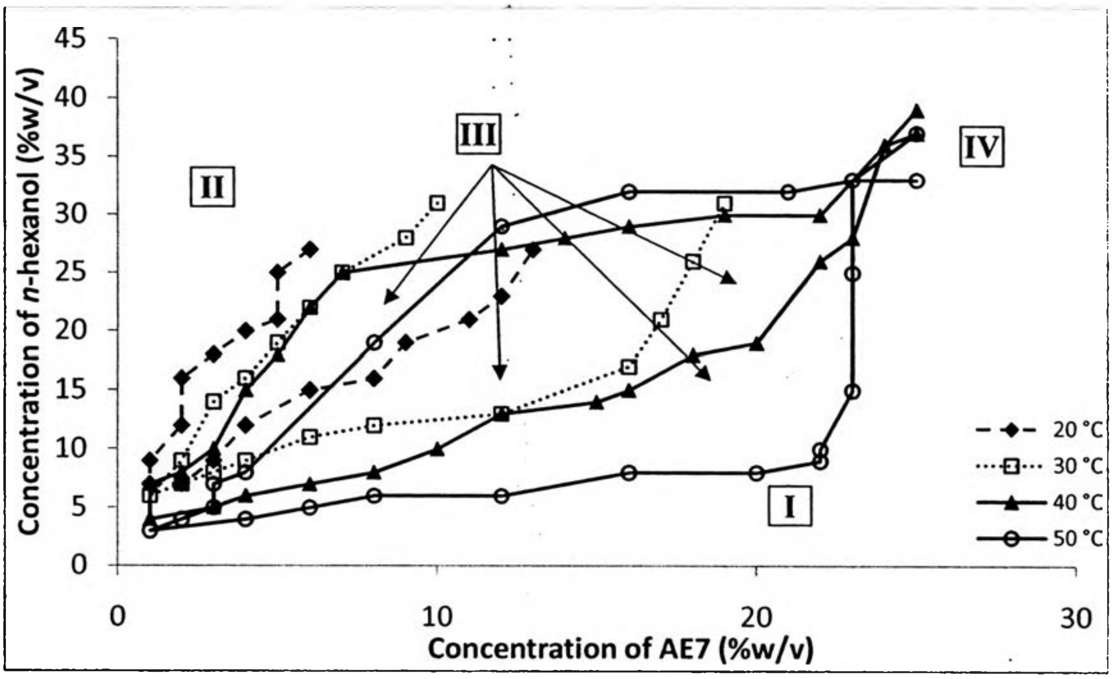

Figure 4.4 Fish diagram of AE7/*n*-hexanol/motor oil/water system at different temperatures.

The fish diagrams of AE9/*n*-hexanol/motor oil/water system, AE3, AE5, and AE7/*n*-octanol/motor oil/water system were indicated in Figure 4.5 to Figure 4.8, respectively. Similarly to Figure 4.4, Winsor Type IV microemulsion cannot be formed at low temperature but it can be formed at high temperature. Moreover, macroemulsions appeared at 20 °C and 30 °C for the first system and at 20 °C for the last 2 systems so that no microemulsions were formed at these temperatures. The hydrogen bonds were break when the temperature increased; therefore, the strength of hydrogen bonds was reduced at higher temperature. In other words, AEs became more hydrophobic at higher temperature which had more similar polarity with motor oil. Hence, Winsor Type IV can be formed at the higher temperatures easier than the lower temperatures.

In the case of AE9/*n*-octanol/motor oil/water system (Figure 4.9), the results show that no Winsor Type IV microemulsion was formed even at the highest temperature (50 °C). The reasons will be discuss in the effect of EO groups on fish diagram section.

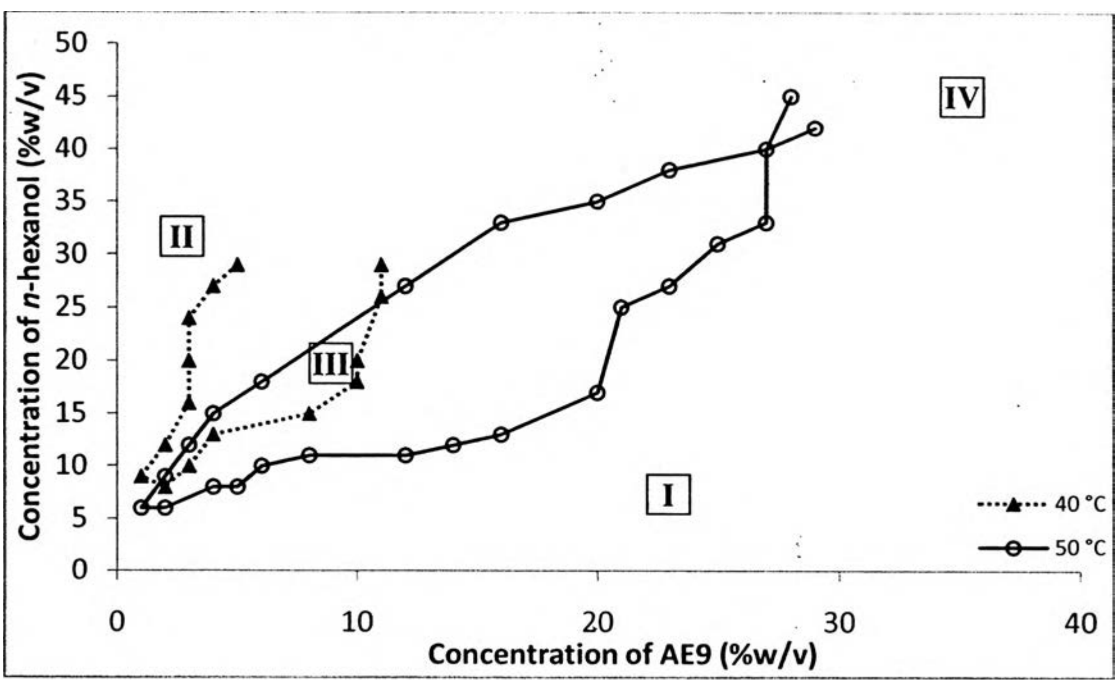

Figure 4.5 Fish diagram of AE9/*n*-hexanol/motor oil/water system at different temperatures. (*Note*: Microemulsion formation at 20 °C, and 30 °C systems were not found).

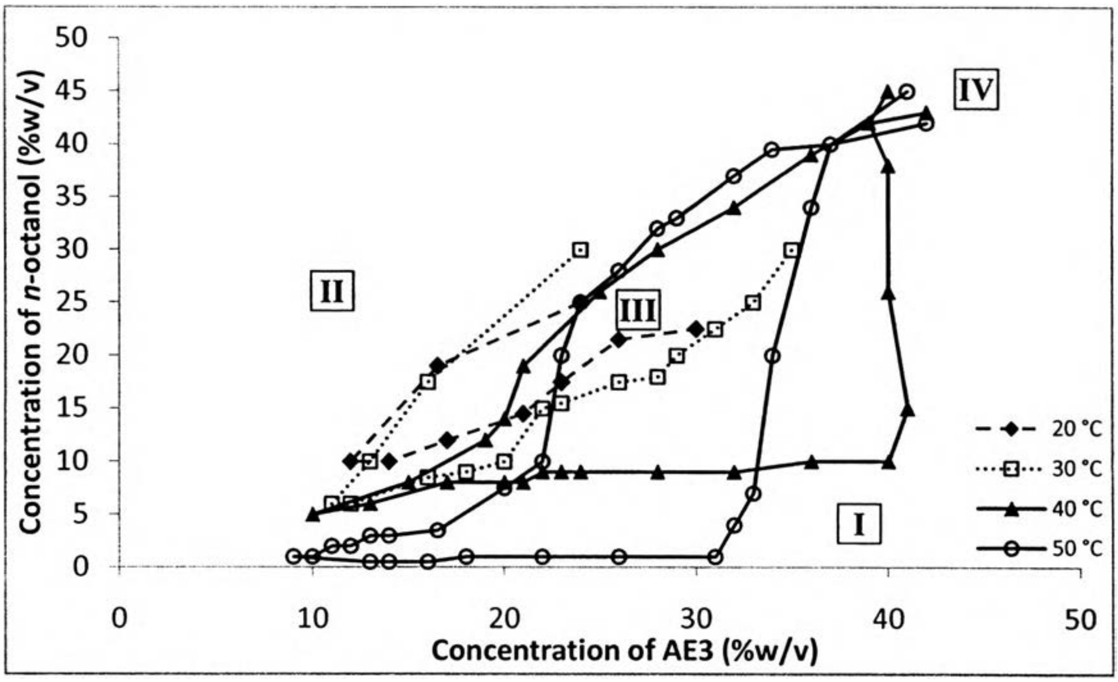

Figure 4.6 Fish diagram of AE3/*n*-octanol/motor oil/water system at different temperatures.

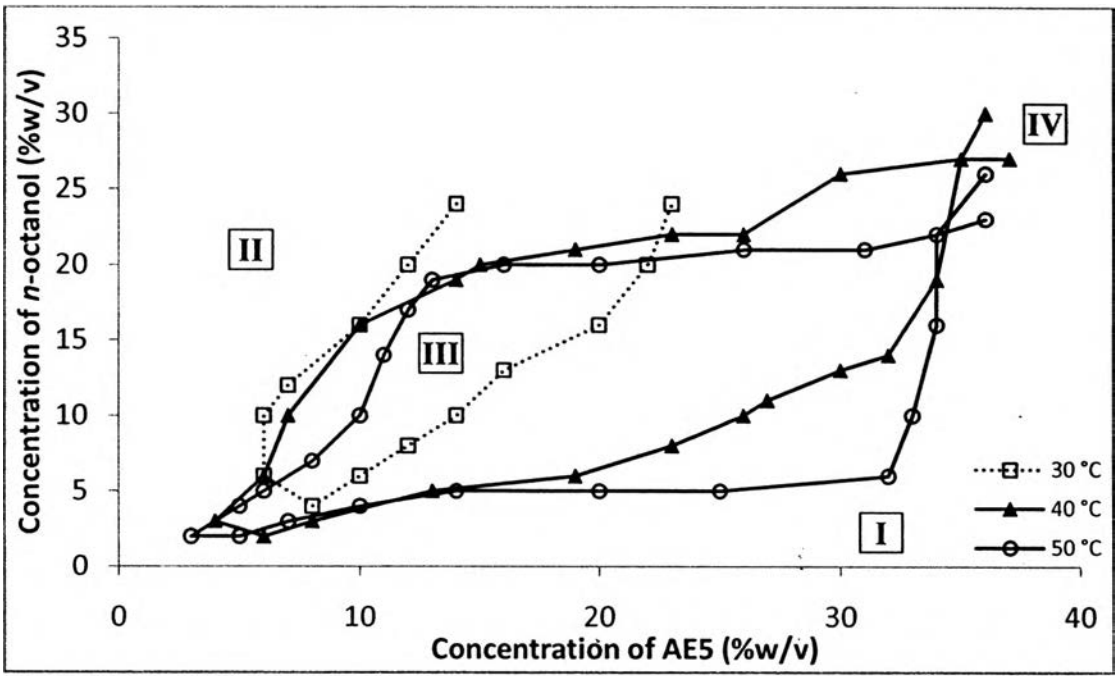

Figure 4.7 Fish diagram of AE5/*n*-octanol/motor oil/water system at different temperatures. (*Note*: Microemulsion formation at 20 °C system was not found).

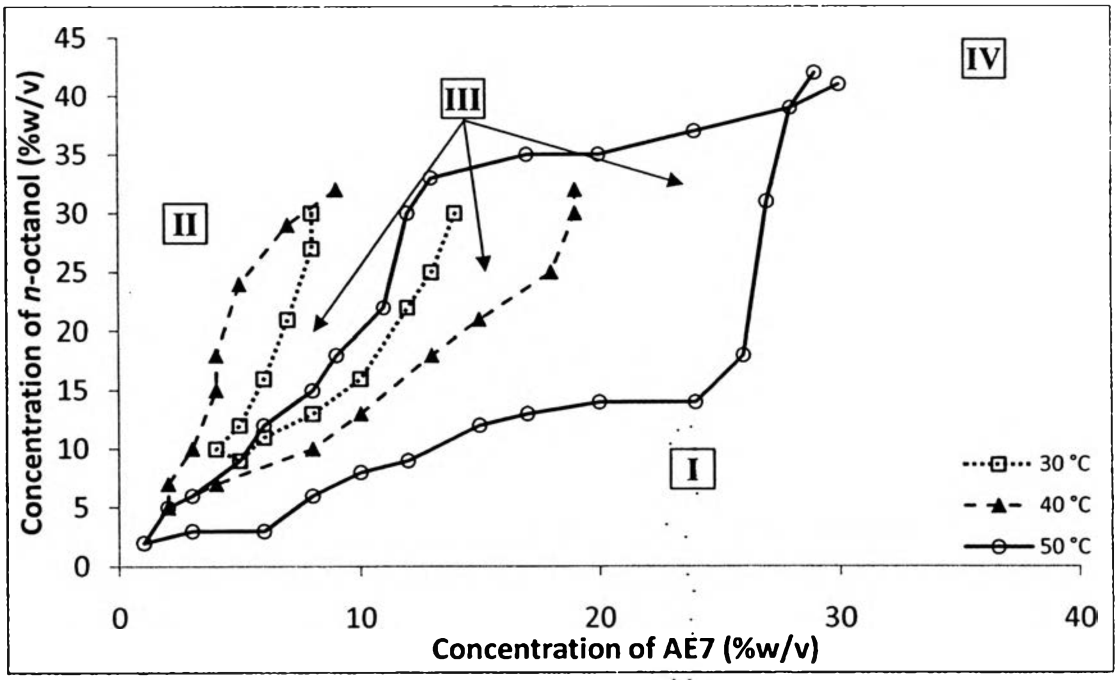

Figure 4.8 Fish diagram of AE7/*n*-octanol/motor oil/water system at different temperatures. (*Note*: Microemulsion formation at 20 °C system was not found).

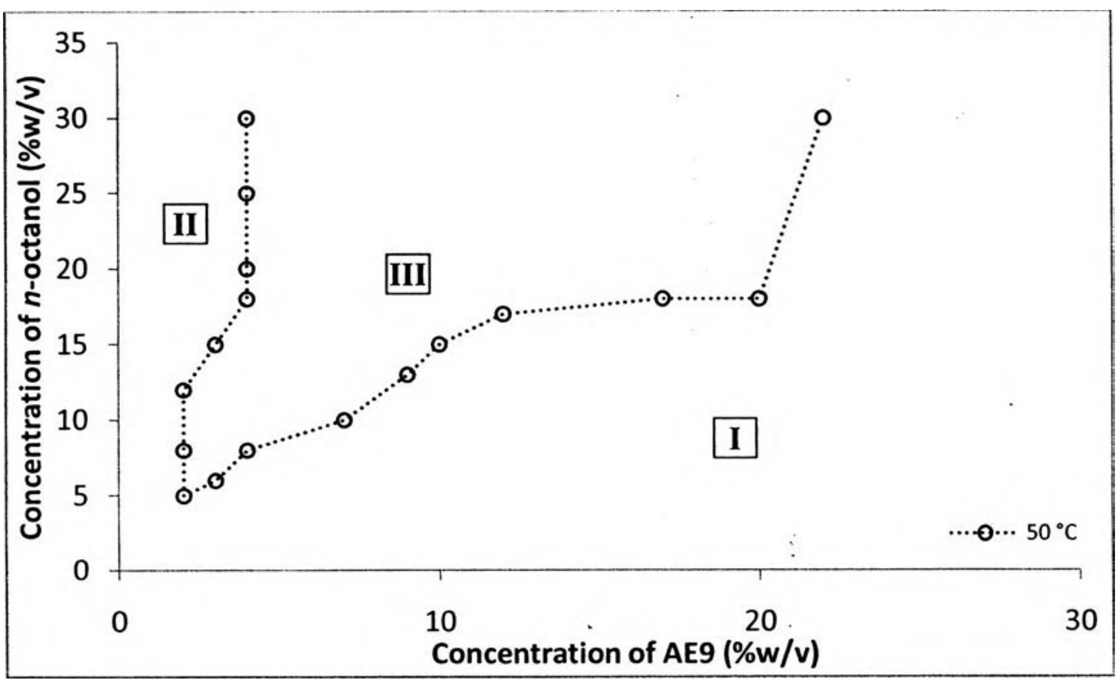

Figure 4.9 Fish diagram of AE9/*n*-octanol/motor oil/water system at different temperatures. (*Note*: Microemulsion formation at 20 °C, 30 °C, and 40 °C systems were not found).

Table 4.1 CµC values and the composition at point E of AE/alcohol/motor oil/water system at different temperatures.

Alcohols	AE	Temperature (°C)	CµC (%w/v)	E ([AE],[Alcohol])
n-butanol	AE3	20	15.0	(48.0, 35.0)
		30	7.0	(45.0, 28.0)
		40	5.0	(43.0, 24.0)
		50	4.0	(38.0, 28.0)
	AE5	20	N/A	N/A
		30	N/A	N/A
		40	N/A	N/A
		50	N/A	N/A
	AE7	20	N/A	N/A
		30	N/A	N/A
		40	N/A	N/A
		50	N/A	N/A
	AE9	20	N/A	N/A
		30	N/A	N/A
		40	N/A	N/A
		50	N/A	N/A
n-hexanol	AE3	20	6.0	(31.5, 37.5)
		30	4.0	(30.0, 42.5)
		40	4.0	(30.0, 37.5)
		50	3.0	(23.5, 42.5)
	AE5	20	3.5	(30.0, 45.0)
		30	3.0	(27.5, 32.5)
		40	3.0	(23.5, 40.0)
		50	2.5	(23.5, 37.5)
	AE7	20	N/A	N/A
		30	1.0	N/A
		40	1.0	(24.0, 36.0)
		50	1.0	(23.0, 33.0)
	AE9	20	N/A	N/A
		30	N/A	N/A
		40	1.0	N/A
		50	1.0	(27.0, 40.0)

Table 4.1 (Cont.)

Alcohols	AE	Temperature (°C)	CμC (%w/v)	E ([AE],[Alcohol])
n-octanol	AE3	20	12.0	N/A
		30	11.0	N/A
		40	10.0	(39.0, 42.0)
		50	9.0	(37.0, 40.0)
	AE5	20	N/A	N/A
		30	6.0	N/A
		40	4.0	(35.0, 27.0)
		50	3.0	(34.0, 22.0)
	AE7	20	N/A	N/A
		30	4.0	N/A
		40	2.0	N/A
		50	1.0	(28.0, 39.0)
	AE9	20	N/A	N/A
		30	N/A	N/A
		40	N/A	N/A
		50	2.0	N/A

4.1.2 The Effect of Cosurfactant Chain Length on Fish Diagram

In order to studied the effect of cosurfactant chain length on the fish diagram, the microemulsion formation of AEs (AE3, AE5, AE7, and AE9)/alcohol (*n*-butanol, *n*-hexanol, and *n*-octanol)/motor oil/water systems was investigated at 20 °C, 30 °C, 40 °C, and 50 °C. The results represent in Figure 4.10 to Figure 4.23 and Table 4.2.

The microemulsion formation of these systems occurred Winsor Types III, and IV microemulsion because there was alcohols (*n*-butanol, *n*-hexanol, and *n*-octanol) which acted as cosurfactants. In other words, the Winsor Types III, and IV microemulsion cannot occur without alcohols.

Figure 4.10 to Figure 4.13 show the effect of various alcohols on phase diagram of AE3/alcohol/motor oil/water system at 20 °C, 30 °C, 40 °C, and 50 °C, respectively. The head of the fish is downward and the tail of the fish is upward. The middle microemulsion region (Winsor Type III microemulsion) is in the body of the fish, the single microemulsion region (Winsor Type IV microemulsion) is located at fish tail. The body lay above is Water-in-Oil microemulsion region

(Winsor Type II microemulsion) and below is Oil-in-Water microemulsion region (Winsor Type I microemulsion). The addition of alcohols as cosurfactants showed a significant effect on both the CμC and the composition at point E. Among the studied alcohols, *n*-hexanol was the most effective cosurfactant in tems of a Winsor Type III microemulsion, and Winsor Type IV microemulsioin. In addition, the systems using *n*-hexanol as cosurfactant gave the lowest CμC values and the concentration of AE at point E. Therefore, an increase in alcohol chain length enhanced the solubilities of both water and oil phases. The surfactant solution with higher alcohol chain length became more hydrophobic as same as motor oil, thus, the solubilities between the interface of the surfactant solution and oil was improved.

However, in the presence of *n*-octanol, only the Winsor Types I, II, and III microemulsion were formed at 20 °C, and 30 °C and the CμC values were about 12% w/vAE3 and 11% w/vAE3, respectively. Winsor Type IV microemulsion was formed at higher temperature (40 °C, and 50 °C) because of the effect of temperature on fish diagram as previously discussed. The results can be explained that an increase in too high alcohol chain length (*n*-octanol, for these systems) results in lowering solubilities in both water and motor oil. As a consequence, the CμC values were higher in microemulsion formation as in good agreement with the wok by Shevachmana *et al.*

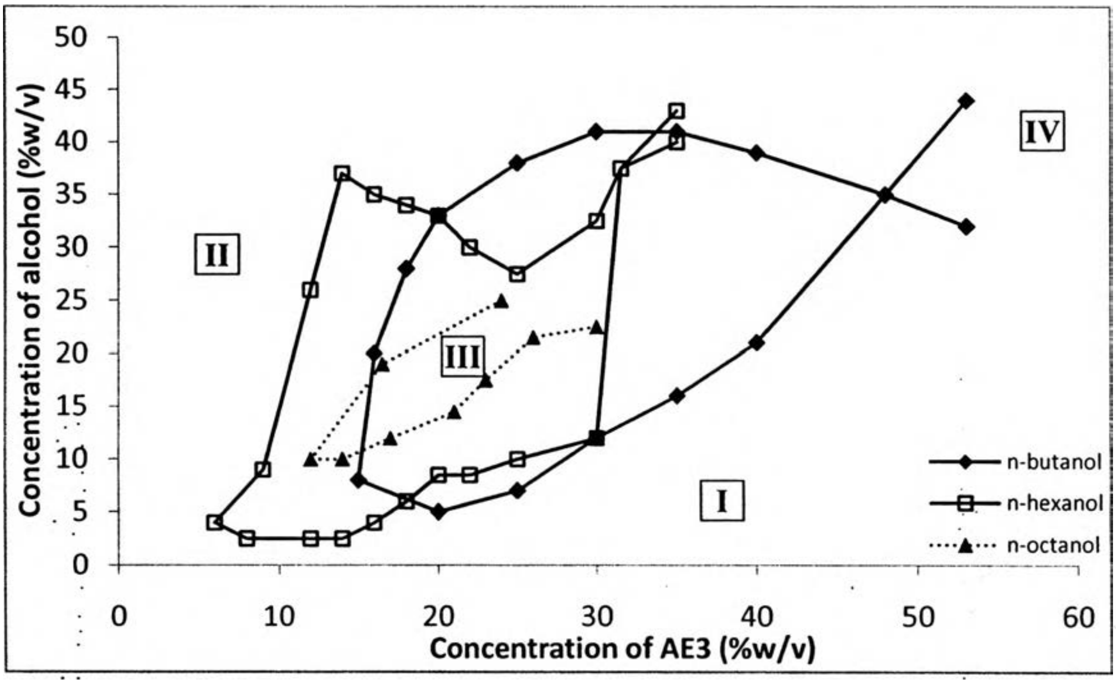

Figure 4.10 The effect of various alcohols on phase diagram (fish diagram) of AE3/alcohol/motor oil/water system at 20 °C.

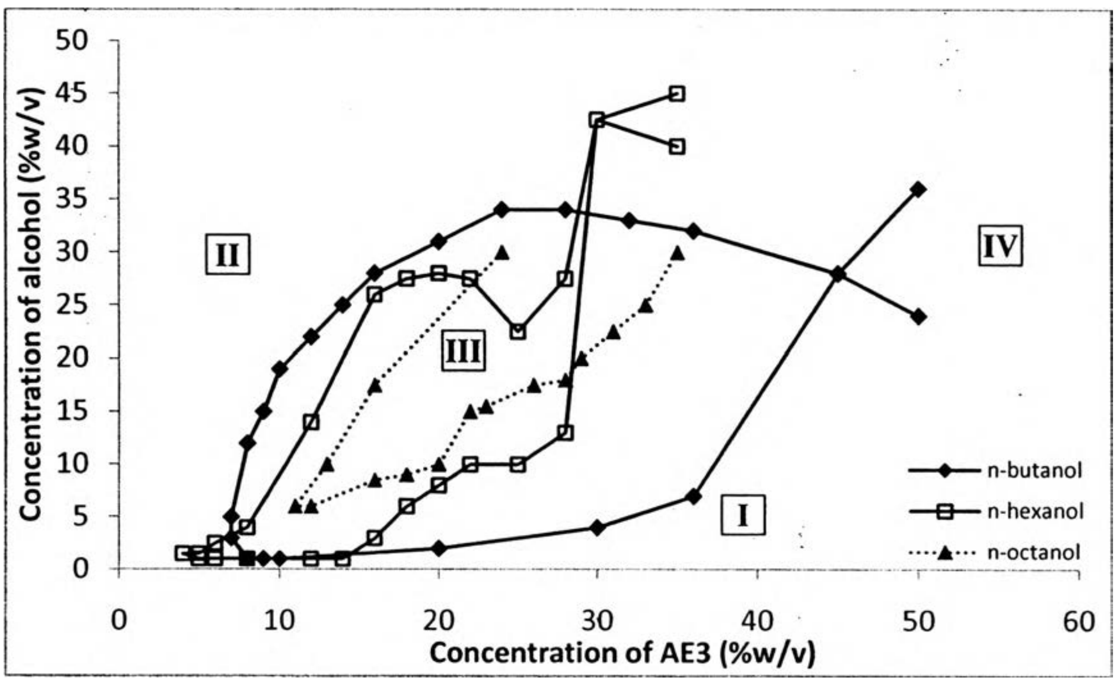

Figure 4.11 The effect of various alcohols on phase diagram (fish diagram) of AE3/alcohol/motor oil/water system at 30 °C.

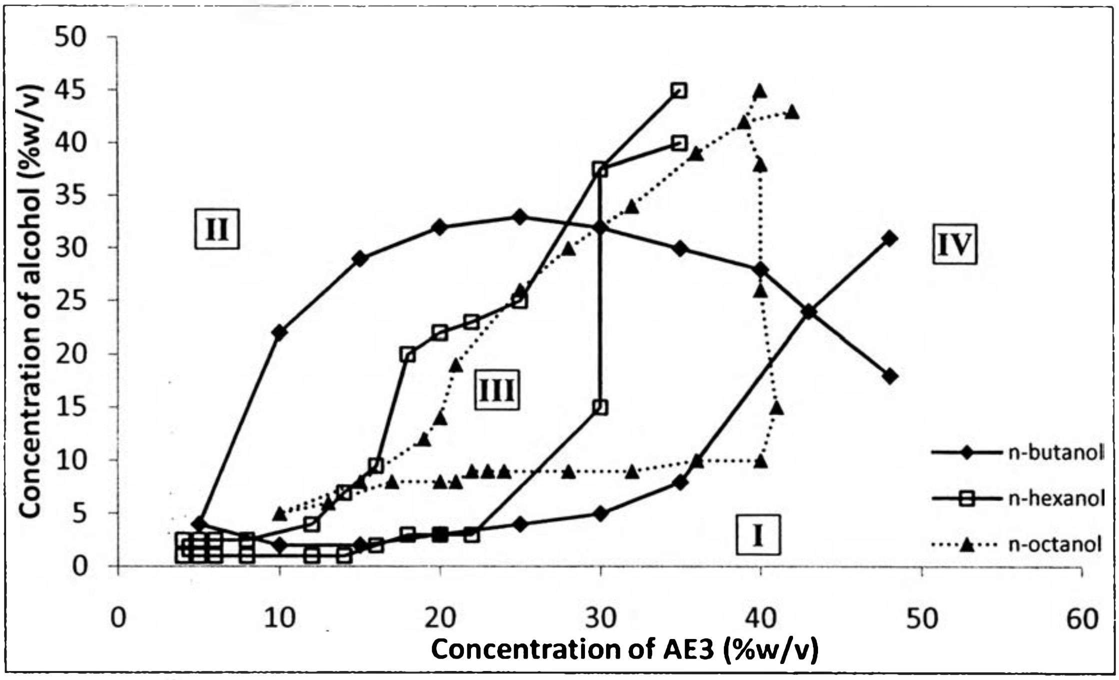

Figure 4.12 The effect of various alcohols on phase diagram (fish diagram) of AE3/alcohol/motor oil/water system at 40 °C.

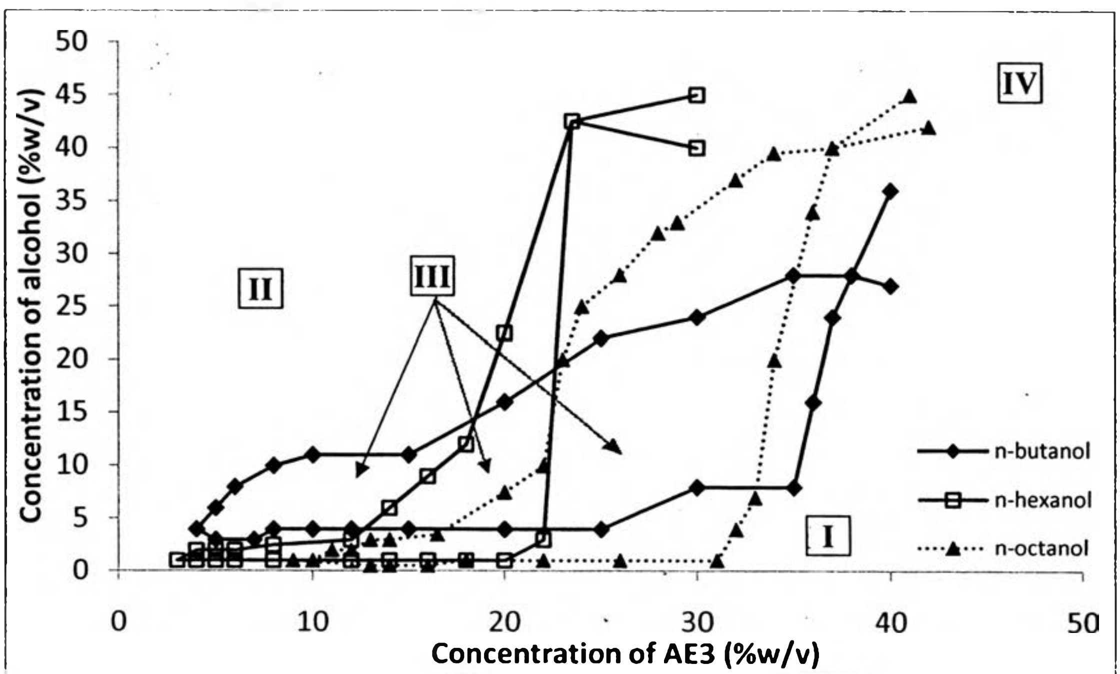

Figure 4.13 The effect of various alcohols on phase diagram (fish diagram) of AE3/alcohol/motor oil/water system at 50 °C.

The systems of AE5/alcohol/motor oil/water at 20 °C, 30 °C, 40 °C, and 50 °C illustrated in Figure 4.14 to Figure 4.17, respectively. The results show that Winsor Type III microemulsion and Winsor Type IV microemulsion occur at such temperatures when using *n*-hexanol as cosurfactant. Winsor Type III of *n*-octanol systems can be formed at every studied temperature except at 20 °C. However, Winsor Type IV microemulsion formation was not found at 30 °C because the gel formation occured at high surfactant concentrations. The CμC values and the concentration of AE5 at point E of *n*-octanol systems were higher than *n*-hexanol systems due to the addition of *n*-octanol lowering the solubilities in both water and motor oil. In addition, the adding *n*-butanol into these systems was not facilitated the Winsor Types I, III, and IV microemulsion formation because the surfactant solutions in the presence of *n*-butanol became more hydrophilic if compare to the surfactant solutions of *n*-hexanol; therefore, the more difference of interface layer between the surfactant solution and motor oil. So, only Winsor Type II microemulsion can be occurring.

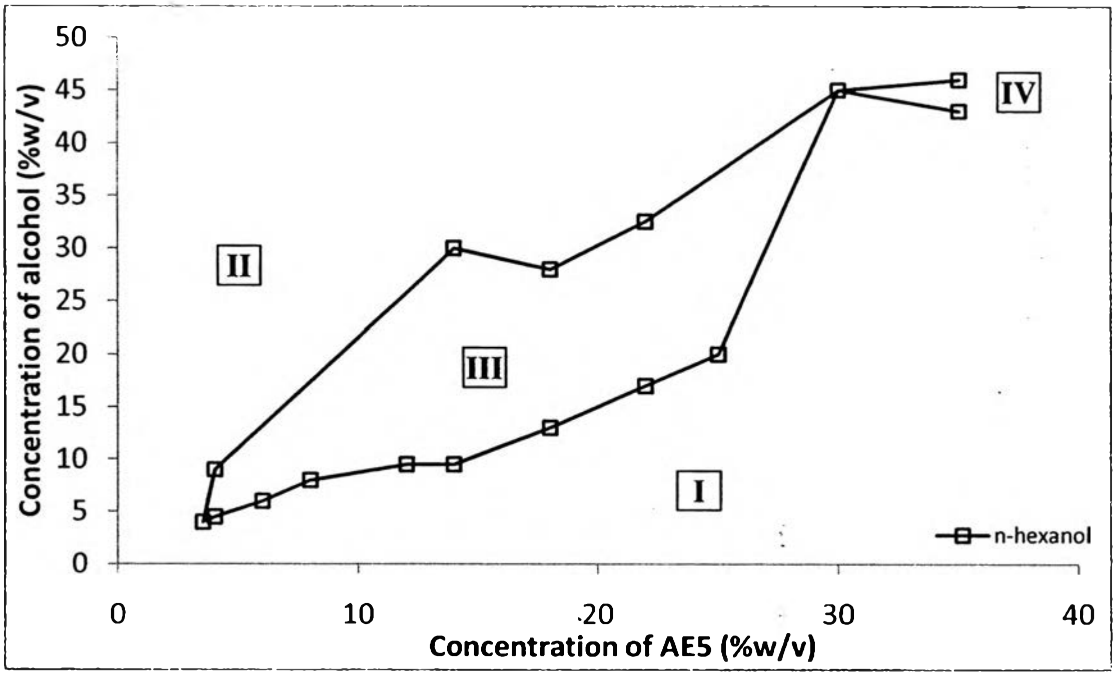

Figure 4.14 The effect of various alcohols on phase diagram (fish diagram) of AE5/alcohol/motor oil/water system at 20 °C. (*Note*: Microemulsion formation of *n*-butanol and *n*-octanol systems were not found).

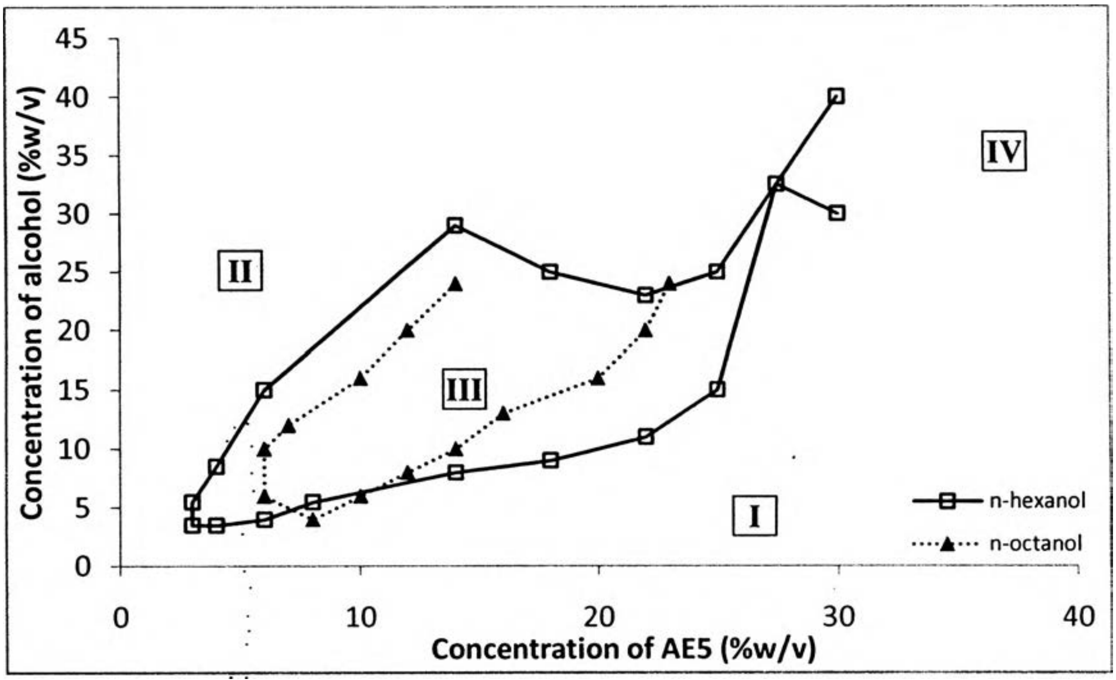

Figure 4.15 The effect of various alcohols on phase diagram (fish diagram) of AE5/alcohol/motor oil/water system at 30 °C. (*Note*: Microemulsion formation of *n*-butanol system was not found).

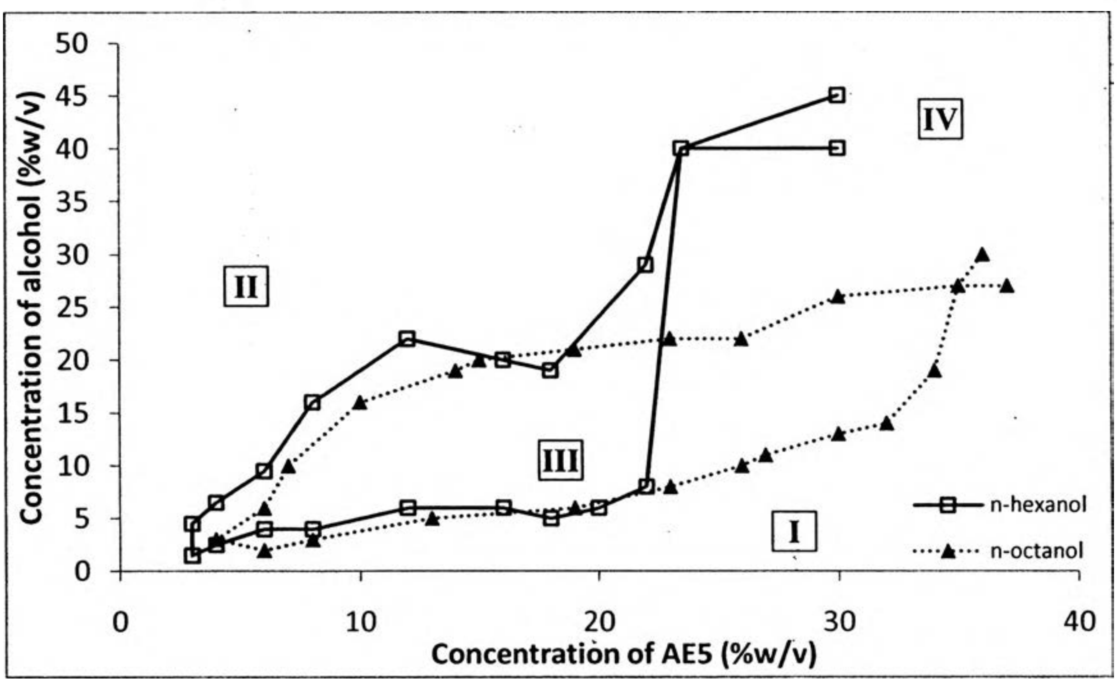

Figure 4.16 The effect of various alcohols on phase diagram (fish diagram) of AE5/alcohol/motor oil/water system at 40 °C. (*Note*: Microemulsion formation of *n*-butanol system was not found).

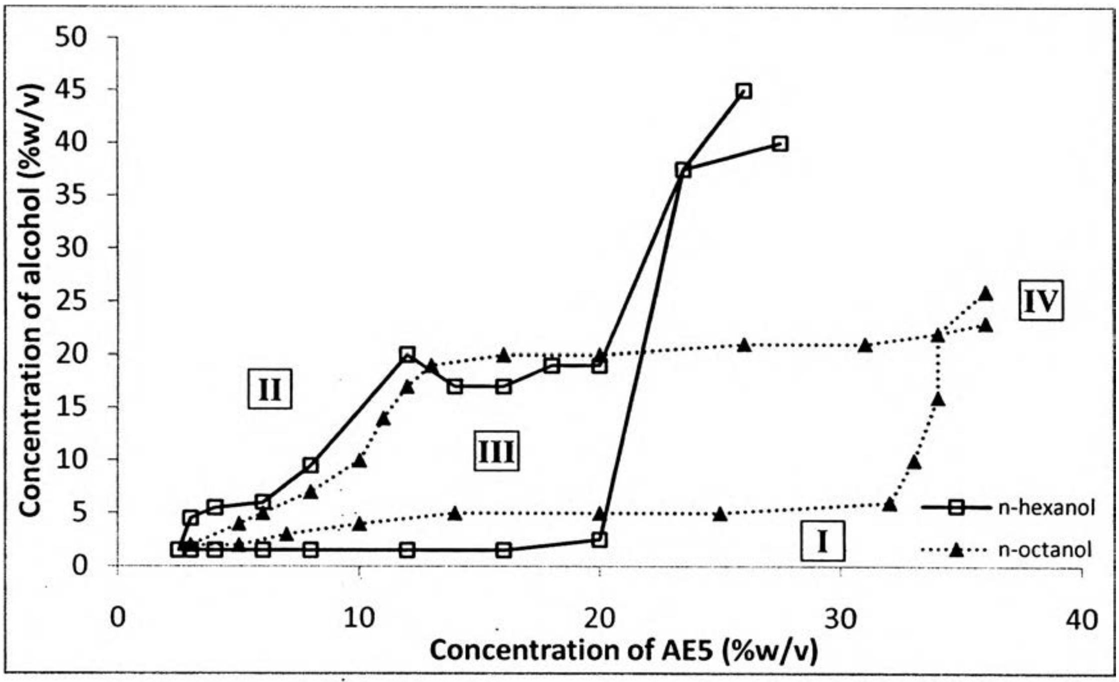

Figure 4.17 The effect of various alcohols on phase diagram (fish diagram) of AE5/alcohol/motor oil/water system at 50 °C. (*Note*: Microemulsion formation of *n*-butanol system was not found).

Similarly with the previous systems, the microemulsion formation of AE7 with various alcohols was illustrated in Figure 4.18 to Figure 4.21. Winsor Type III microemulsion of only *n*-hexanol systems can occur at every studied temperature. By using *n*-octanol as cosurfactant, Winsor Type III appeared starting from 30 °C and got Winsor Type IV microemulsion at 50 °C while *n*-hexanol system got Winsor Type IV microemulison at lower temperature (40 °C). Moreover, the CμC values and the concentration of AE7 at point E of added *n*-hexanol into the systems were lower than added *n*-octanol. In addition, the adding *n*-butanol into these systems was not facilitated the Winsor Types II, III, and IV microemulsion formation. As the previous discussion, the surfactant solutions in the presence of *n*-butanol became more hydrophilic if compare to the surfactant solutions of *n*-hexanol, and *n*-octanol, respectively; therefore, the more difference of interface layer between the surfactant solution and motor oil. So, only Winsor Type I microemulsion can be occur.

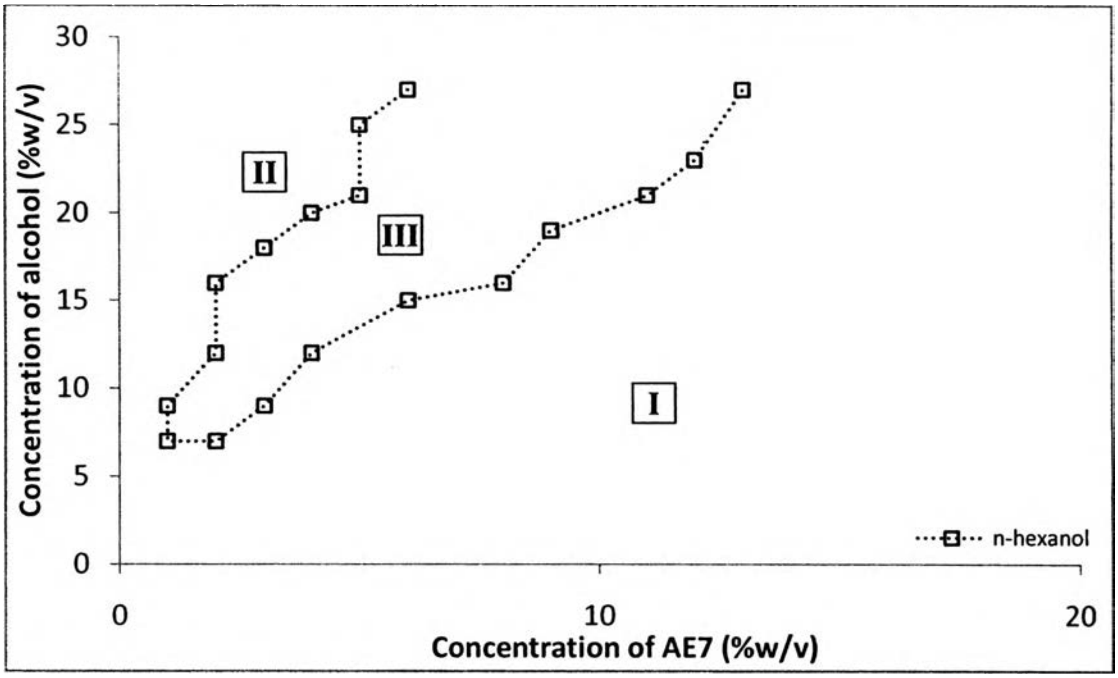

Figure 4.18 The effect of various alcohols on phase diagram (fish diagram) of AE7/alcohol/motor oil/water system at 20 °C. (Note: Microemulsion formation of *n*-butanol and *n*-octanol systems were not found).

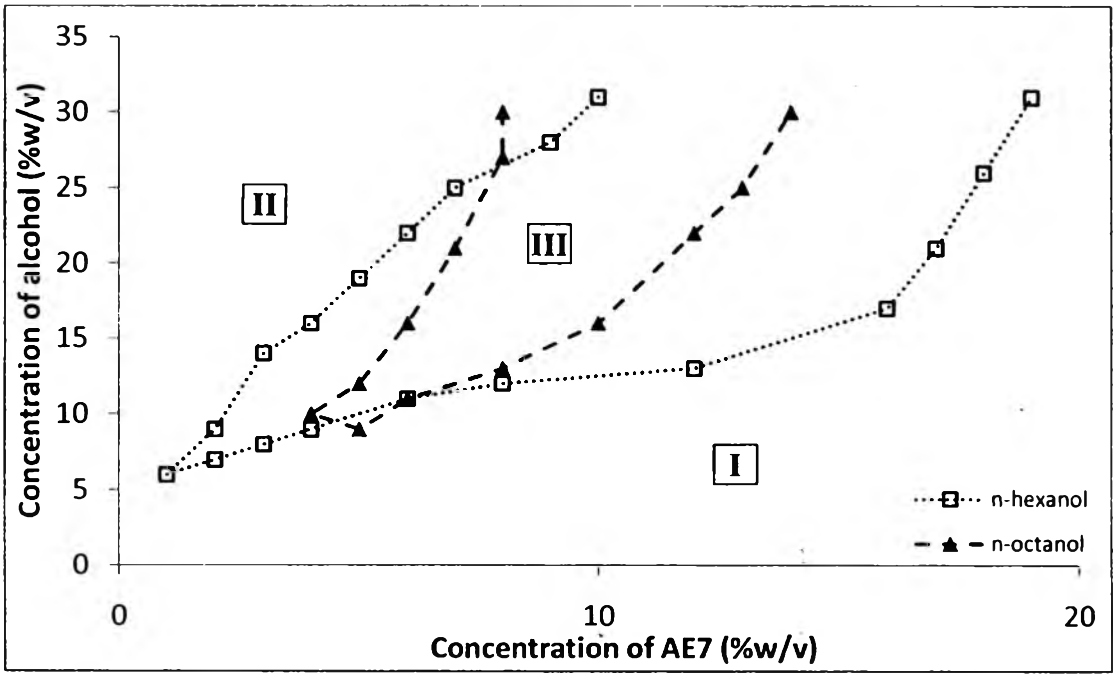

Figure 4.19 The effect of various alcohols on phase diagram (fish diagram) of AE7/alcohol/motor oil/water system at 30 °C. (Note: Microemulsion formation of *n*-butanol system was not found).

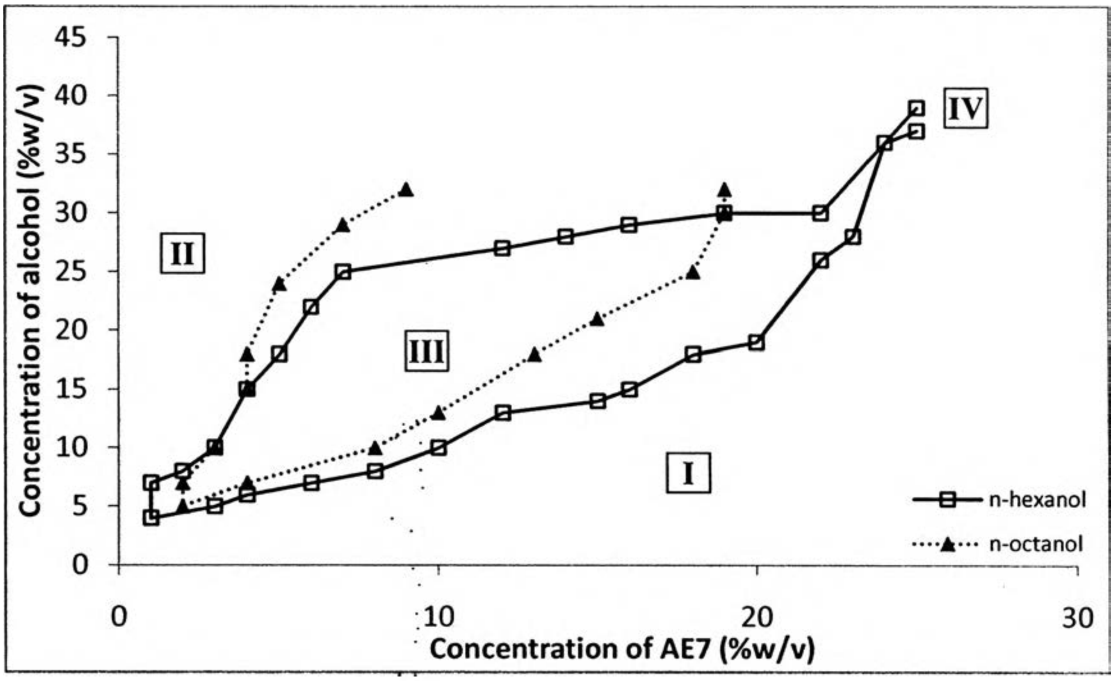

Figure 4.20 The effect of various alcohols on phase diagram (fish diagram) of AE7/alcohol/motor oil/water system at 40 °C. (Note: Microemulsion formation of *n*-butanol system was not found).

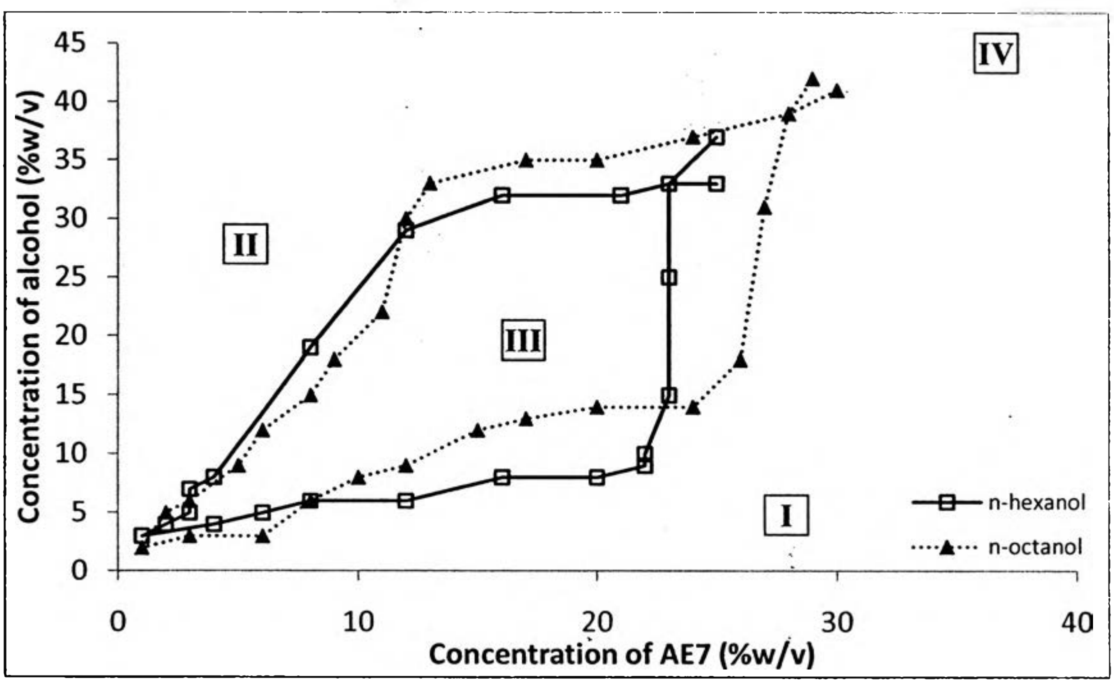

Figure 4.21 The effect of various alcohols on phase diagram (fish diagram) of AE7/alcohol/motor oil/water system at 50 °C. (Note: Microemulsion formation of *n*-butanol system was not found).

The results of the AE9/alcohol/motor oil/water system at 40 °C and 50 °C show in Figures 4.22 and 4.23, respectively. The AE9 cannot form the Winsor Types I, II, II, and IV microemulsion with *n*-butanol. Nevertheless, only *n*-hexanol system formed the Winsor Types I, II, III, and IV microemulison at 50 °C while *n*-octanol system was not formed Winsor Type IV microemulison at this temperature. The CμC value of *n*-hexanol system at 50 °C was less than *n*-octanol (Table 4.2).

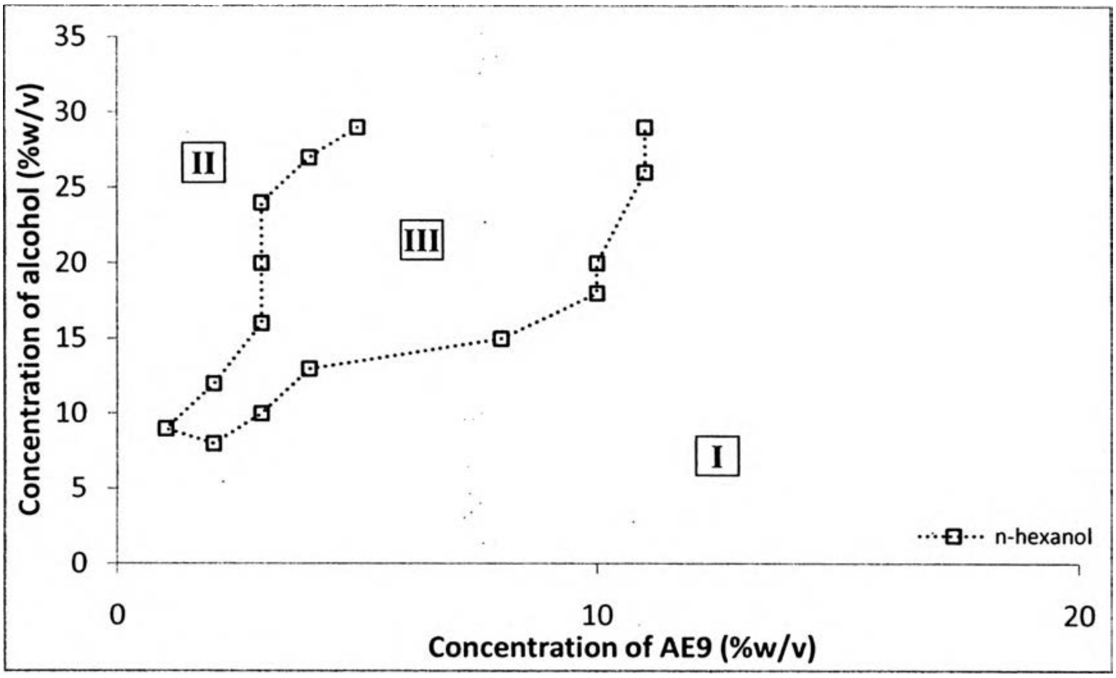

Figure 4.22 The effect of various alcohols on phase diagram (fish diagram) of AE9/alcohol/motor oil/water system at 40 °C. (*Note*: Microemulsion formation of *n*-butanol and *n*-octanol systems were not found).

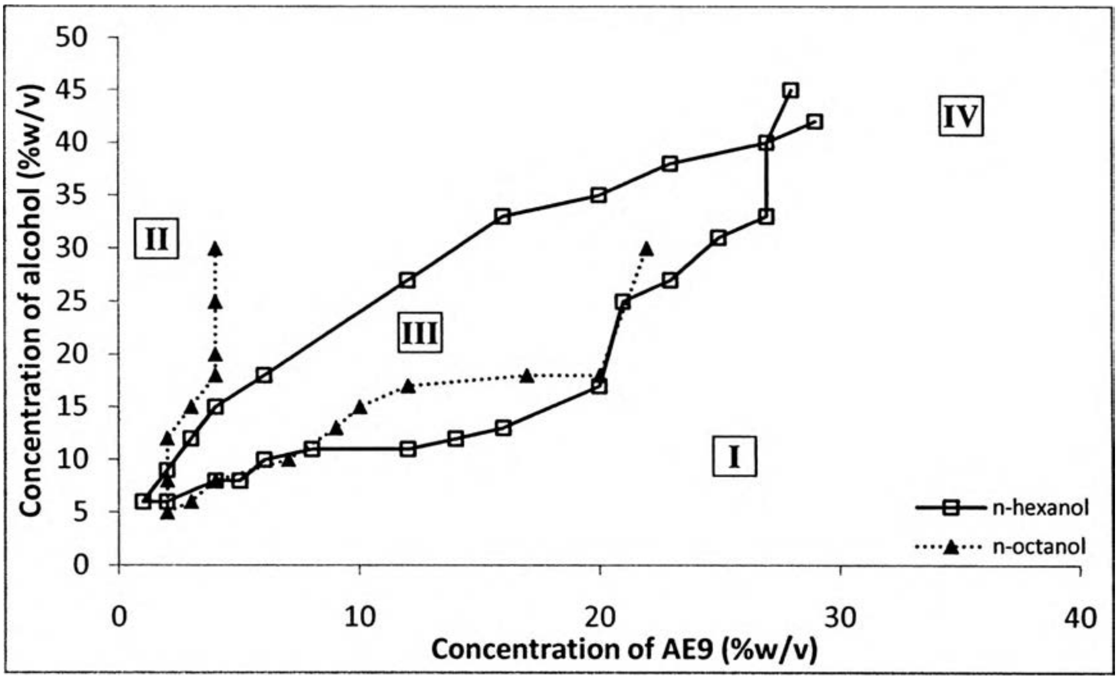

Figure 4.23 The effect of various alcohols on phase diagram (fish diagram) of AE9/alcohol/motor oil/water system at 50 °C. (*Note*: Microemulsion formation of *n*-butanol system was not found).

Table 4.2 CμC values and the composition at point E of AE/alcohol/motor oil/water system at various alcohol chain lengths.

AE	Temperature (°C)	Alcohols	CμC (%w/v)	E ([AE],[Alcohol])
AE3	20	*n*-butanol	15.0	(48.0, 35.0)
		n-hexanol	6.0	(31.5, 37.5)
		n-octanol	12.0	N/A
	30	*n*-butanol	17.0	(45.0, 28.0)
		n-hexanol	4.0	(30.0, 42.5)
		n-octanol	11.0	N/A
	40	*n*-butanol	5.0	(43.0, 24.0)
		n-hexanol	4.0	(30.0, 37.5)
		n-octanol	10.0	(39.0, 42.0)
	50	*n*-butanol	4.0	(38.0, 28.0)
		n-hexanol	3.0	(23.5, 42.5)
		n-octanol	9.0	(37.0, 40.0)

Table 4.2 (Cont.)

AE	Temperature (°C)	Alcohols	CμC (%w/v)	E ([AE],[Alcohol])
AE5	20	*n*-butanol	N/A	N/A
		n-hexanol	3.5	(30.0, 45.0)
		n-octanol	N/A	N/A
	30	*n*-butanol	N/A	N/A
		n-hexanol	3.0	(27.5, 32.5)
		n-octanol	6.0	N/A
	40	*n*-butanol	N/A	N/A
		n-hexanol	3.0	(23.5, 40.0)
		n-octanol	4.0	(35.0, 27.0)
	50	*n*-butanol	N/A	N/A
		n-hexanol	2.5	(23.5, 37.5)
		n-octanol	3.0	(34.0, 22.0)
AE7	20	*n*-butanol	N/A	N/A
		n-hexanol	N/A	N/A
		n-octanol	N/A	N/A
	30	*n*-butanol	N/A	N/A
		n-hexanol	1.0	N/A
		n-octanol	4.0	N/A
	40	*n*-butanol	N/A	N/A
		n-hexanol	1.0	(24.0, 36.0)
		n-octanol	2.0	N/A
	50	*n*-butanol	N/A	N/A
		n-hexanol	1.0	(23.0, 33.0)
		n-octanol	1.0	(28.0, 39.0)
AE9	20	*n*-butanol	N/A	N/A
		n-hexanol	N/A	N/A
		n-octanol	N/A	N/A
	30	*n*-butanol	N/A	N/A
		n-hexanol	N/A	N/A
		n-octanol	N/A	N/A
	40	*n*-butanol	N/A	N/A
		n-hexanol	1.0	N/A
		n-octanol	N/A	N/A
	50	*n*-butanol	N/A	N/A
		n-hexanol	1.0	(27.0, 40.0)
		n-octanol	2.0	N/A

4.1.3 Effect of EO Groups on Fish Diagram

The effect of EO groups of AE on fish diagram was investigated. AE with three EO groups (AE3), five EO groups (AE5), seven EO groups (AE7), and nine EO groups (EO9), nonionic surfactants were used as surfactants in microemulsion formation. Surfactant which has bigger EO groups has higher hydrophilicity increasing in the order: AE9 > AE7 > AE5 > AE3. The results show in Figures 4.24 to 4.35 and Table 4.3.

The microemulsion formation was formed with only AE3 for every studied systems because it was the least hydrophilic of these surfactants and addition of cosurfactant made interfacial layer less hydrophilic therefore motor oil could be dissolved in the interfacial layer. For the higher EO groups (e.g. AE5, AE7, and AE9), the alcohols with longer hydrocarbon chain and an increase in temperature are needed in order to make the interfacial layer less hydrophilic.

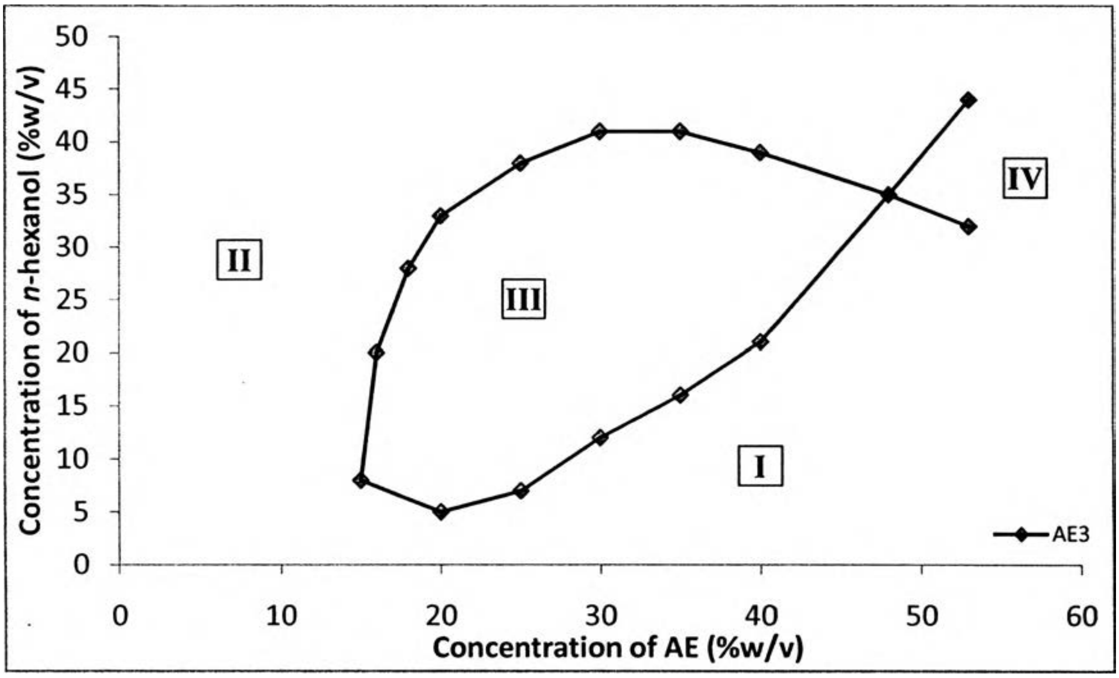

Figure 4.24 The effect of EO groups on phase diagram (fish diagram) of various AEs/n-butanol/motor oil/water system at 20 °C. (*Note*: Microemulsion formation of AE5, AE7 and AE9 systems were not found).

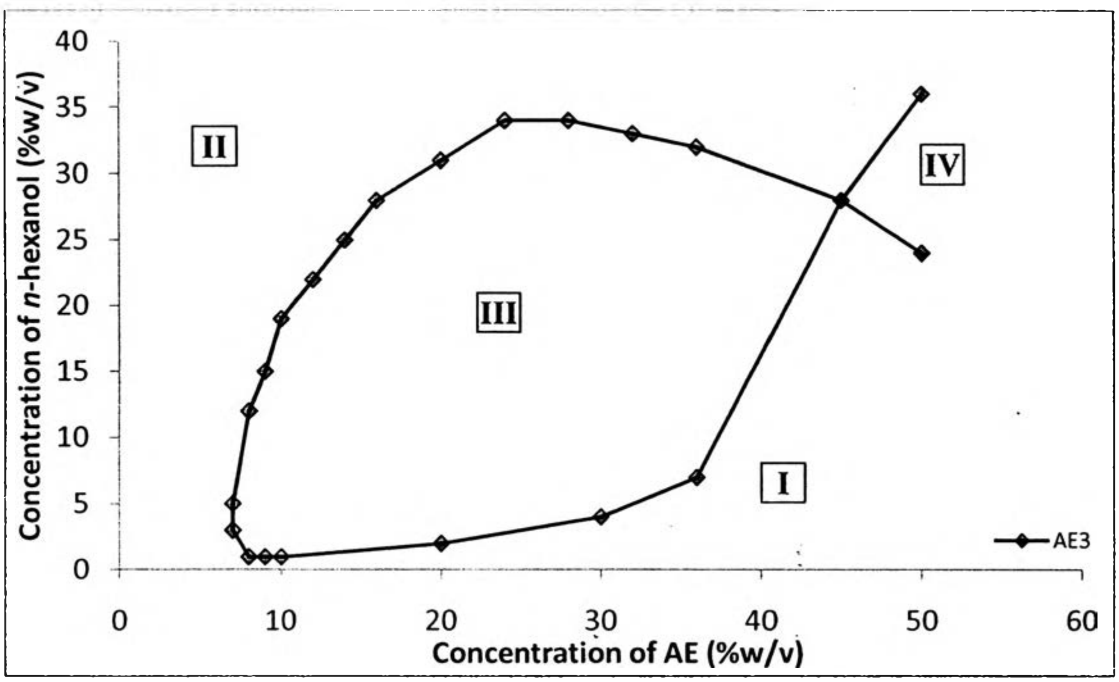

Figure 4.25 The effect of EO groups on phase diagram (fish diagram) of various AEs/n-butanol/motor oil/water system at 30 °C. (*Note*: Microemulsion formation of AE5, AE7 and AE9 systems were not found).

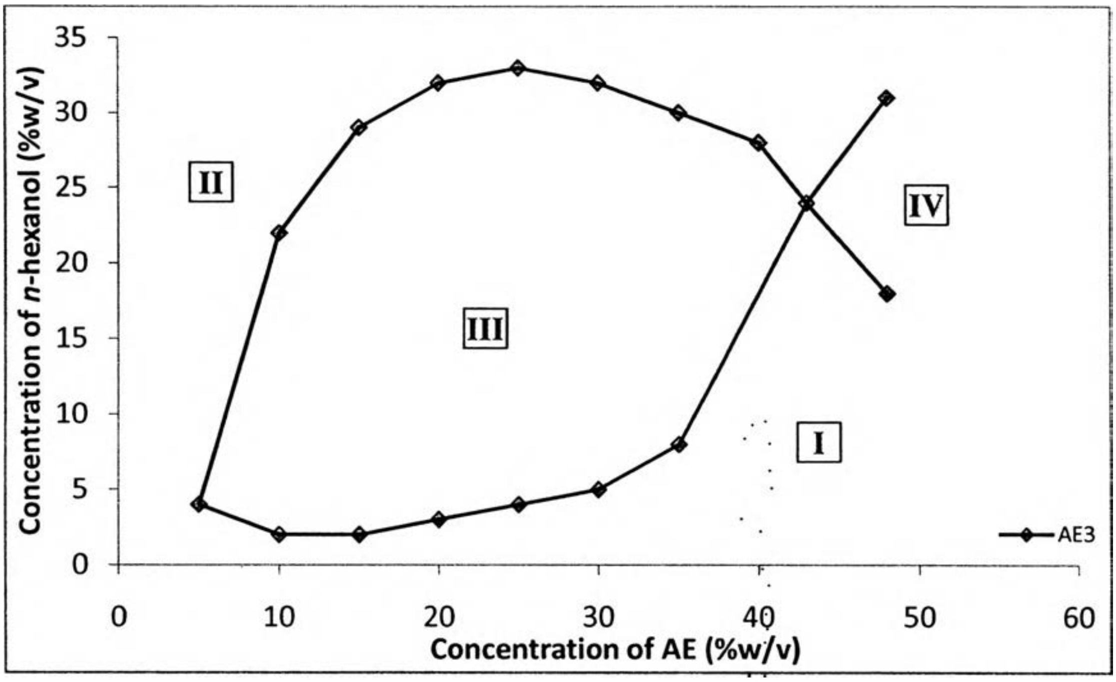

Figure 4.26 The effect of EO groups on phase diagram (fish diagram) of various AEs/*n*-butanol/motor oil/water system at 40 °C. (*Note*: Microemulsion formation of AE5, AE7 and AE9 systems were not found).

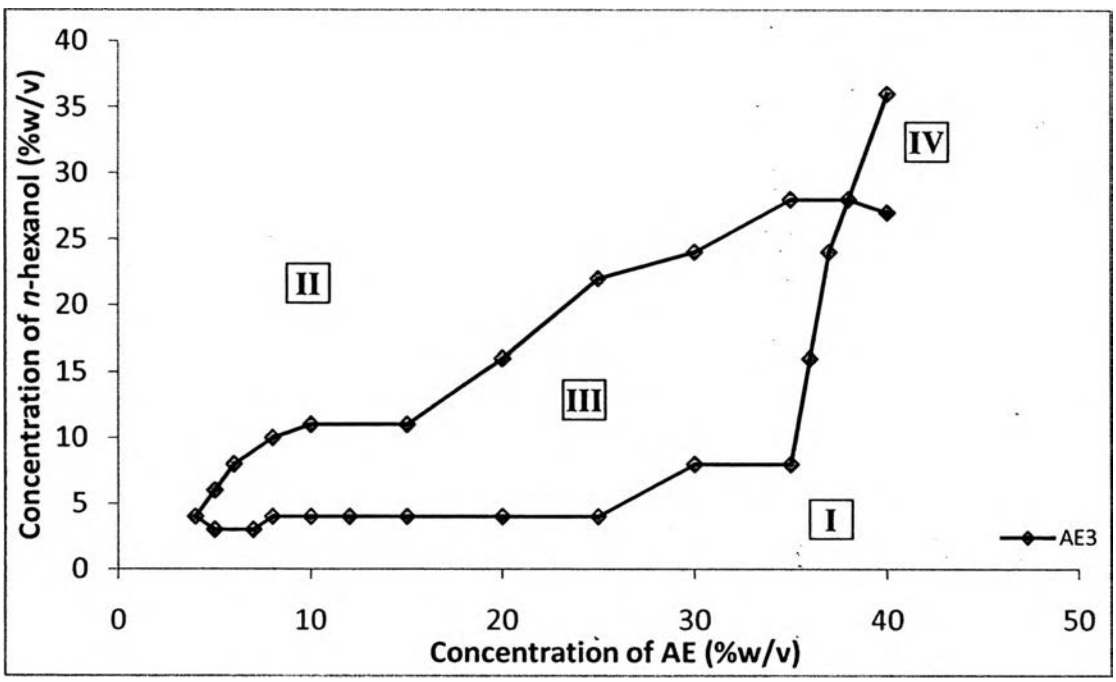

Figure 4.27 The effect of EO groups on phase diagram (fish diagram) of various AEs/*n*-butanol/motor oil/water system at 50 °C. (*Note*: Microemulsion formation of AE5, AE7 and AE9 systems were not found).

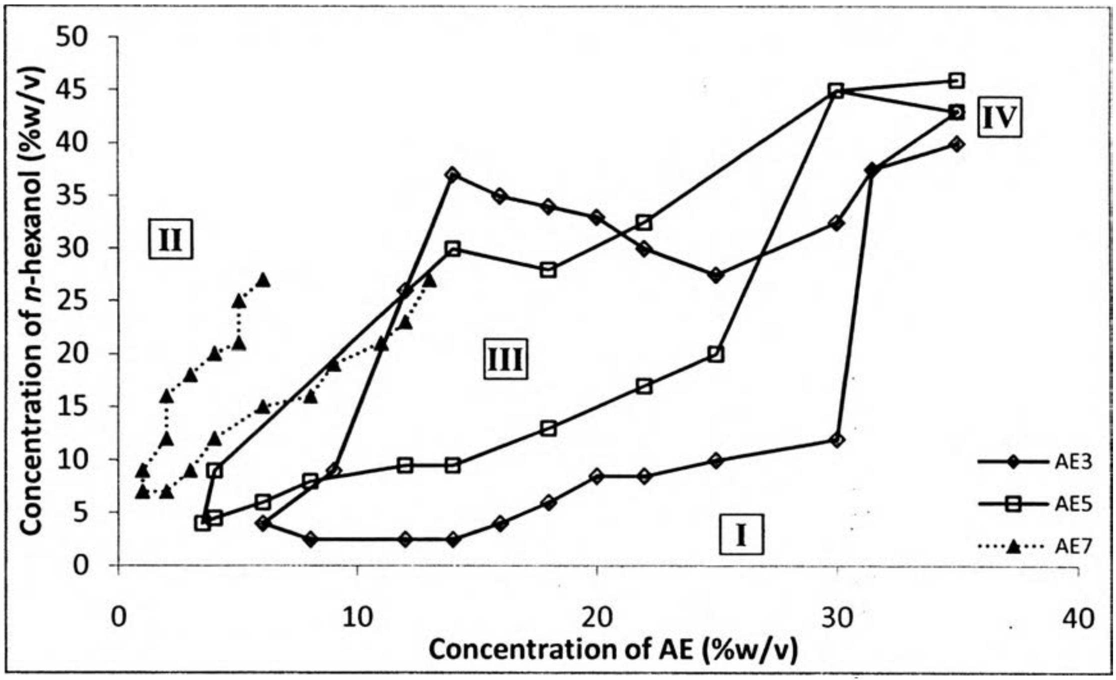

Figure 4.28 The effect of EO groups on phase diagram (fish diagram) of various AEs/*n*-hexanol/motor oil/water system at 20 °C. (*Note*: Microemulsion formation of AE9 system was not found).

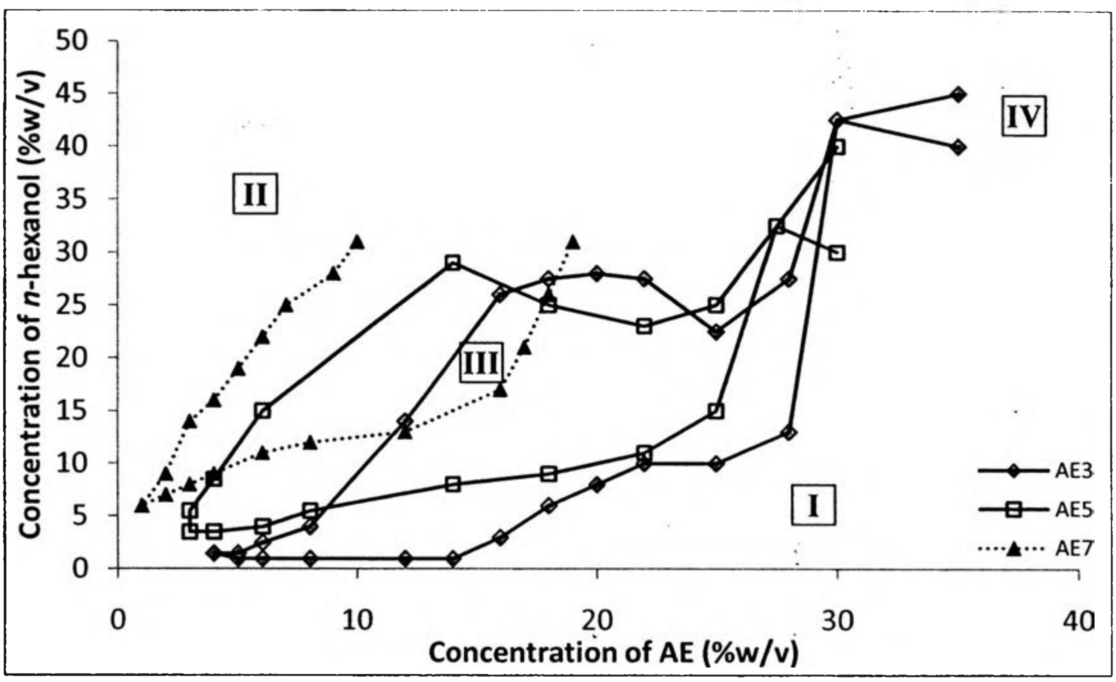

Figure 4.29 The effect of EO groups on phase diagram (fish diagram) of various AEs/*n*-hexanol/motor oil/water system at 30 °C. (*Note*: Microemulsion formation of AE9 system was not found).

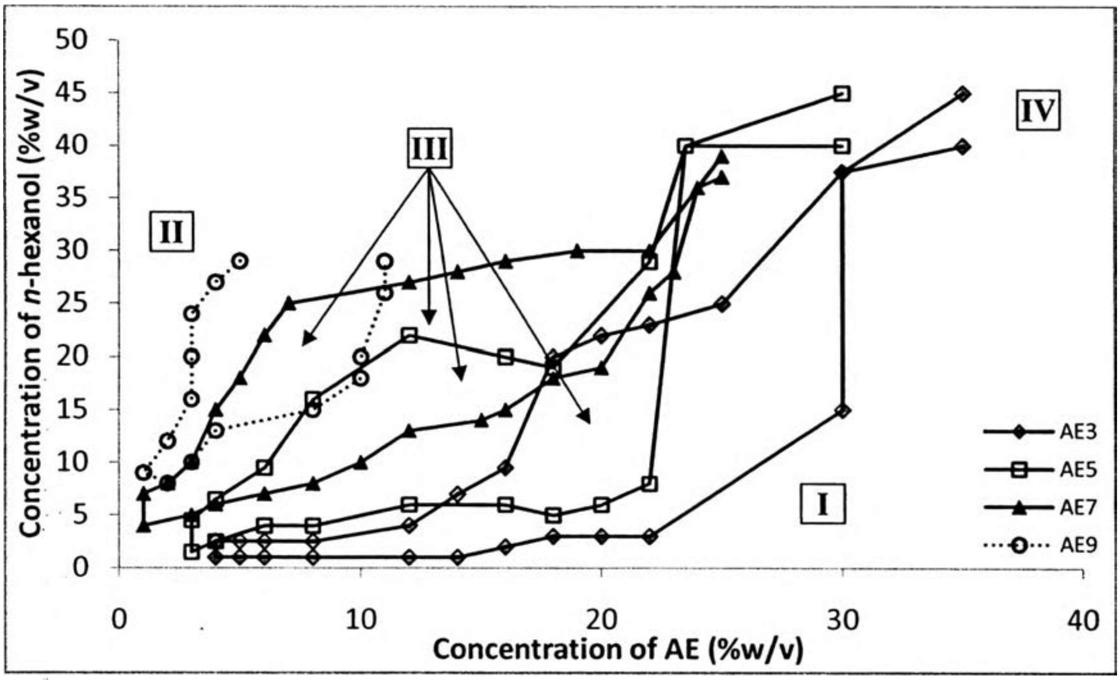

Figure 4.30 The effect of EO groups on phase diagram (fish diagram) of various AEs/*n*-hexanol/motor oil/water system at 40 °C.

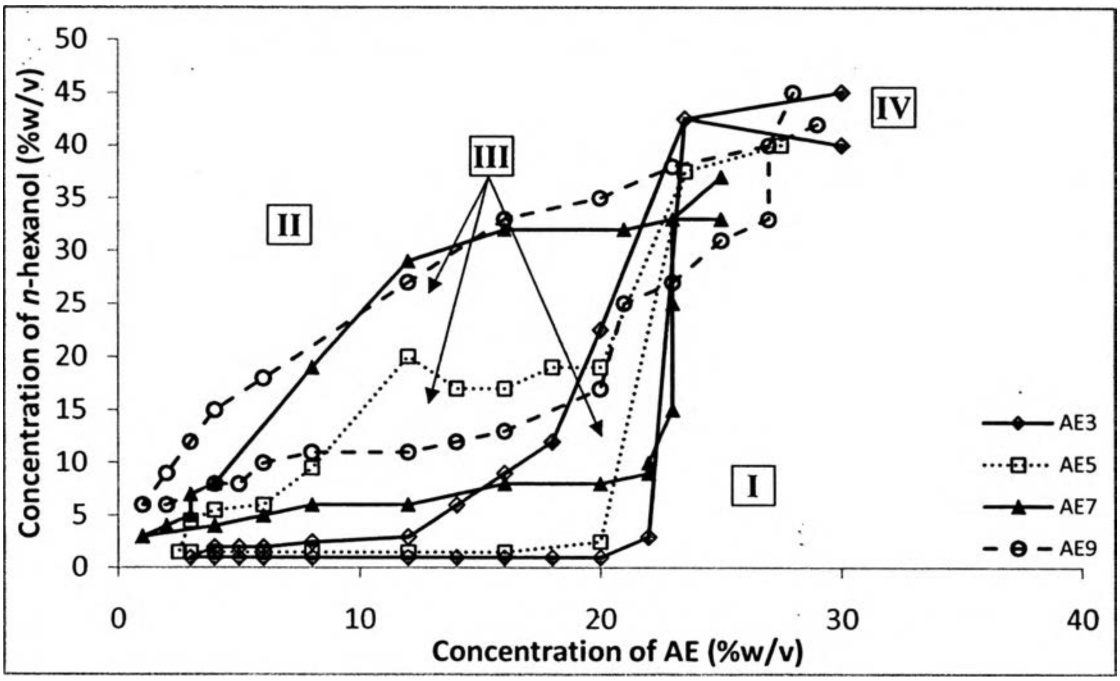

Figure 4.31 The effect of EO groups on phase diagram (fish diagram) of various AEs/*n*-hexanol/motor oil/water system at 50 °C.

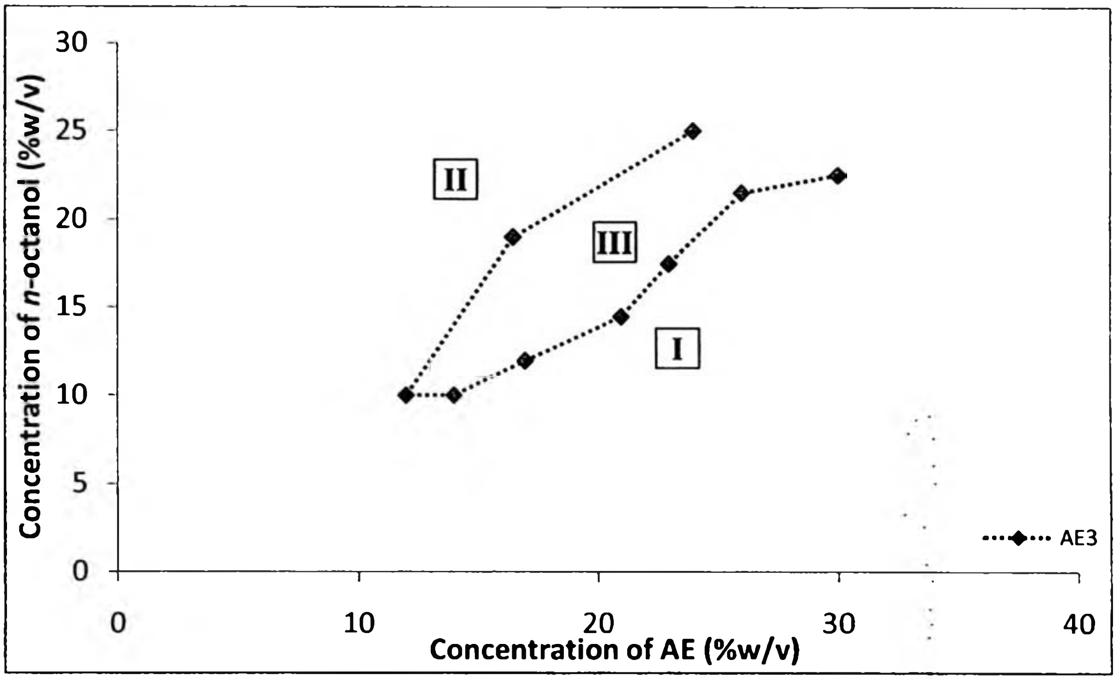

Figure 4.32 The effect of EO groups on phase diagram (fish diagram) of various AEs/*n*-octanol/motor oil/water system at 20 °C. (*Note*: Microemulsion formation of AE5, AE7 and AE9 systems were not found).

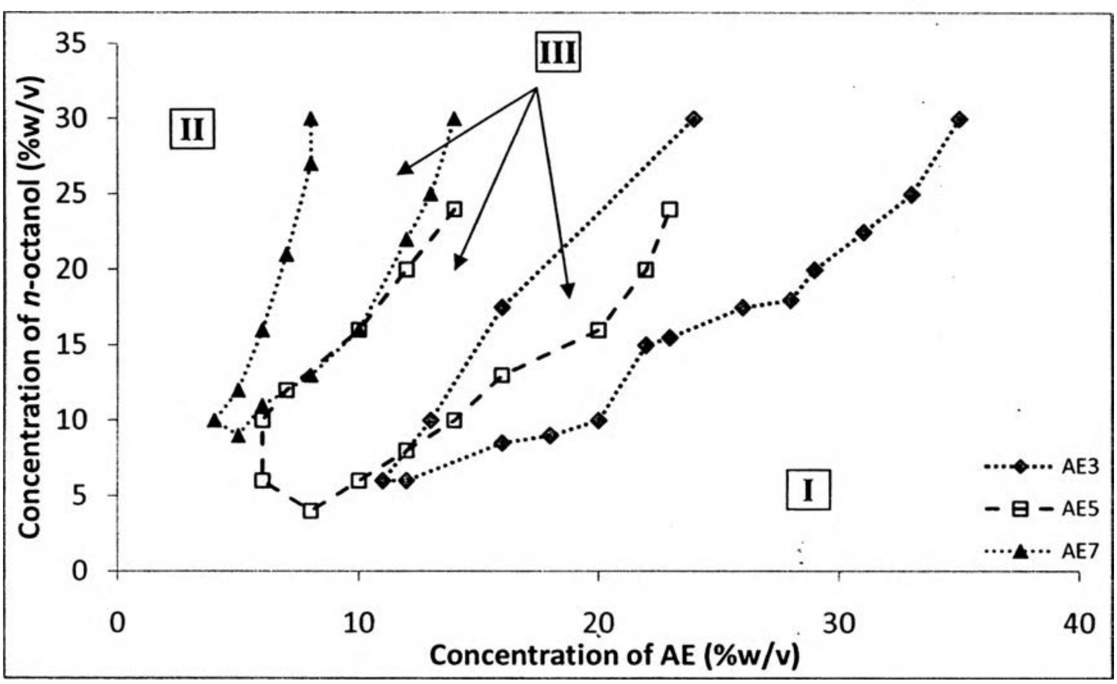

Figure 4.33 The effect of EO groups on phase diagram (fish diagram) of various AEs/*n*-octanol/motor oil/water system at 30 °C. (*Note*: Microemulsion formation of AE9 system was not found).

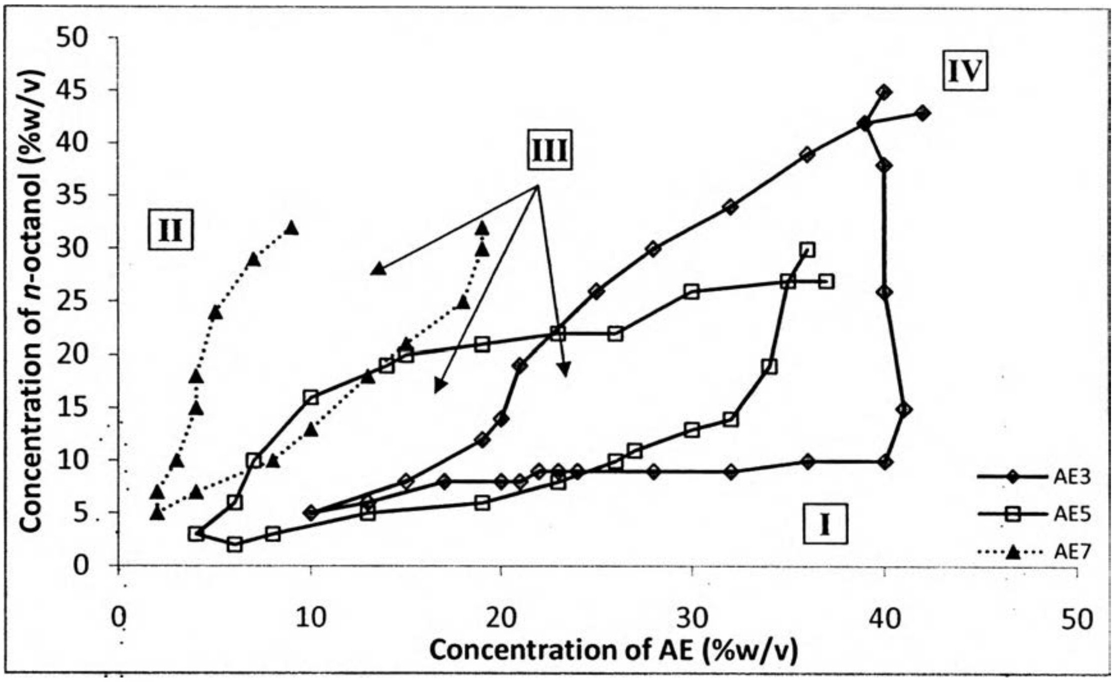

Figure 4.34 The effect of EO groups on phase diagram (fish diagram) of various AEs/*n*-octanol/motor oil/water system at 40 °C. (*Note*: Microemulsion formation of AE9 system was not found).

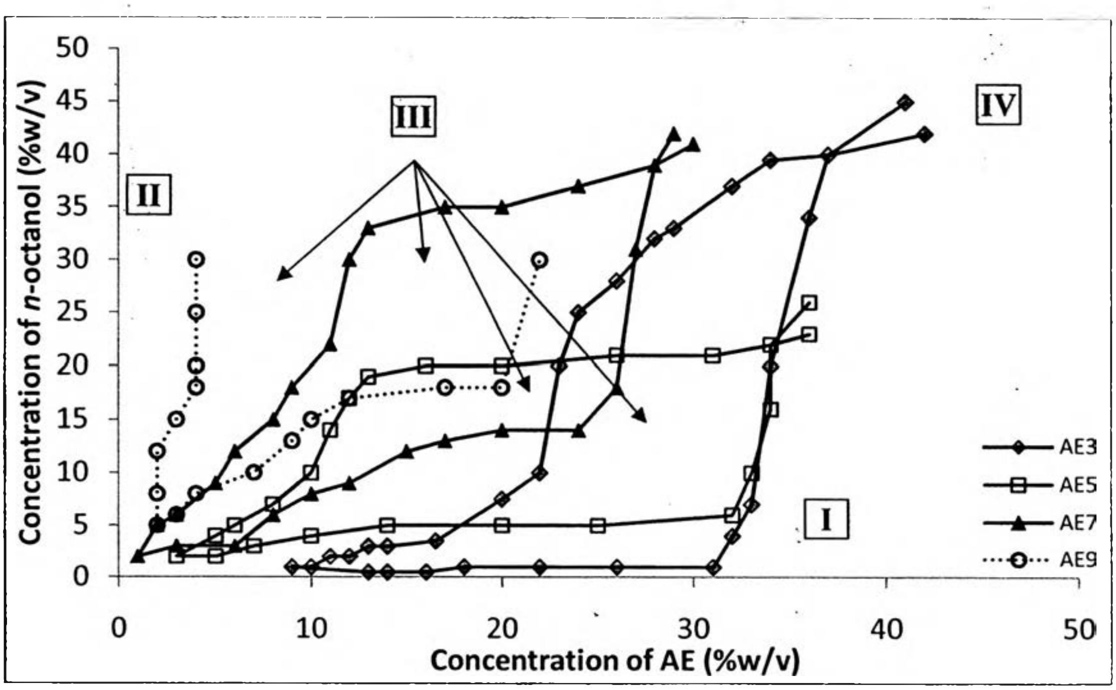

Figure 4.35 The effect of EO groups on phase diagram (fish diagram) of various AEs/*n*-octanol/motor oil/water system at 50 °C.

Table 4.3 CμC values and the concentration of and the composition at point E of AE/alcohol/motor oil/water system at various AEs.

Alcohols	Temperature (°C)	AE	CμC (%w/v)	E ([AE],[Alcohol])
n-butanol	20	AE3	15.0	(48.0, 35.0)
		AE5	N/A	N/A
		AE7	N/A	N/A
		AE9	N/A	N/A
	30	AE3	7.0	(45.0, 28.0)
		AE5	N/A	N/A
		AE7	N/A	N/A
		AE9	N/A	N/A
	40	AE3	5.0	(43.0, 24.0)
		AE5	N/A	N/A
		AE7	N/A	N/A
		AE9	N/A	N/A
	50	AE3	4.0	(38.0, 28.0)
		AE5	N/A	N/A
		AE7	N/A	N/A
		AE9	N/A	N/A
n-hexanol	20	AE3	6.0	(31.5, 37.5)
		AE5	3.5	(30.0, 45.0)
		AE7	N/A	N/A
		AE9	N/A	N/A
	30	AE3	4.0	(30.0, 42.5)
		AE5	3.0	(27.5, 32.5)
		AE7	1.0	N/A
		AE9	N/A	N/A
	40	AE3	4.0	(30.0, 37.5)
		AE5	3.0	(23.5, 40.0)
		AE7	1.0	(24.0, 36.0)
		AE9	1.0	N/A
	50	AE3	3.0	(23.5, 42.5)
		AE5	2.5	(23.5, 37.5)
		AE7	1.0	(23.0, 33.0)
		AE9	1.0	(27.0, 40.0)

Table 4.3 (Cont.)

Alcohols	Temperature (°C)	AE	CµC (%w/v)	E ([AE],[Alcohol])
n-octanol	20	AE3	12.0	N/A
		AE5	N/A	N/A
		AE7	N/A	N/A
		AE9	N/A	N/A
	30	AE3	11.0	N/A
		AE5	6.0	N/A
		AE7	4.0	N/A
		AE9	N/A	N/A
	40	AE3	10.0	(39.0, 42.0)
		AE5	4.0	(35.0, 27.0)
		AE7	2.0	N/A
		AE9	N/A	N/A
	50	AE3	9.0	(37.0, 40.0)
		AE5	3.0	(34.0, 22.0)
		AE7	1.0	(28.0, 39.0)
		AE9	2.0	N/A

4.2 Solubilization Parameters (SP)

After equilibration, the height of each liquid phase was measured using a cathetometer. The solubilization capacities were calculated in terms of the Solubilization Parameters, which is the volume of either oil or water dissolved per weight of total surfactants.

4.2.1 Effect of Temperature on Solubilization Parameters (SP)

Solubilization Parameters (SP) of the nonionic surfactant system consisting of AE/alcohol/motor oil/water system were examined at four different temperatures (20 °C, 30 °C, 40 °C, and 50 °C) for a constant of alcohol concentration of 10 %w/v. The SP is defined as the volume of oil solubilized (SPo) or of water solubilized (SPw) per weight of total surfactants in the microemulsion phase (Tantakit *et al.*, 2009)

Figure 4.36 to Figure 4.44 illustrate the phase behavior of motor oil in terms of SPw and SPo. The transition of microemulsion phase shifted from Winsor

Type II microemulsion or Water-in- Oil (W/O) to Winsor Type III microemulsion or middle (M) to Winsor Type I microemulsion or Oil-in-Water (O/W) microemulsion phases with increasing in the AE concentration. At highest temperature (50 °C), the volume fraction of the middle phase was larger than those at the other low temperatures. Moreover, for the relatively low temperature (20 °C, and 30 °C), the macroemulsion appeared at high AE concentrations, but it disappeared at higher temperatures. In the case of AE3 and AE5 which are hydrophobic molecules, the SPw slightly decreased and then remained constant with increasing AE concentration while the SPo was high in the W/O microemulsion region and dramatically dropped in the middle phase region. The value of SPo in the O/W microemulsion region became lower than SPw at any given AE concentration. While on the contrary AE7 and AE9 which are hydrophilic molecules, the SPo slightly changed and then remained constant with increasing AE concentration while the SPw was high in the O/W microemulsion region and dramatically dropped with an increase AE concentration. The value of SPw in the O/W microemulsion region became higher than SPo at any given AE concentration except the case of AE7 with both *n*-hexanol and *n*-octanol at 50 °C which show the W/O microemulsion at 4 %w/v of AE. From the results, it might be explained by the fact that the hydrophobic molecules (AE3 and AE5) are formed Winsor Type III microemulsion easier than the hydrophilic molecules (AE7 and AE9) because motor oil are more solubilized in the micelle core of hydrophobic molecule (SPo is higher than SPw) and vice versa. Moreover, the results can be concluded that temperature facilitates the solubilization of oil, helping the formation of Winsor Type III microemulsion.

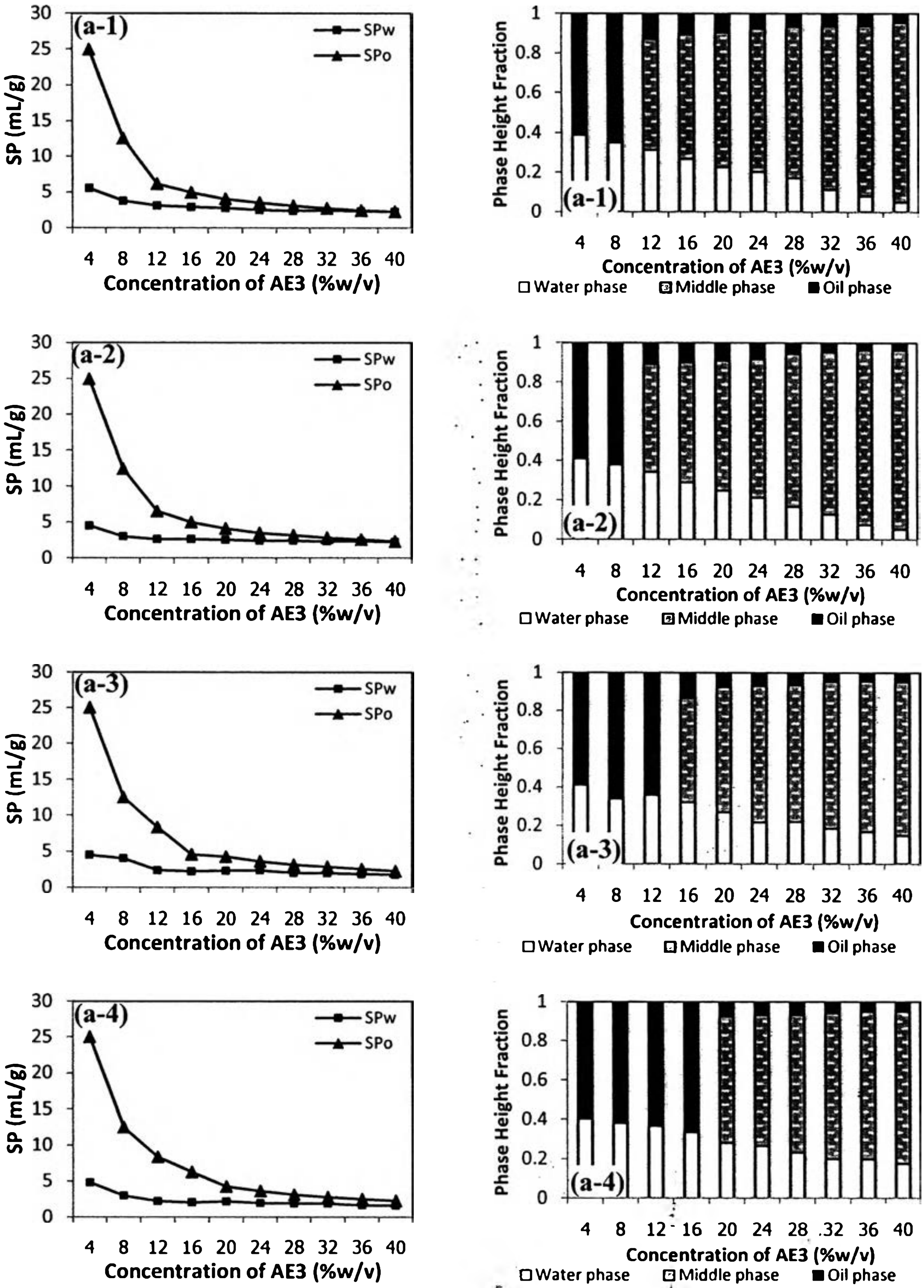

Figure 4.36 Solubilization Parameters (SP) and phase height fraction as a function of AE3 concentration comprising AE3/*n*-hexanol/motor oil/water: (a-1) at 20 °C, (a-2) at 30 °C, (a-3) at 40 °C, and (a-4) at 50 °C.

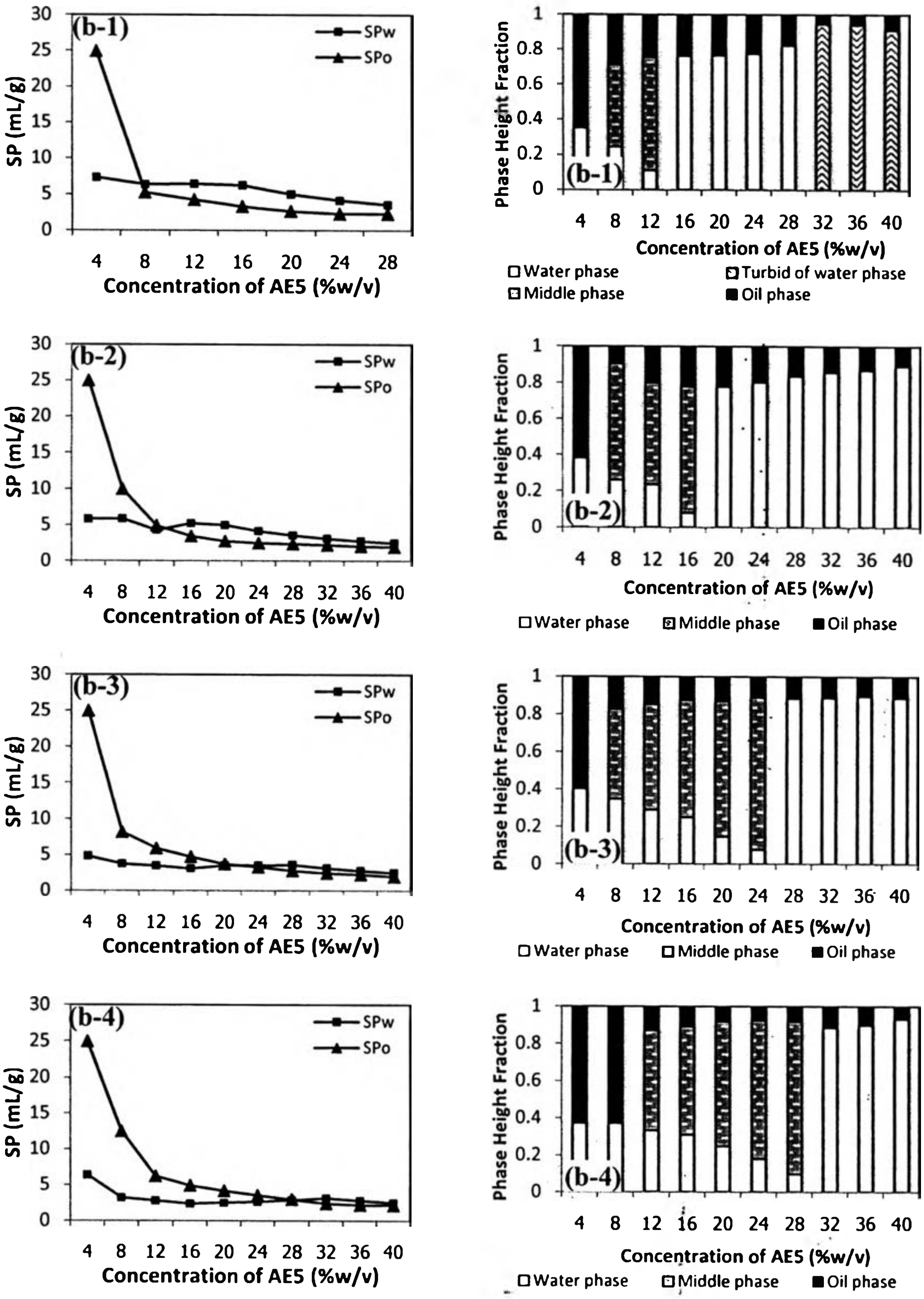

Figure 4.37 Solubilization Parameters (SP) and phase height fraction as a function of AE5 concentration comprising AE5/*n*-hexanol/motor oil/water: (b-1) at 20 °C, (b-2) at 30 °C, (b-3) at 40 °C, and (b-4) at 50 °C.

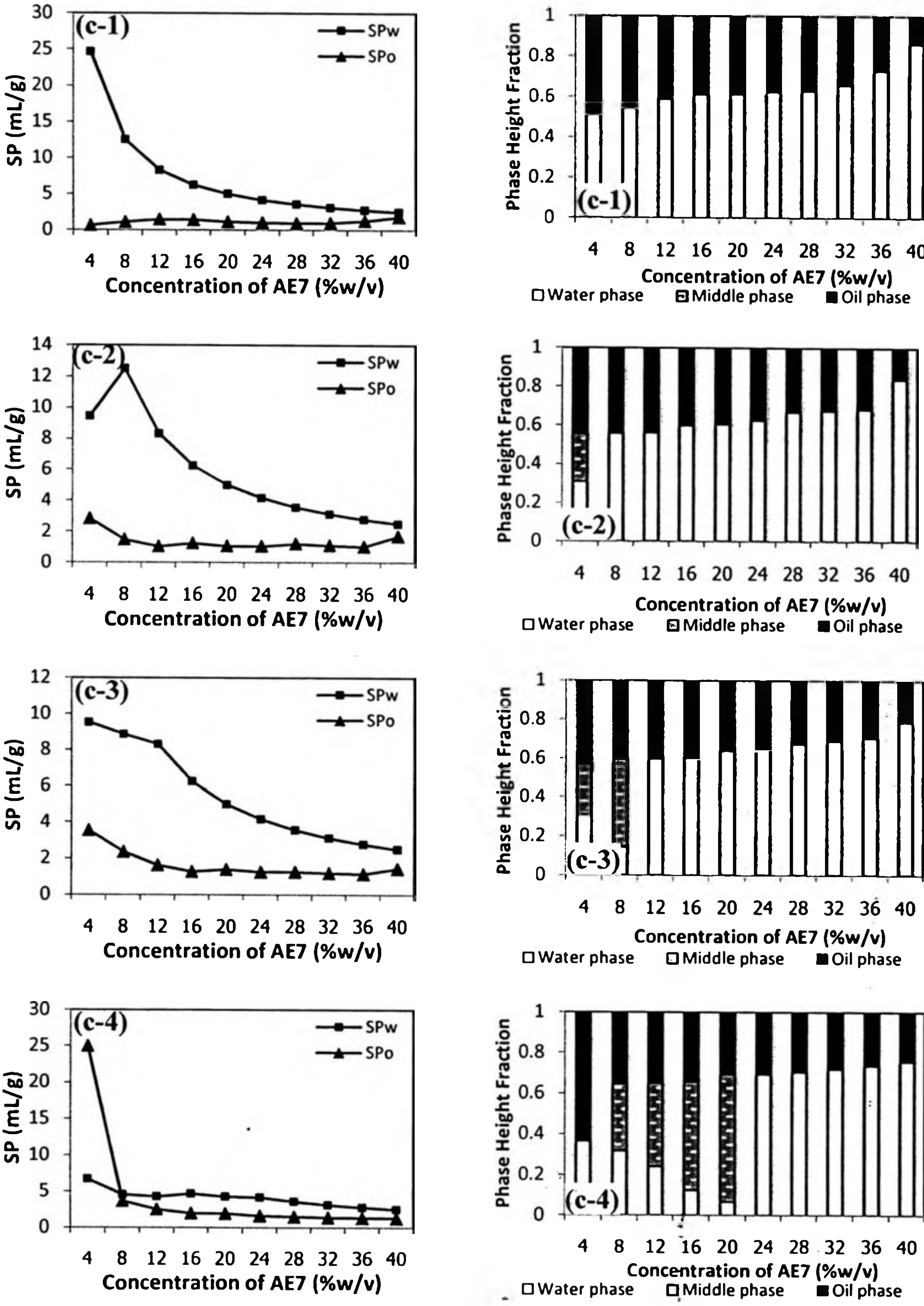

Figure 4.38 Solubilization Parameters (SP) and phase height fraction as a function of AE7 concentration comprising AE7/*n*-hexanol/motor oil/water: (c-1) at 20 °C, (c-2) at 30 °C, (c-3) at 40 °C, and (c-4) at 50 °C.

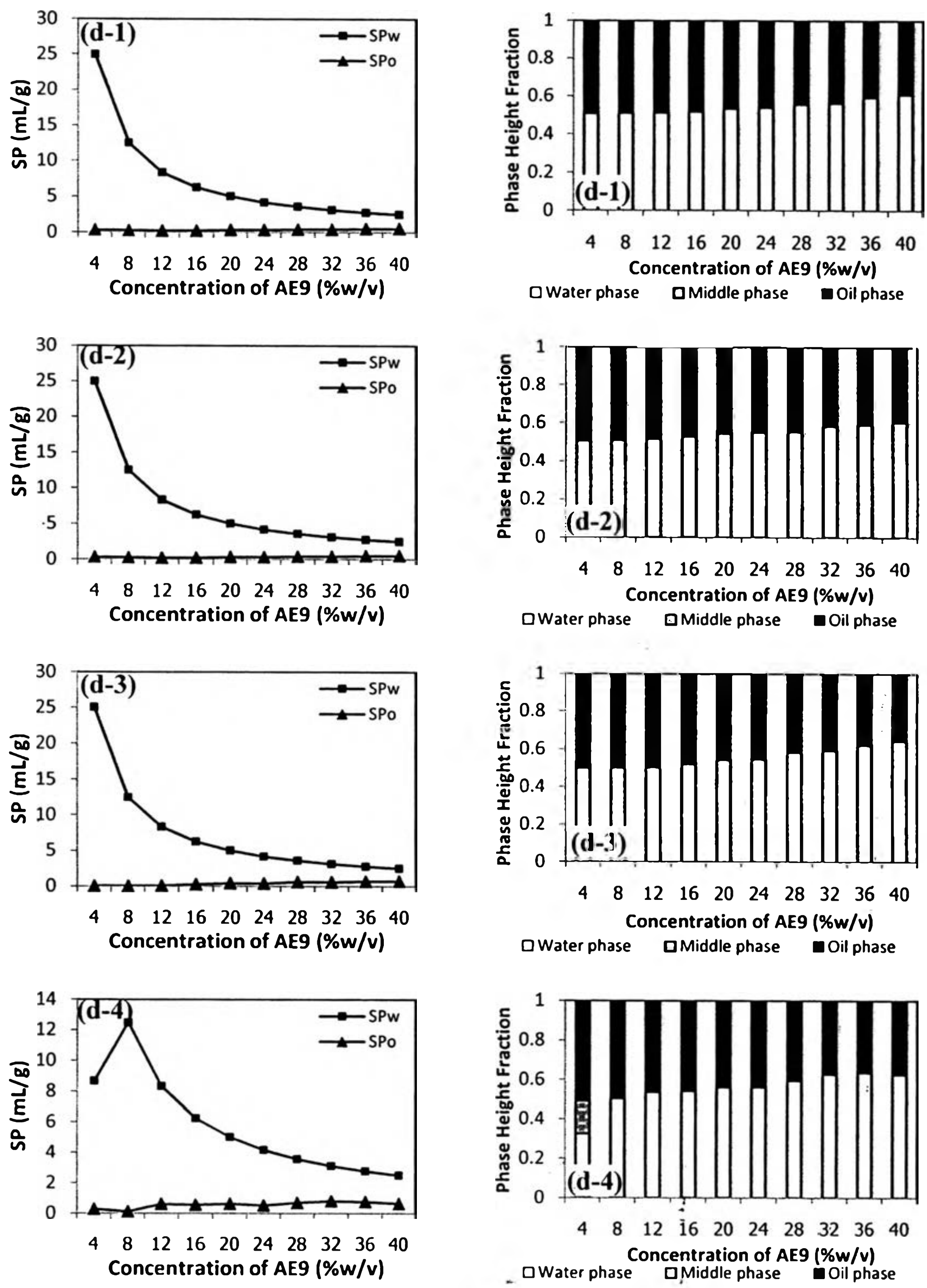

Figure 4.39 Solubilization Parameters (SP) and phase height fraction as a function of AE9 concentration comprising AE9/*n*-hexanol/motor oil/water: (d-1) at 20 °C, (d-2) at 30 °C, (d-3) at 40 °C, and (d-4) at 50 °C.

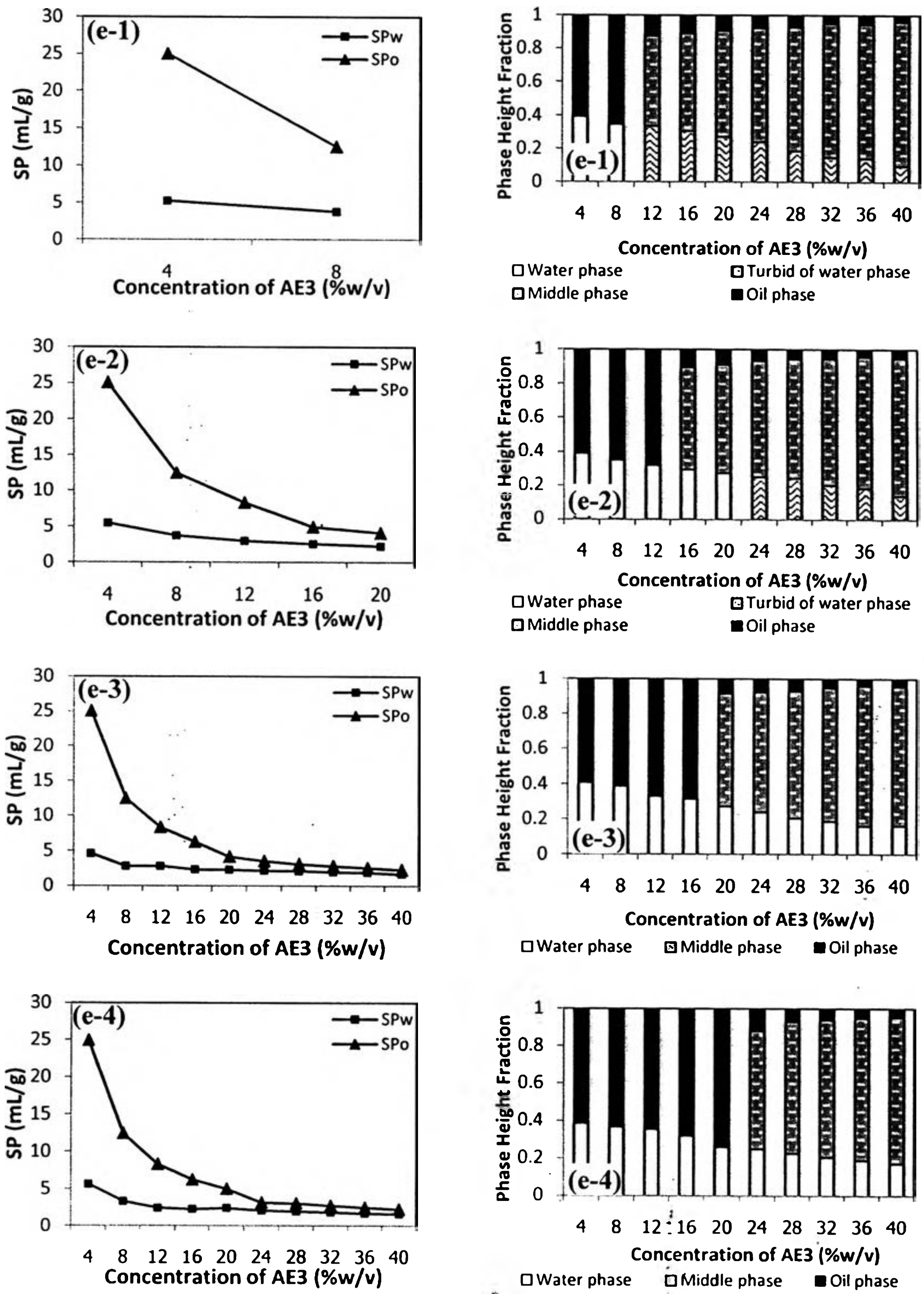

Figure 4.40 Solubilization Parameters (SP) and phase height fraction as a function of AE3 concentration comprising AE3/*n*-octanol/motor oil/water: (e-1) at 20 °C, (e-2) at 30 °C, (e-3) at 40 °C, and (e-4) at 50 °C.

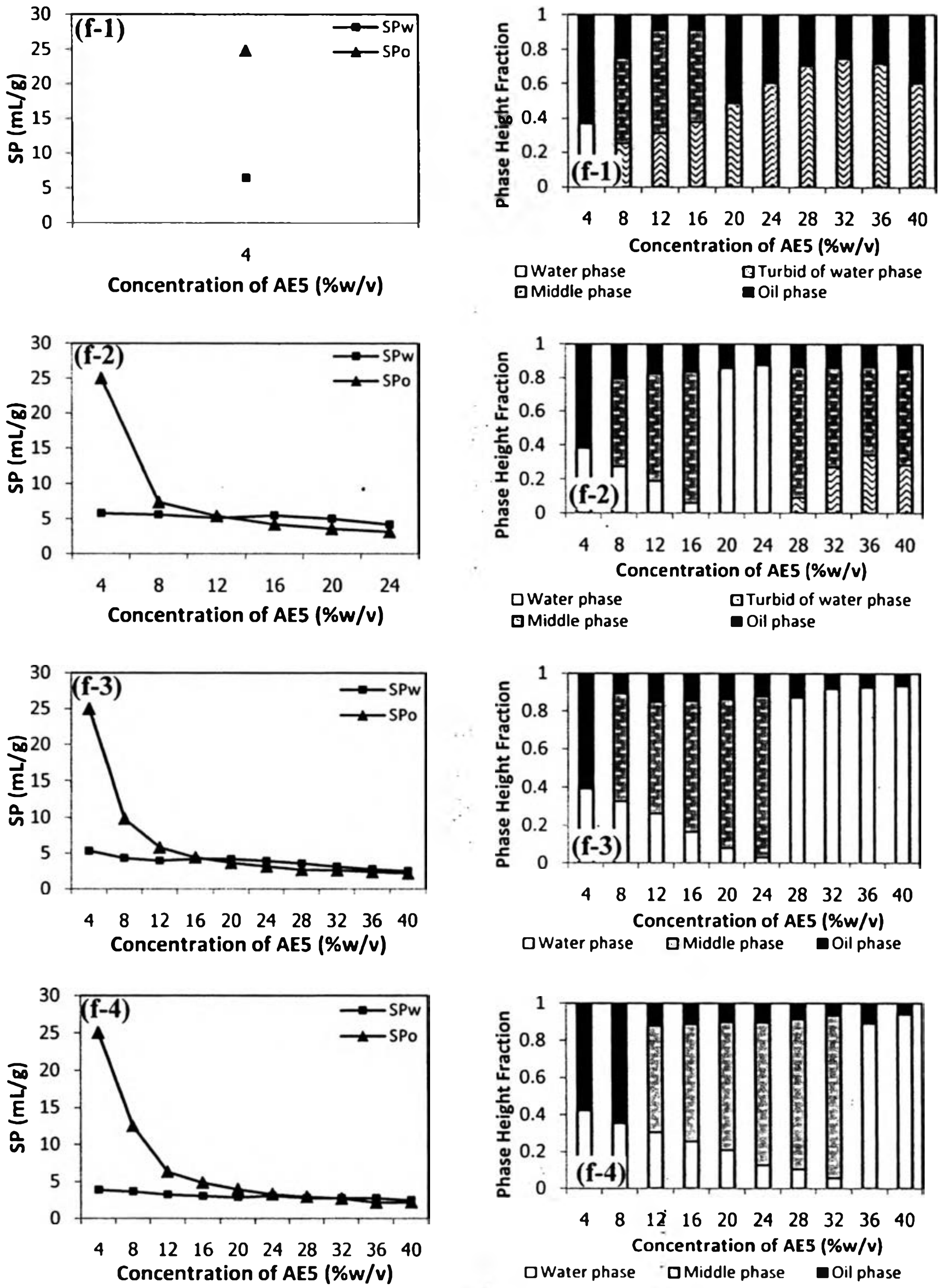

Figure 4.41 Solubilization Parameters (SP) and phase height fraction as a function of AE5 concentration comprising AE5/*n*-octanol/motor oil/water: (f-1) at 20 °C, (f-2) at 30 °C, (f-3) at 40 °C, and (f-4) at 50 °C.

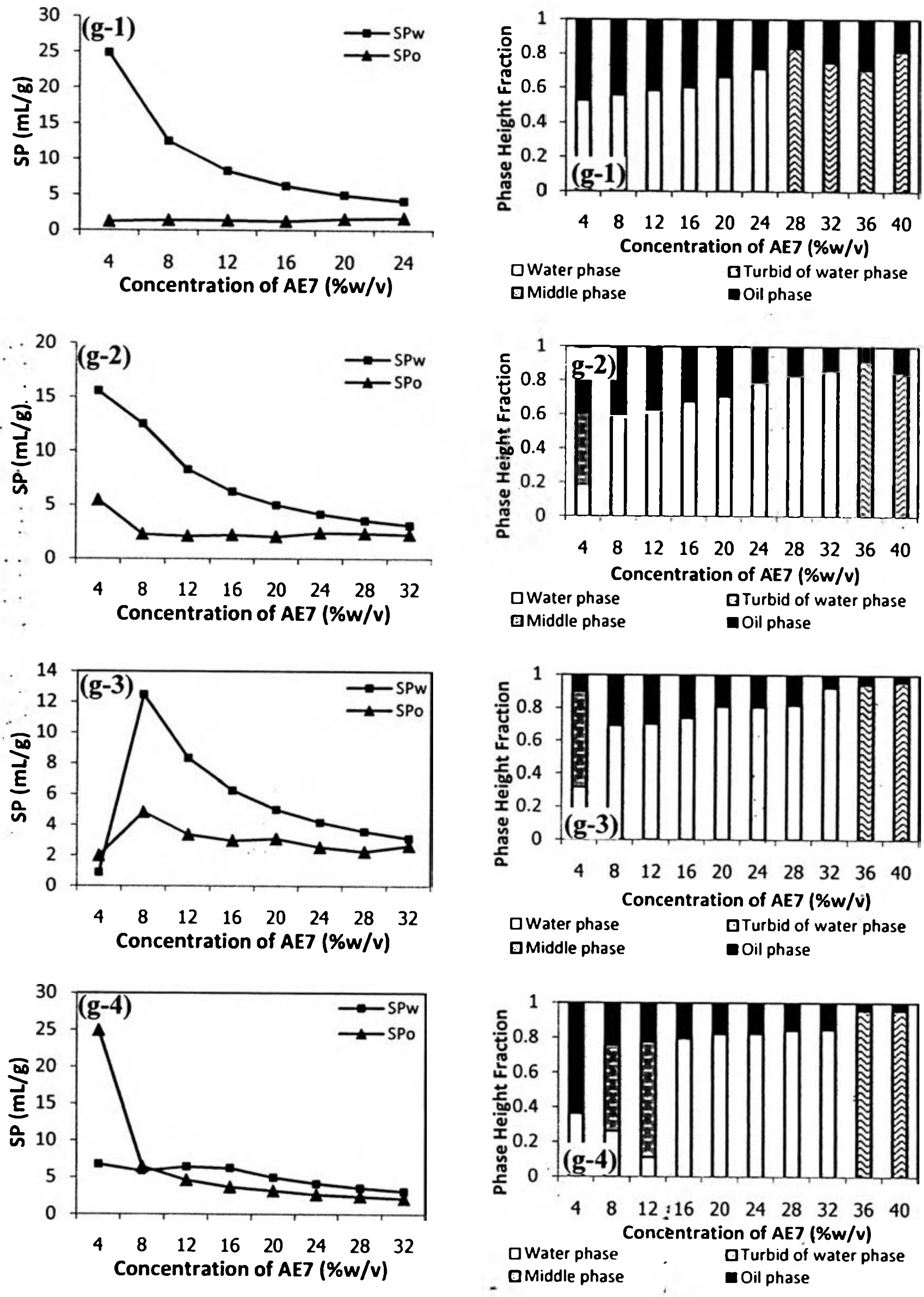

Figure 4.42 Solubilization Parameters (SP) and phase height fraction as a function of AE7 concentration comprising AE7/*n*-octanol/motor oil/water: (g-1) at 20 °C, (g-2) at 30 °C, (g-3) at 40 °C, and (g-4) at 50 °C.

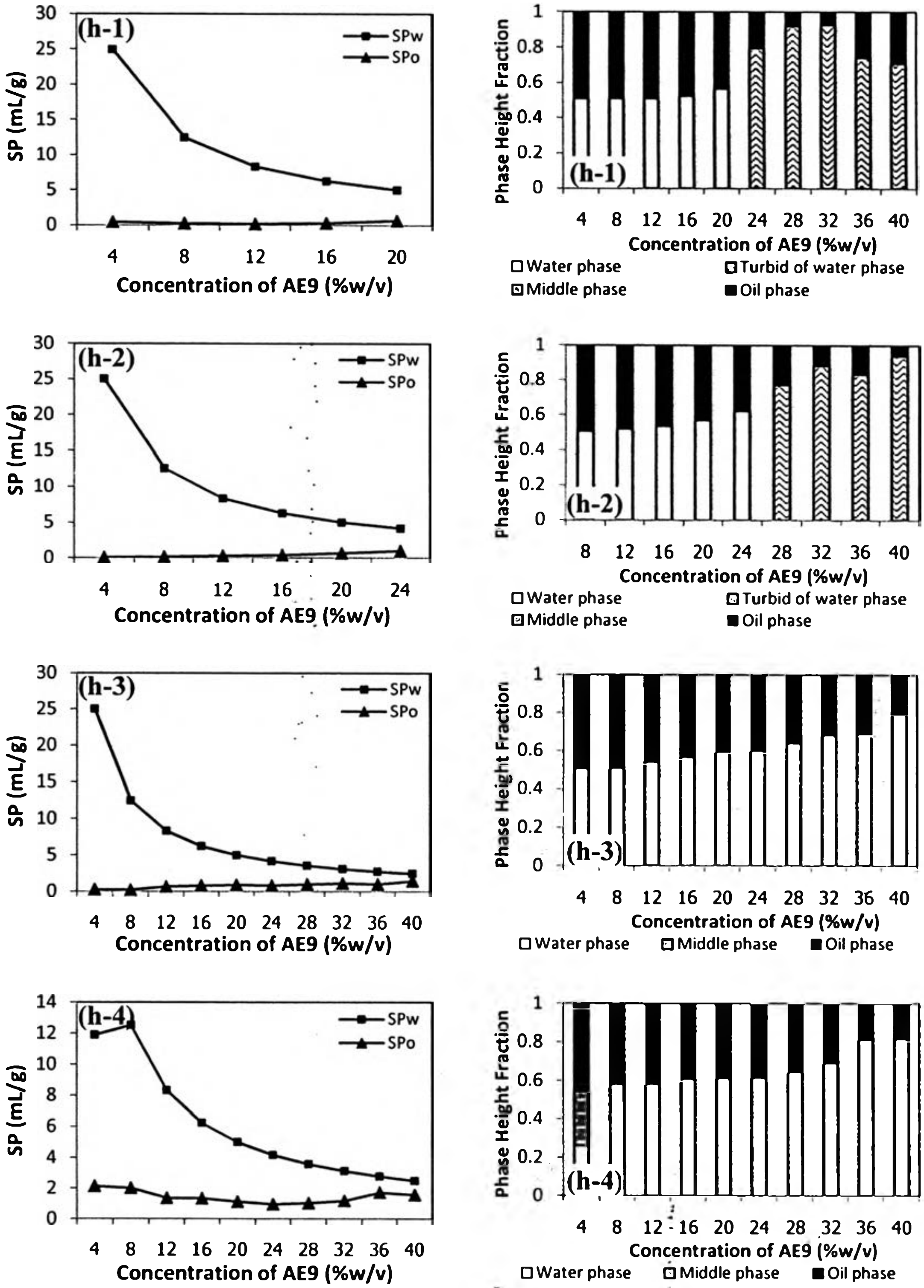

Figure 4.43 Solubilization Parameters (SP) and phase height fraction as a function of AE9 concentration comprising AE9/*n*-octanol/motor oil/water: (h-1) at 20 °C, (h-2) at 30 °C, (h-3) at 40 °C, and (h-4) at 50 °C.

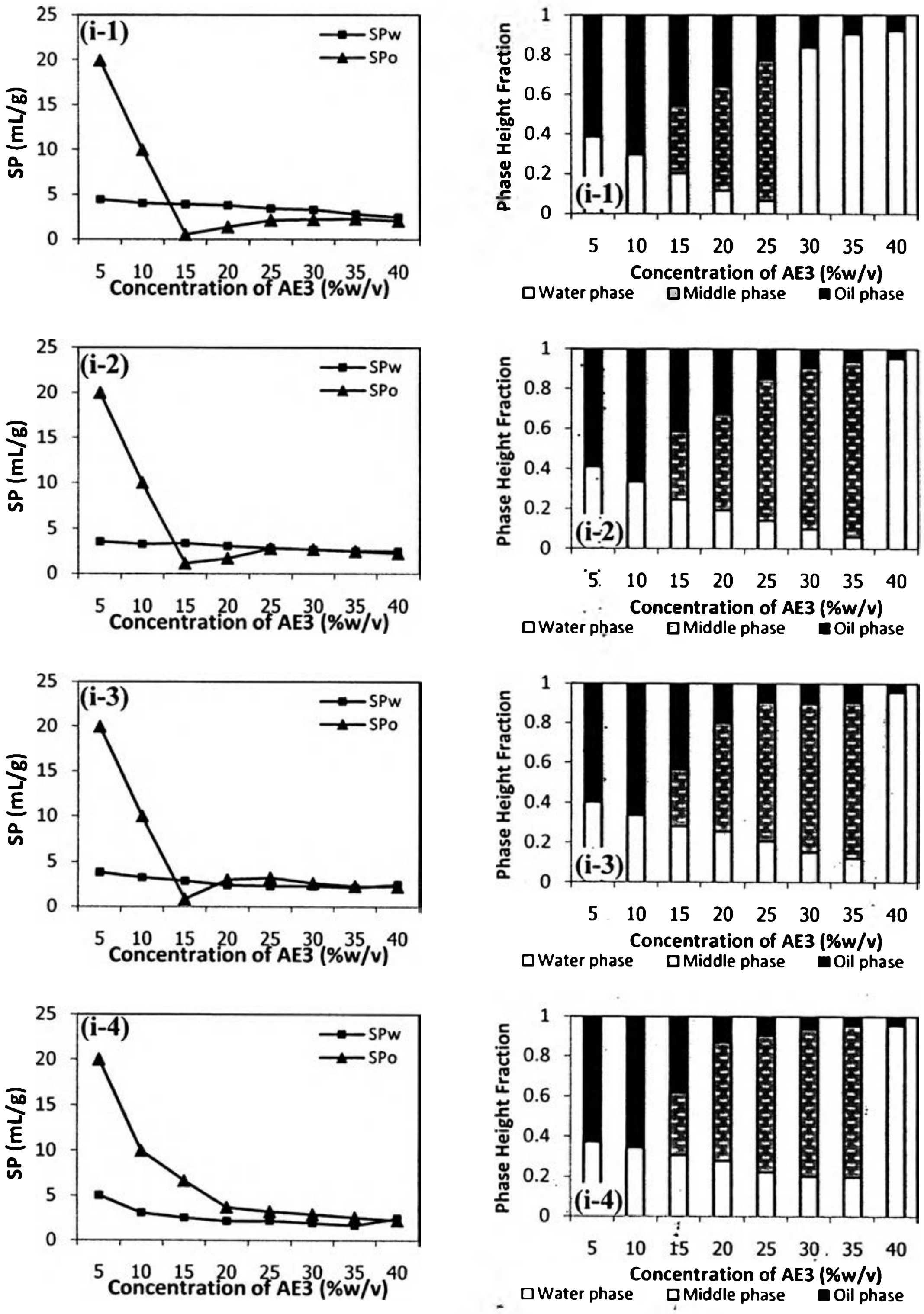

Figure 4.44 Solubilization Parameters (SP) and phase height fraction as a function of AE9 concentration comprising AE9/*n*-octanol/motor oil/water: (i-1) at 20 °C, (i-2) at 30 °C, (i-3) at 40 °C, and (i-4) at 50 °C.

4.2.2 Effect of Cosurfactant Chain Length on Solubilization Parameters (SP)

In order to study the effect of cosurfactant chain length on SP, the system AE3/alcohol/motor oil/water at 20 °C, 30 °C, 40 °C, and 50 °C was chosen because the microemulsion formation of AE3 can be formed with all cosurfactants (*n*-butanol, *n*-hexanol, and *n*-octanol) and alcohol concentration was kept constant at 10 %w/v as same as the previous studied.

Figure 4.45 to Figure 4.48 indicate the phase behavior of motor oil in terms of SPw and SPo and the phase height fraction of water, middle, and oil phases. The transition of microemulsion phase shifted from Winsor Type II microemulsion or Water-in-Oil (W/O) to Winsor Type III microemulsion or middle (M) to Winsor Type I microemulsion or Oil-in-Water (O/W) microemulsion phases with increasing in the AE3 concentration. The SPw slightly decreased and then remained constant with increasing AE3 concentration while the SPo was high in the W/O microemulsion region and dramatically dropped in the middle phase region. The value of SPo in the O/W microemulsion region became lower than SPw at any given AE3 concentration. Among the studied alcohols, *n*-haxanol was the most effective cosurfactant in terms of Winsor Type III microemulsion formation because it provide wider middle phase region at every studied temperatures than the other two cosurfactants. Moreover, for the *n*-octanol system at 20 °C, and 30 °C, the macroemulsion appeared at high AE concentrations according to *n*-octanol is the hydrophobic molecules so that it less solubilized into the water phase, hence, the macroemulsion can be formed.

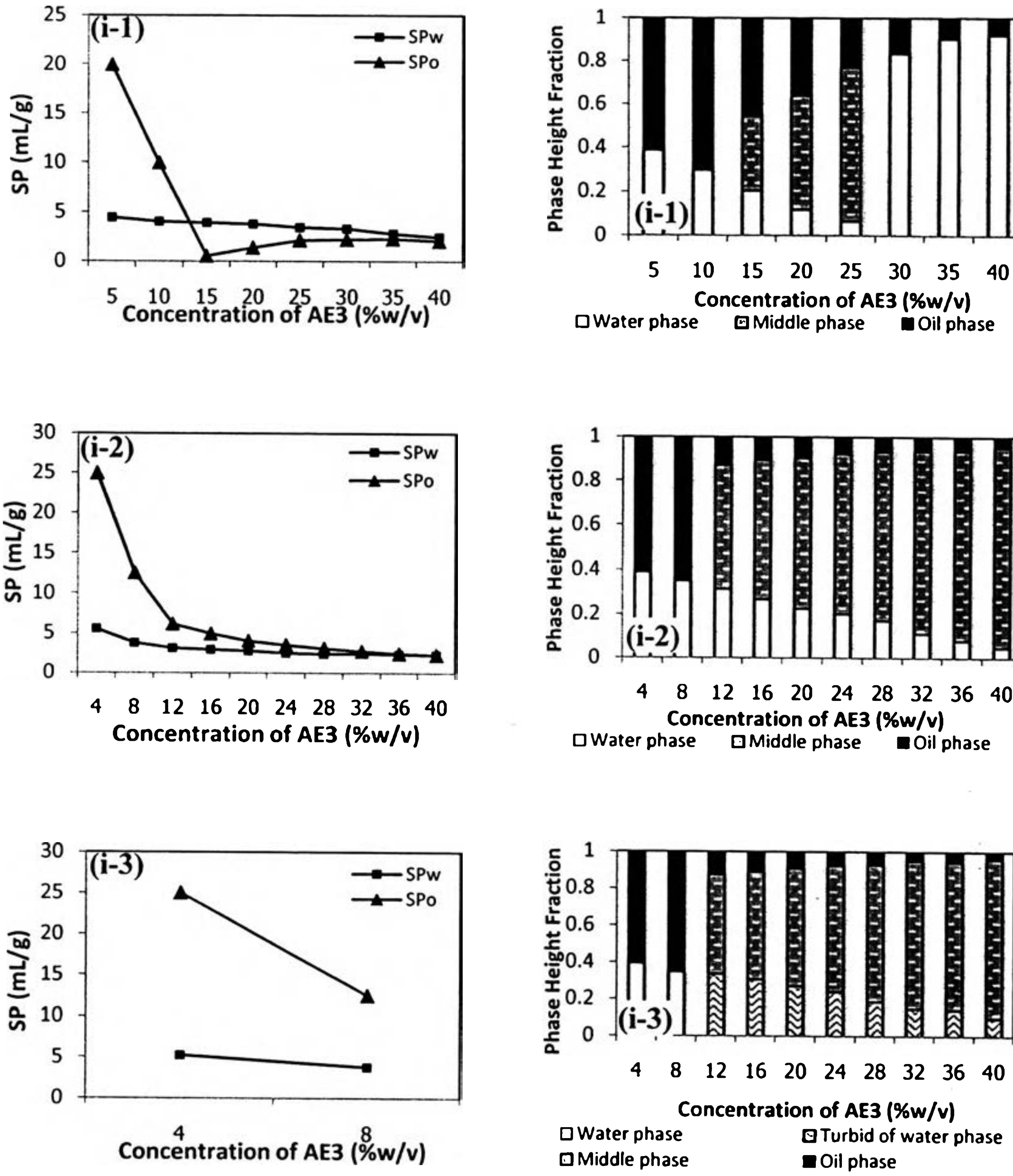

Figure 4.45 Solubilization Parameters (SP) and phase height fraction as a function of AE3 concentration comprising AE3/*alcohol*/motor oil/water at 20 °C (i-1) with *n*-butanol, (i-2) with *n*-hexanol, and (i-3) with *n*-octanol.

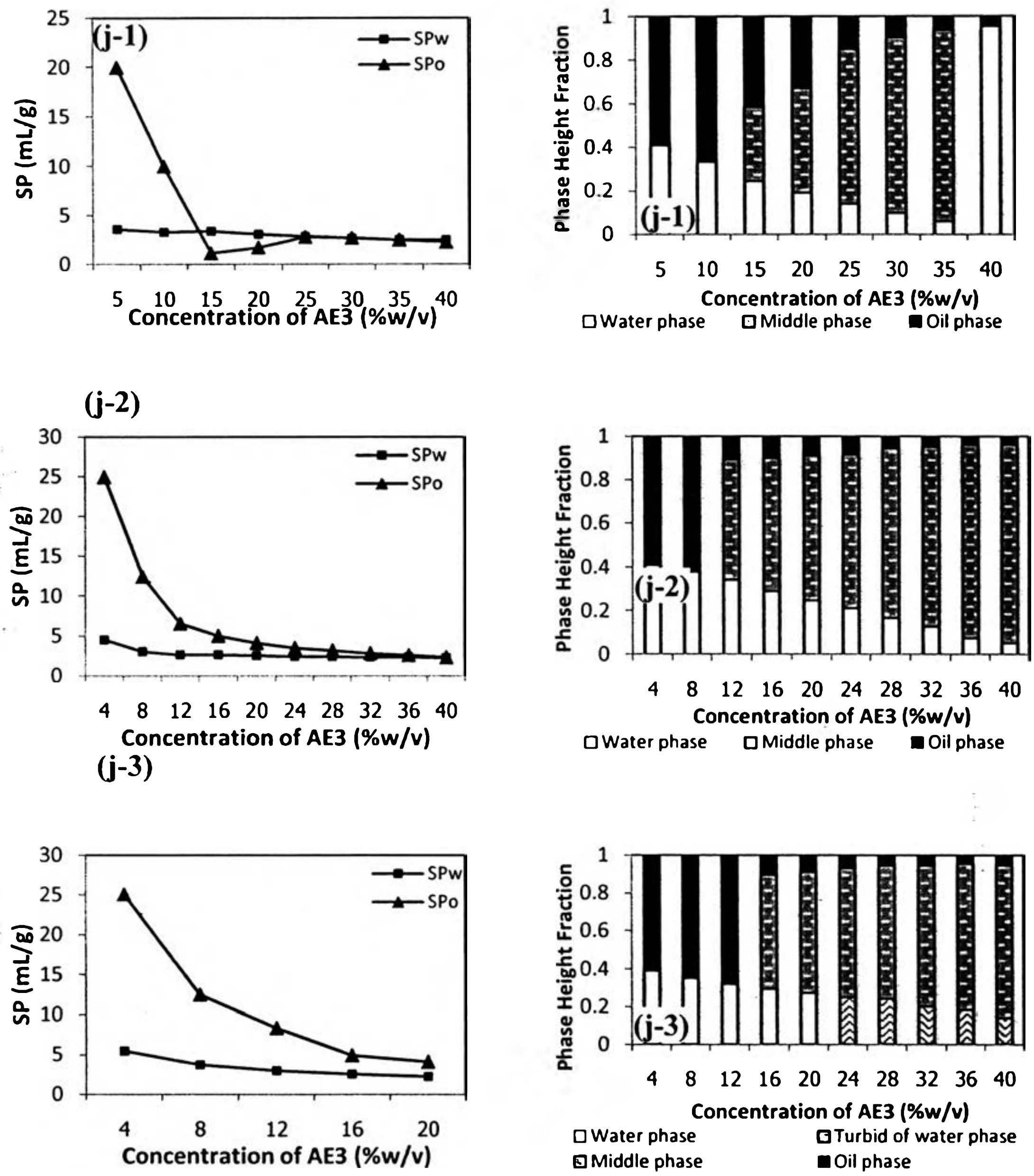

Figure 4.46 Solubilization Parameters (SP) and phase height fraction as a function of AE3 concentration comprising AE3/*alcohol*/motor oil/water at 30 °C (j-1) with *n*-butanol, (j-2) with *n*-hexanol, and (j-3) with *n*-octanol.

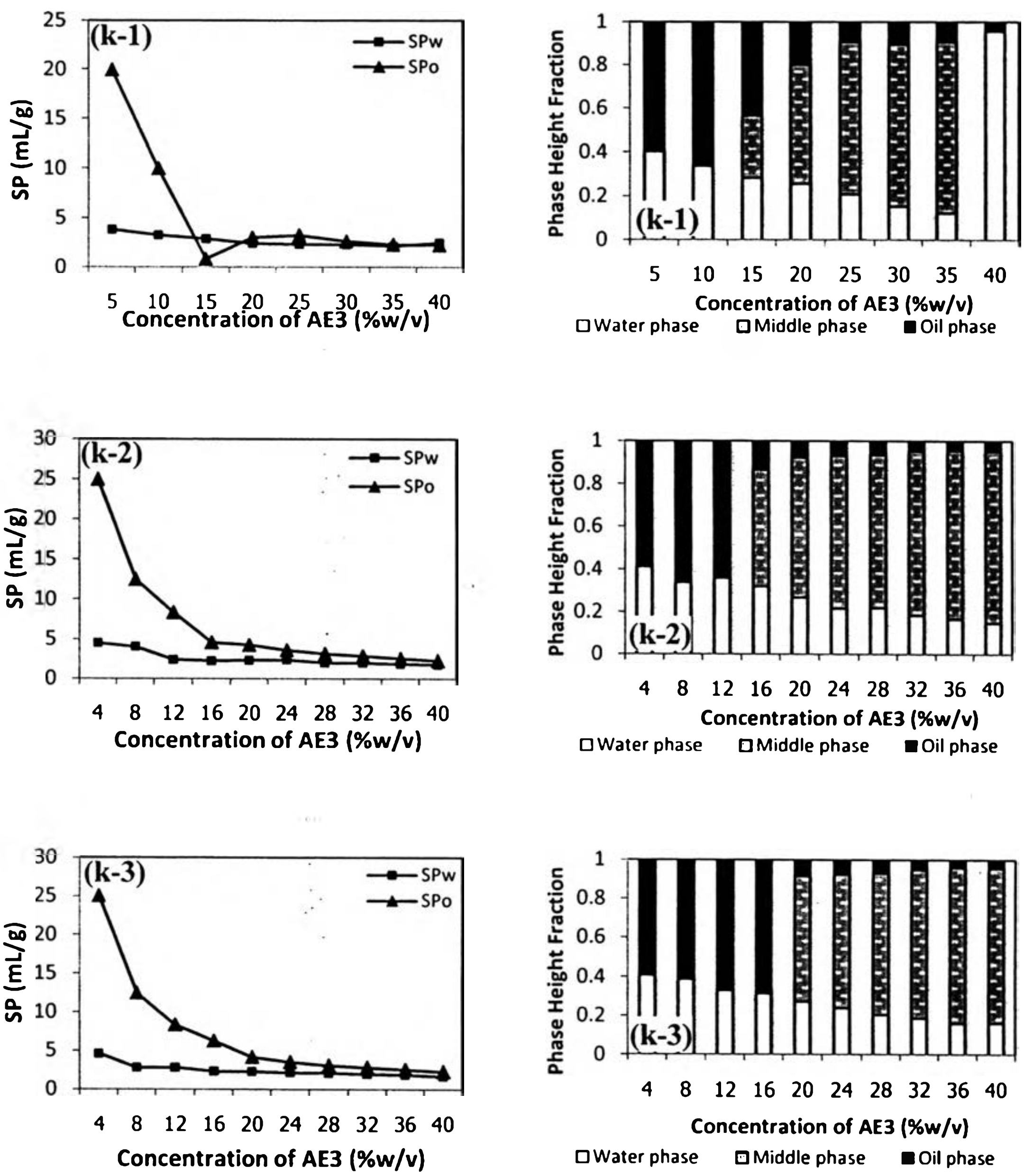

Figure 4.47 Solubilization Parameters (SP) and phase height fraction as a function of AE3 concentration comprising AE3/*alcohol*/motor oil/water at 40 °C (k-1) with *n*-butanol, (k-2) with *n*-hexanol, and (k-3) with *n*-octanol.

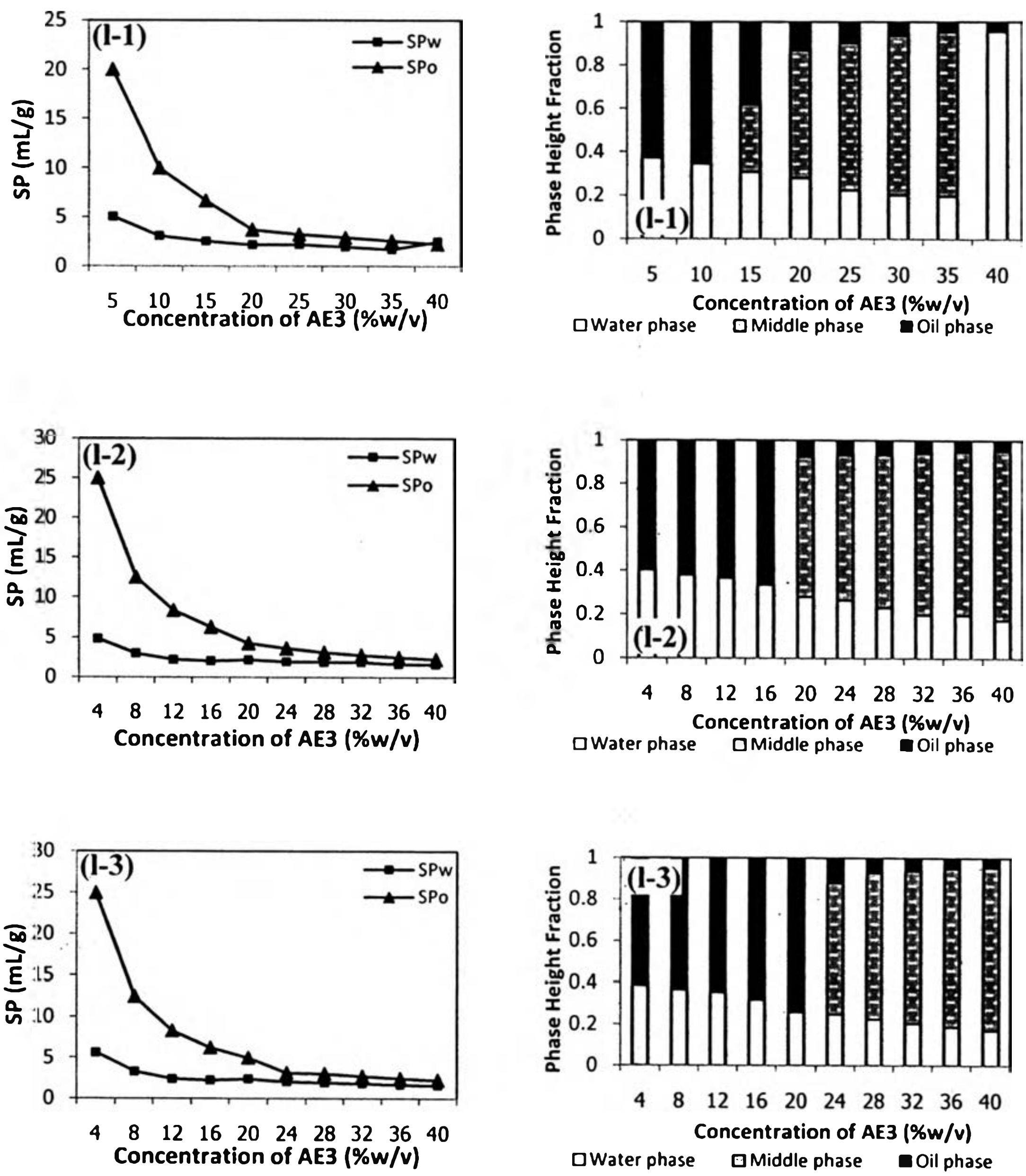

Figure 4.48 Solubilization Parameters (SP) and phase height fraction as a function of AE3 concentration comprising AE3/*alcohol*/motor oil/water at 50 °C (l-1) with *n*-butanol, (l-2) with *n*-hexanol, and (l-3) with *n*-octanol.

4.3 Cloud Point Temperature

The cloud point measurement was modified from the standard test method D 2024-65 (Rosen, 2004). The cloud point of aqueous surfactant solutions were determined visually by noting the turbid temperature and separated-phase temperature while heating 5 ml of such surfactant solution in the screw-capped vial. Therefore, cloud point was taken as the average temperature between the surfactant solutions turned into turbidity and separated into 2 phases upon being heated. The determination was repeated 3 times for each solution and the heating rate was kept at 0.5 °C for 2 hours.

4.3.1 Effect of EO groups on cloud point temperature

The effect of EO groups on cloud point temperature at 1 %w/v of AEs is reported in Table 4.4. Increasing EO groups result in an increased in cloud point temperature. Increasing number of EO groups tended to increase the water solubility because the molecules of such surfactant became more hydrophilic, resulting in an increase in cloud point temperature. In the case of AE3 and AE5 surfactant solutions, they are both definitely cloudy at 0 °C, suggesting that the cloud point temperatures of both surfactant solutions are below 0 °C.

Table 4.4. Cloud point temperature at 1%w/v of AEs

Surfactant	Cloud Point Temperature (°C)
AE3	< 0
AE5	< 0
AE7	57
AE9	77

4.3.2 Effect of concentration of AEs on cloud point temperature

In order to study the effect of concentration of AE on cloud point temperarue, the system of AE3/alcohol/motor oil/water was selected because it can form Winsor Type III microemulsion with all cosurfactants. Figure 4.49 illustrates the cloud point temperature as a function of AEs concentration. The result shows that the cloud point temperature increases with increasing AEs concentration. As temperature increases, nonionic surfactants will be lose its water solubilitiy and change from water-soluble to oil-soluble. As the temperature reaches a certain level, the balance between the hydrophilic and hydrophobic interactions will be broken and the surfactant molecules will be separate out from the originally homogeneous micellar solution. As a result, the homogeneous micellar solution phase-separates into two coexisting phases (Jing *et al.*, 2009).

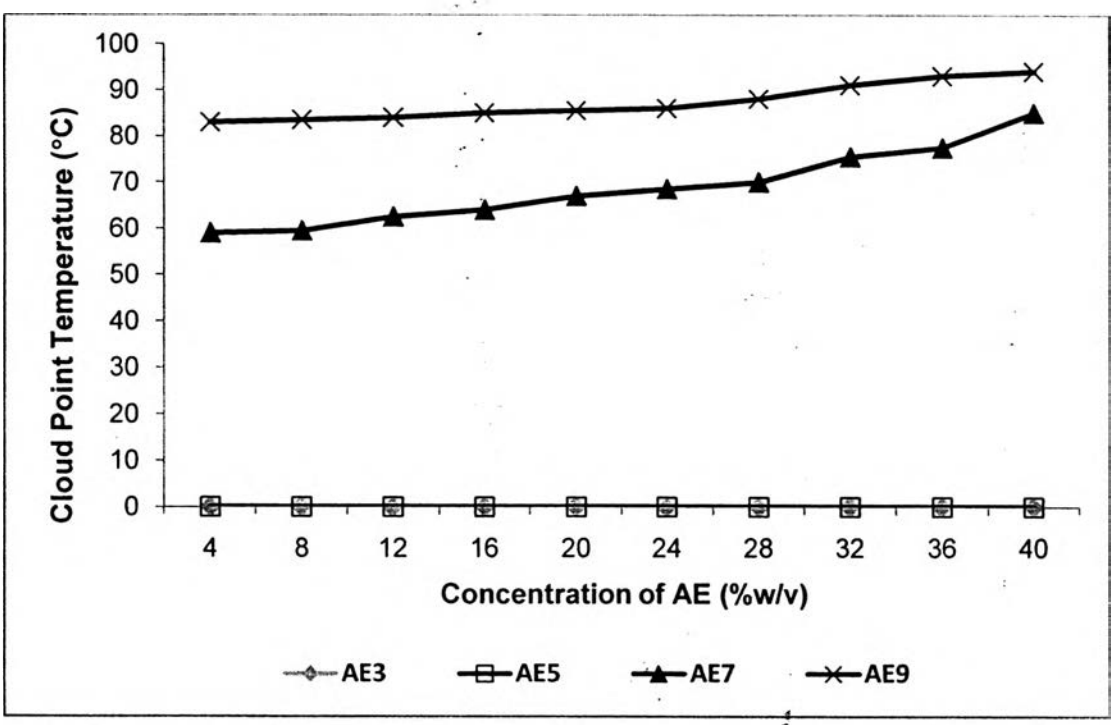

Figure 4.49 The cloud point temperature as a function of AEs concentration.

4.3.3 Effect of added alcohols on cloud point temperature

Figure 4.50 shows the effect of added alcohols on the cloud point temperature at different AE3 concentrations. As indicated in the figure, the addition of alcohol including *n*-butanol, *n*-hexanol, and *n*-octanol increased the cloud point temperature. In general, shorter chain alcohols have better solubility in water. In other words, alcohols with longer chain length are partially soluble in water (Jing *et al.*, 2009). Therefore, *n*-butanol is soluble in water and form strong hydrogen bond more than *n*-hexanol, and *n*-octanol, respectively. As a result, an addition of alcohol increases the cloud point temperature. The lower the alcohol molecular weight, the higher the cloud point temperature. For any given alcohol, the cloud point of AE3 was found to increase with increasing AE3 concentration.

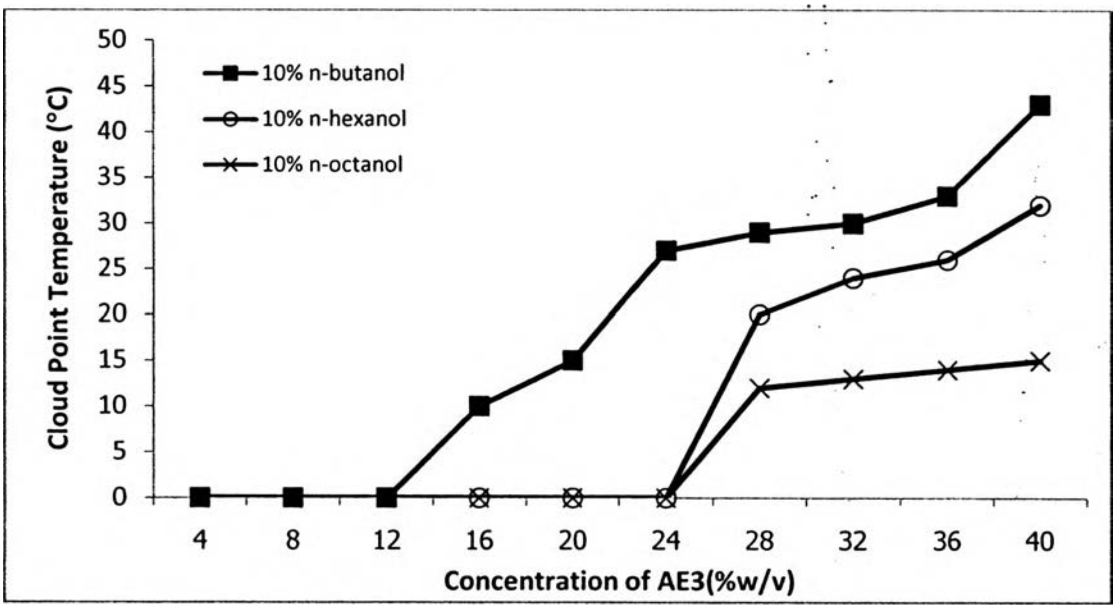

Figure 4.50 The effect of various alcohols on the cloud point temperature at different AE3 concentrations.