

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Phase Diagram of Microemulsion

Phase diagrams of the microemulsion systems using the C₃-C₇ fatty acids are shown in Figure 4.1. The diagram indicates the Winsor phase boundaries for type I-IV microemulsions. For example, the microemulsion phase containing the C₃ fatty acid shows that increasing salinity causes the system to change from Winsor type I to III to II at lower SDS concentrations and I to IV to II at higher SDS concentrations. Addition of an adequate quantity of SDS produced a single-phase microemulsion, Winsor IV.

This figure also shows the effect of fatty acid chain length on the phase behavior of the microemulsion: the longer the chain length of fatty acid, the lower the amount of salt required for phase transition. This result can be described on the basis of modified Winsor's R-ratio:

$$R = \frac{A_{co} - A_{oo} - A_{ll}}{A_{cw} - A_{ww} - A_{hh}} \quad (4.1)$$

Term "A" represents interaction energy per unit interfacial area. Subscriptions c, w, and o are interfacial surfactant, water and oil molecules, respectively, whereas subscriptions l and h represent the lipophilic and hydrophilic parts of surfactant. A Winsor I system has an R-ratio less than one because the interaction energy between the surfactant and the water is larger than that between the surfactant and the oil. On the other hand, the R-ratio is greater than unity in a Winsor II system. As the R-ratio approaches one, conditions are favorable to formation of a Winsor III system. The interaction between

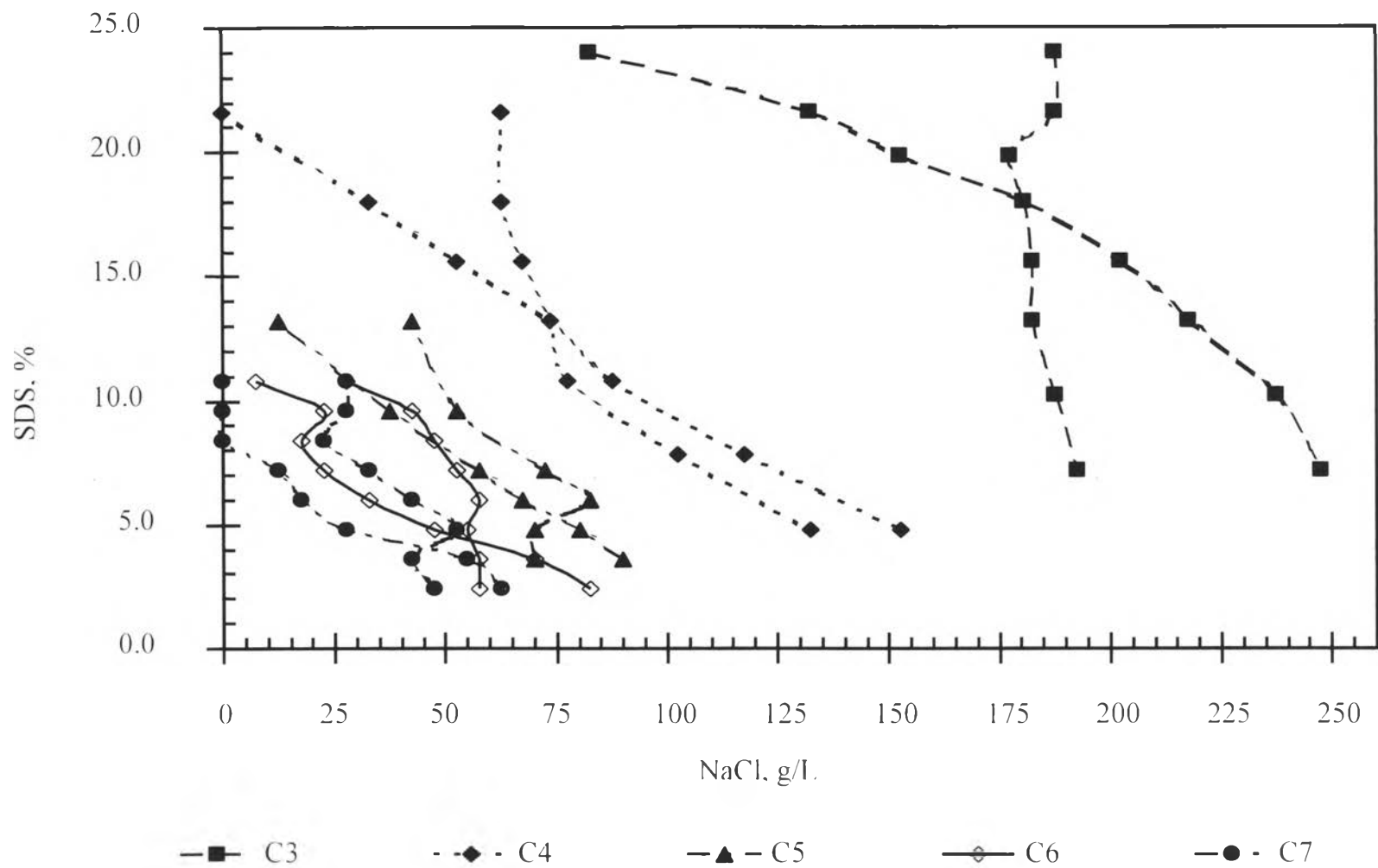


Figure 4.1 Phase diagrams of microemulsion systems containing fatty acids (C₃-C₇) at 25°C.

surfactant and oil molecules (A_{co}) can be enhanced by increasing the chain length of cosurfactant. As a result, R-ratio increases.

Increasing the chain length of fatty acid would promote the interaction between surfactant and oil molecules. Therefore, the surfactant affinity for the aqueous phase decreased and the numerator in equation (4.1) increases. Consequently, less electrolyte is required to drive the surfactant from the aqueous phase to the oil phase.

The results also showed that the microemulsions containing short chain fatty acid, $n=3-4$, formed a clear solution while the systems containing long chain fatty acid, $n=5-7$, resulted in gel formation that could be observed in any condition of the system. The occurrence of gel was found in excess oil, middle phase, and excess water for the Winsor type I, III and II, respectively. This could be due to the lack of dilution property for long-chained fatty acid. The cosurfactant molecules with an adequate chain length enter the interfacial area and pull apart the interfacial surfactant molecules. Consequently, interfacial surfactant concentration decreases and the formation of liquid crystal or gel is inhibited. If the chain length of cosurfactant is too long, the cosurfactant molecules mostly participate in the oil phase causing the lack of this dilution property. Accordingly, the lateral interactions between the interfacial surfactant molecules augment and the interfacial region tends to crystallize (Graciaa *et al.*, 1993).

4.2 Effect of Temperature on Equilibrium of Microemulsion

The results illustrated that the microemulsion contained C3 or C4 fatty acid broke while the gel volume of the system containing C5 - C7 fatty acid continuously dropped as increasing temperature. Finally, the gel volume diminished for the 3.6% and 9.6% pentanoic acid and 9.6% hexanoic acid systems and disappeared for the 2.4% hexanoic acid system, and the 2.4% and

6.0% heptanoic systems when the temperature reached 85°C. Phase volume in the system did not change when the temperature was reduced from 85°C to 25°C. It was reported by Kahlweit (1995c) that increasing temperature decreased tendency to form liquid crystalline mesophase in microemulsion. Moreover, it implies that the gel system requires a very long time to reach equilibrium state.

4.3 Solubilization Study

Solubilization parameter curves of oil and water in the microemulsion phase were plotted against NaCl concentration in the systems in order to determine the optimum condition. Plots of the SP^* vs. SDS concentration in the microemulsion using the C_3 - C_7 fatty acids are shown in Figure 4.2. When increasing the amount of SDS in the system, the solubilizing power of the microemulsion decreased. Moreover, the SP^* obviously increased when the chain length was increased from 3 to 5. Because the increasing of fatty acid chain length enhanced the interaction between the surfactant and the oil, the solubilization of oil in the systems increased. Beyond $n=5$, the SP^* did not change significantly. This was probably because the gel formation prevented further enrichment in the solubilization.

Figure 4.3 shows the variation of S^* with the amount of SDS in the systems. As the SDS concentration increased, the S^* clearly decreased. Increasing the SDS concentration in the system while keeping the ratio of SDS to fatty acid constant resulted in the increase in the amount of fatty acid in the system. The increasing of cosurfactant concentration also promotes the I-III-II transition (Bourrel and Schechter, 1988b). Therefore, less amount of NaCl was required to reach the optimum condition at higher SDS concentration.

The fatty acid chain length also showed an effect on the S^* . At a constant SDS concentration, lower salinity was required to achieve the

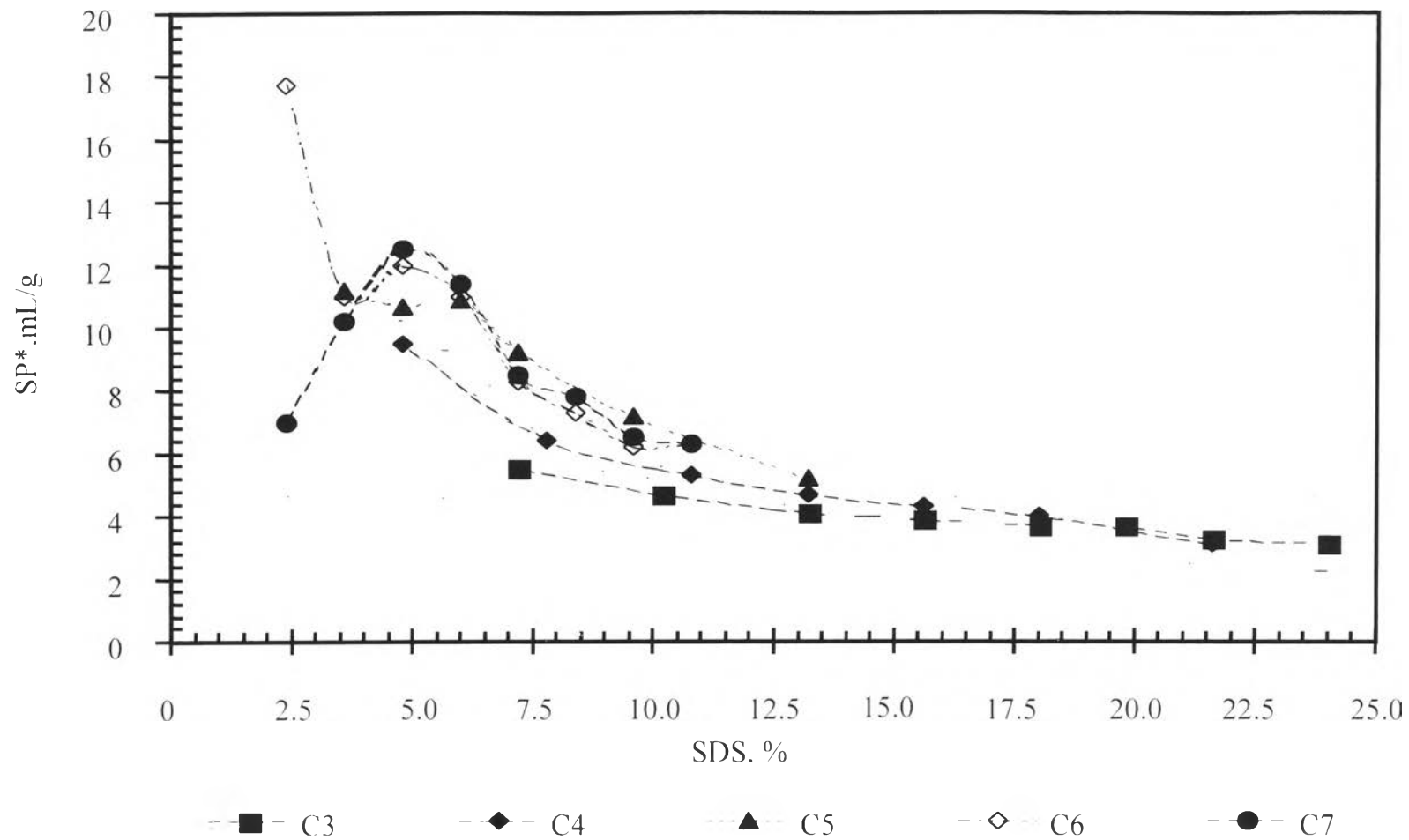


Figure 4.2 Optimum solubilization parameter of various SDS concentrations for the microemulsion systems containing fatty acids.

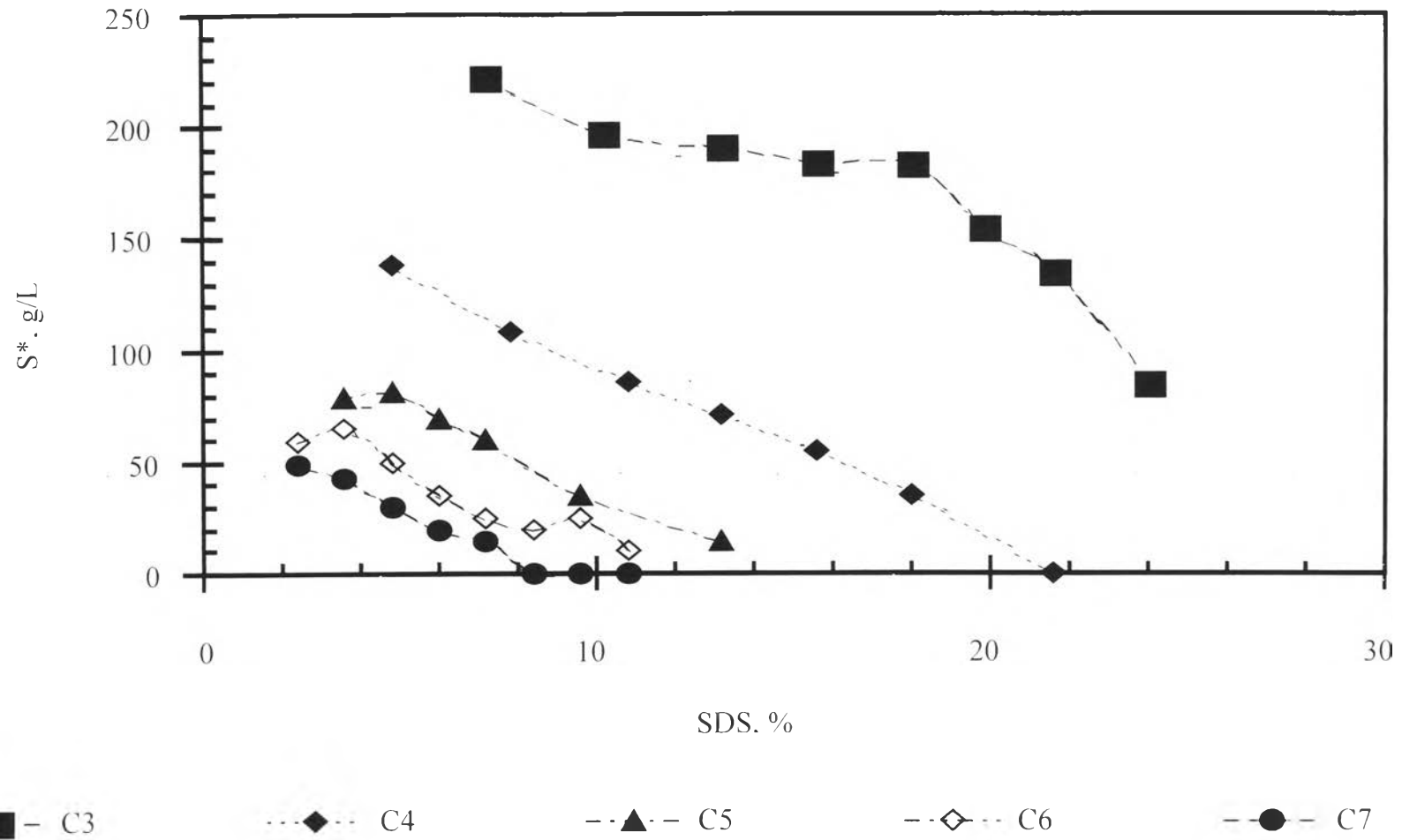


Figure 4.3 Optimum salinity of various SDS concentrations for the microemulsion systems containing fatty acids.

optimum condition for the system containing longer fatty acid chain length. Increasing fatty acid hydrophobicity will primarily increase the interaction between surfactant and oil molecules. As a result, the denominator in equation (1) decreased and the R-ratio increased. Therefore, the S^* was expected to decrease, as observed. It could be concluded that longer chain length yielded higher solubilization and used up less amount of SDS to reach the maximum solubilization of the system. However, the solubilization in the long chain system is limited by the gel formation.

For systems containing fatty acids with alkyl groups ranging from 5 to 7, the SP^* is plotted against the S^* as shown in Figure 4.4 to Figure 4.6. The plots show that as SDS concentration increased, the SP^* increased until reaching a maximum and then decreased while the S^* continuously decreased. This maximum point should be the optimum condition that produces the maximum solubilization with less amount of salt required. Therefore, it is not worth to increase the surfactant concentration beyond this maximum point to solubilize both oil and water.

4.4 pH Measurement of Microemulsion

The pH of microemulsion Winsor type I, III and IV containing C_3 to C_7 fatty acids are shown in Table 4.1. The salinity scan causing the phase transition had no effect on the pH of microemulsion because all the systems that formed by salinity scan gave the same pH of the microemulsion phase. The deionized water (pH 5.62) used to prepare microemulsion for this study possibly had an effect on the pH of microemulsion. The pH of microemulsion was calculated from the value of pKa and acid solubility in water listed in Table 4.2 and compared with the experimental results. The result showed that pH of microemulsion was similar to the pH of fatty acid in saturated aqueous solution. This indicated that the fatty acid concentration in continuous phase

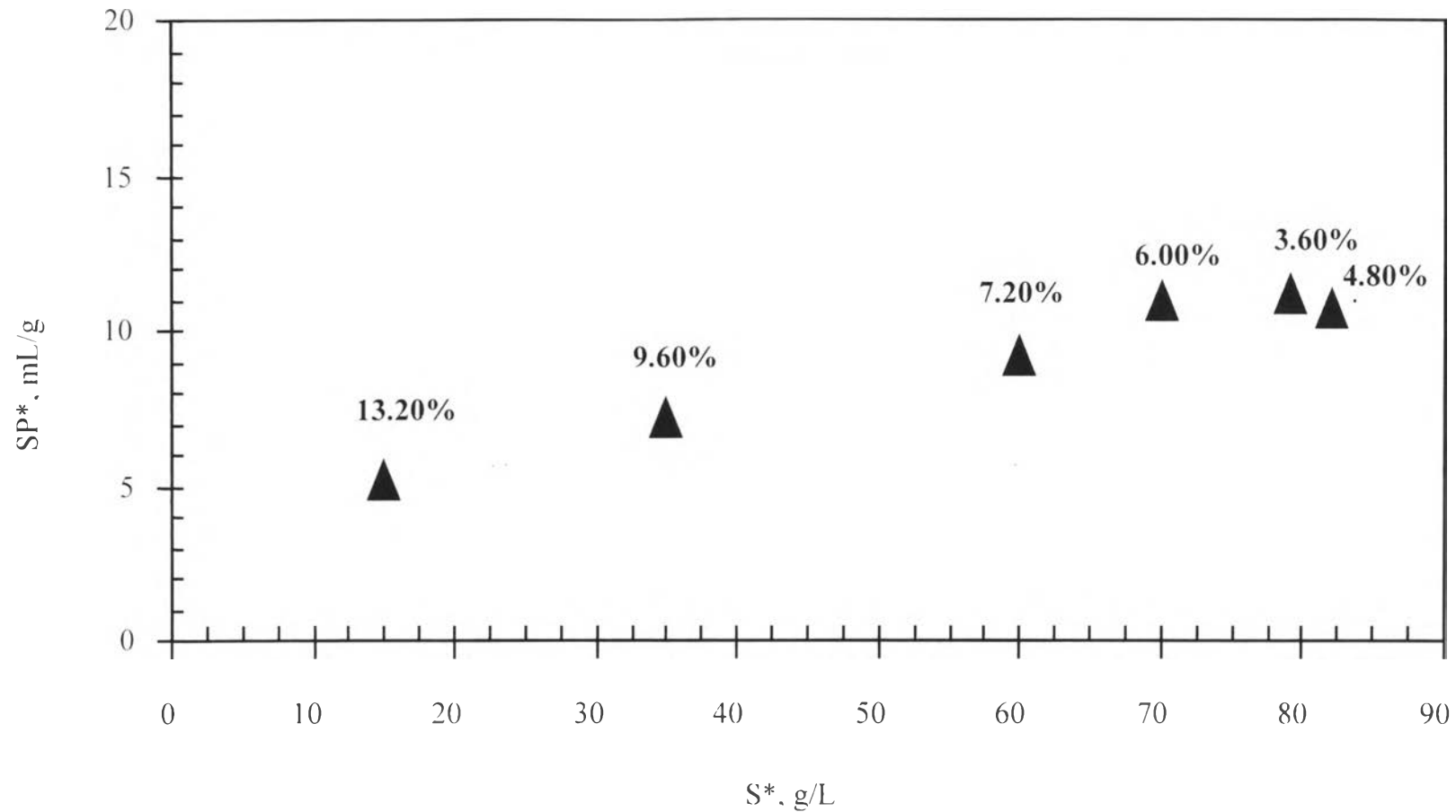


Figure 4.4 Optimum solubilization parameter (SP^*) and optimum salinity (S^*) at different percentage of SDS when the cosurfactant was pentanoic acid.

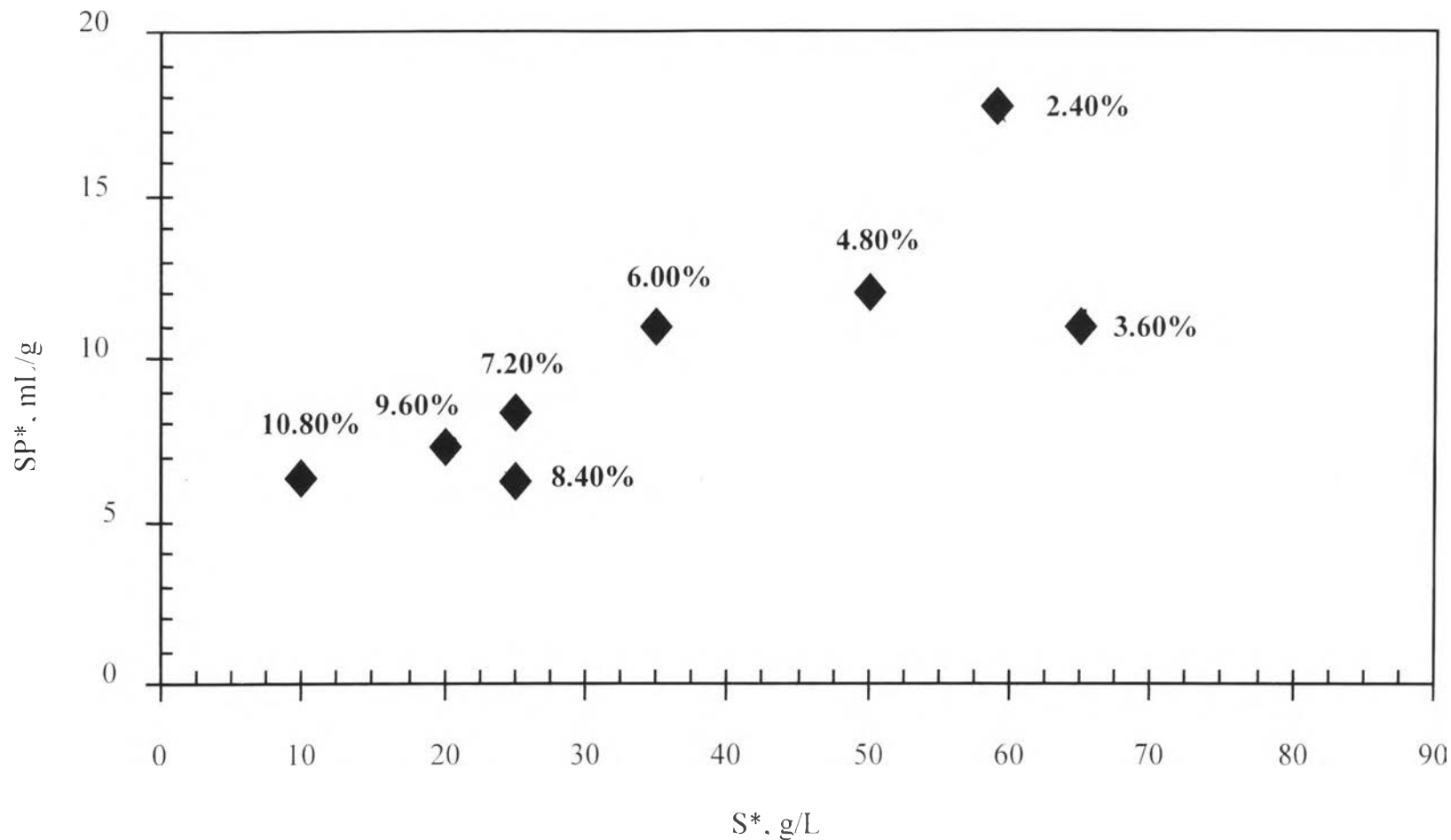


Figure 4.5 Optimum solubilization parameter (SP^*) and optimum salinity (S^*) at different percentage of SDS when the cosurfactant was hexanoic acid.

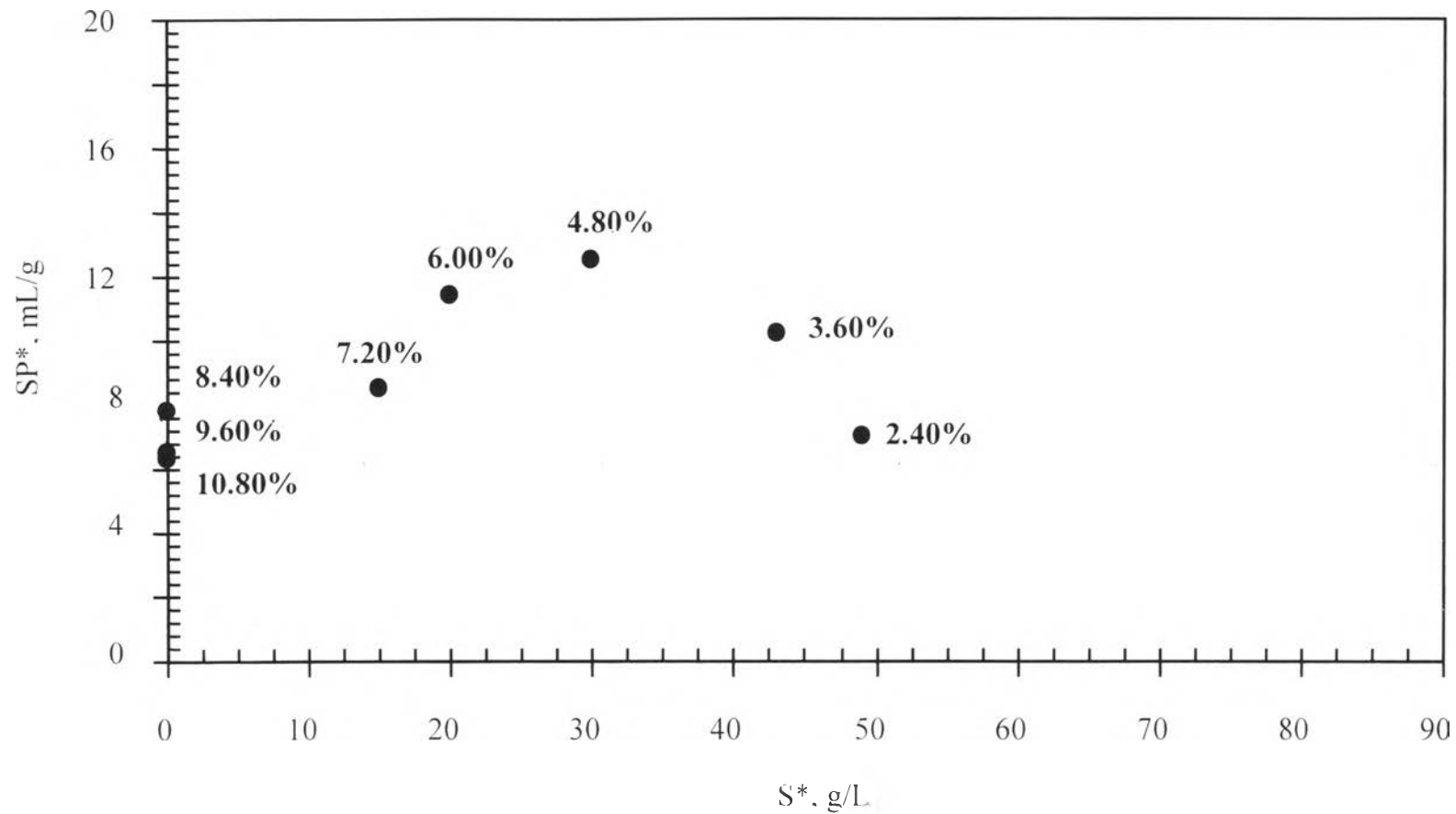


Figure 4.6 Optimum solubilization parameter (SP^*) and optimum salinity (S^*) at different percentage of SDS when the cosurfactant was heptanoic acid.

of microemulsion was at saturation state. By calculating the pH of microemulsion from acid dissociation (pK_a) only, the estimated value was similar to the experimental results for systems containing C_3 and C_4 fatty acids only. The solubility of C_5 to C_7 fatty acids in an aqueous solution is very low, therefore their solubility constants were taken into account for the pH calculation. The results showed good agreement with the experimental results for all of the systems.

Table 4.1 pH of microemulsion Winsor type I, III, and IV containing C_3 to C_7 fatty acids at 25°C.

Fatty acid \ pH	pH from experiment of		pH estimated from	
	Microemulsion	Saturated fatty acid in water	pK_a	pK_a and solubility of acid in water
Propanoic acid	2	-	1.99-2.31	1.99-2.31
Butanoic acid	2-2.5	-	2.06-2.39	2.06-2.39
Pentanoic acid	2.5	2.5	2.24-2.60	2.64
Hexanoic acid	3	3	2.27-2.72	2.96
Heptanoic acid	3-3.5	3-3.5	2.42-2.77	3.28

Table 4.2 pK_a and aqueous solubility of fatty acid at 25°C (Lide, 2000).

Fatty acid \ Value of	pK_a at 25°C	Aqueous solubility at 25°C (g/100g water)
Propanoic acid	4.86	Miscible
Butanoic acid	4.83	Miscible
Pentanoic acid	4.84	3.7
Hexanoic acid	4.85	1.0
Heptanoic acid	4.89	0.28

4.5 Measurement of Microemulsion Conductivity

The conductivity of microemulsion at 25°C was examined corresponding to phase transition as shown in Figure 4.7 to Figure 4.11. For the system containing propanoic acid at 7.2% and 13.2% SDS, high conductivity occurred at low salinity (Winsor type I region) and low conductivity values occurred at high electrolyte concentration (Winsor type II region). In the intermediate salt concentration (Winsor type III region), the conductivity first raised to a maximum and then decreased. For the propanoic acid system at 18.0% and 21.6% SDS, the conductivity of the microemulsion phase was relatively unchanged. For butanoic acid system, the conductivity continuously dropped from low to high electrolyte concentration at 4.8% SDS while the conductivity did not change markedly at 10.8%, 15.6%, and 21.6% SDS. For pentanoic acid system at 3.6% SDS, the conductivity raised in Winsor type I region and then dropped and remained constant in Winsor type III and II region. The conductivity of microemulsion phase was almost constant for pentanoic acid system at 6.0%, 9.6%, and 13.2% SDS. For hexanoic acid system at 2.4% SDS, the conductivity was high in Winsor type I and low in Winsor type II. In Winsor type III region, the conductivity rapidly decreased. For hexanoic acid system at 4.8%, 7.2% and 9.6% SDS, the conductivity was nearly unchanged. For heptanoic acid system at 2.4% SDS, the conductivity first increased in Winsor type I region and then decreased significantly in Winsor type III region and remained constant in Winsor type II region. For heptanoic acid system at 4.8%, 7.2%, and 9.6% SDS, the conductivity was constant.

The results show that the conductivity changed significantly for the systems that had I-III-II phase transition. This change in conductivity can be categorized into two trends. First, the conductivity continuously decreased, i.e. the systems containing butanoic acid at 4.8% SDS and hexanoic acid at

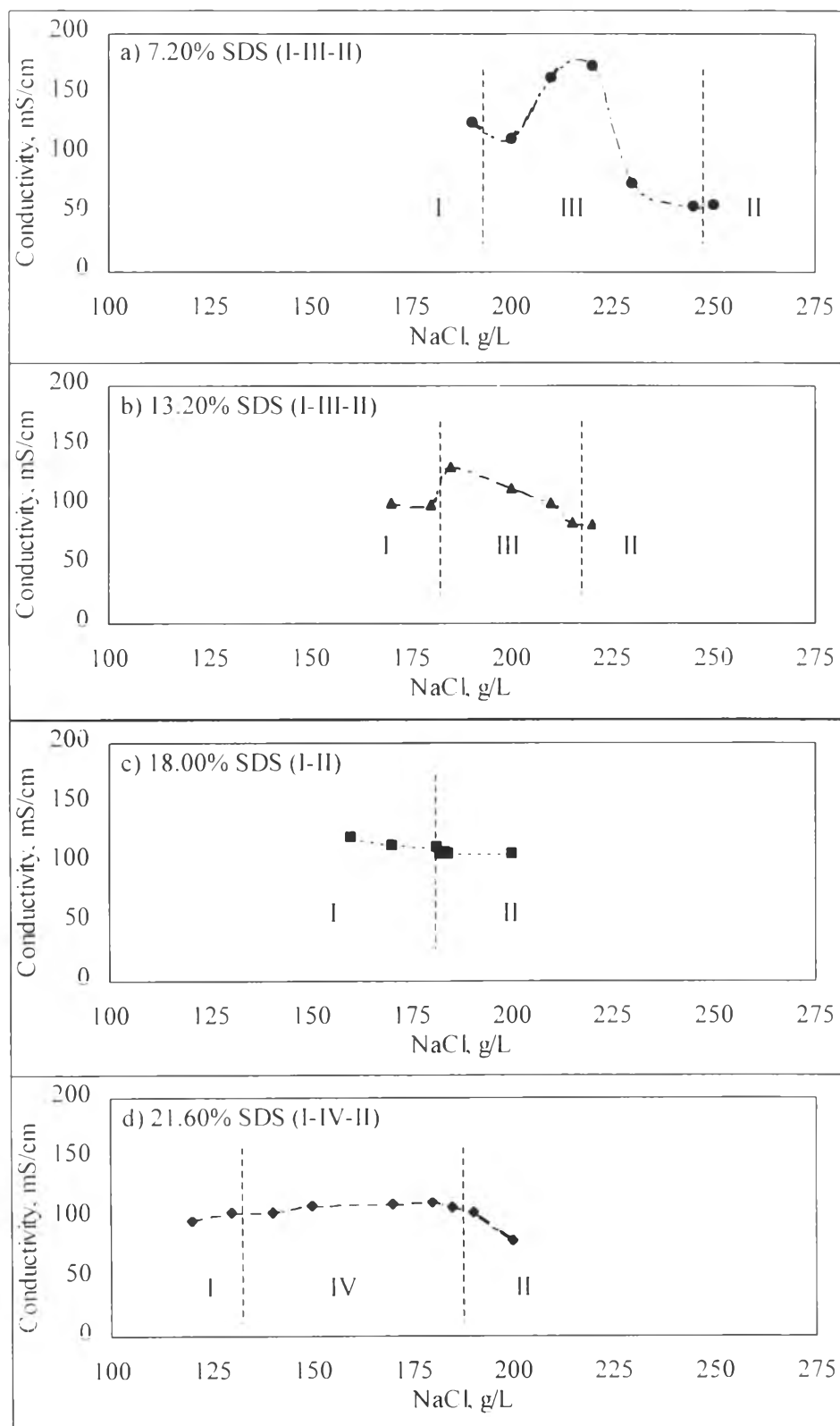


Figure 4.7 The electrical conductivity of the microemulsion systems containing propanoic acid.

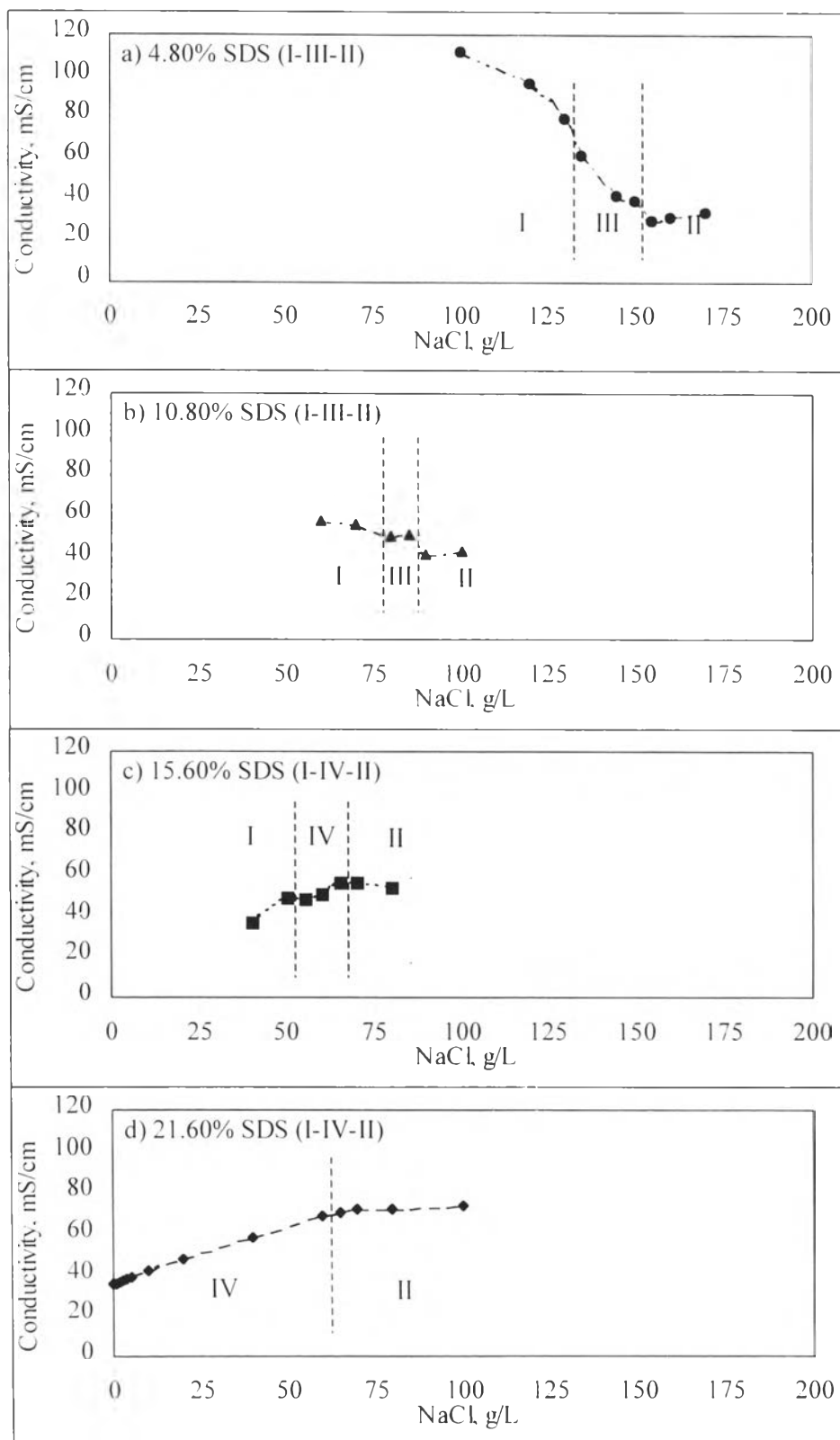


Figure 4.8 The electrical conductivity of the microemulsion systems containing butanoic acid.

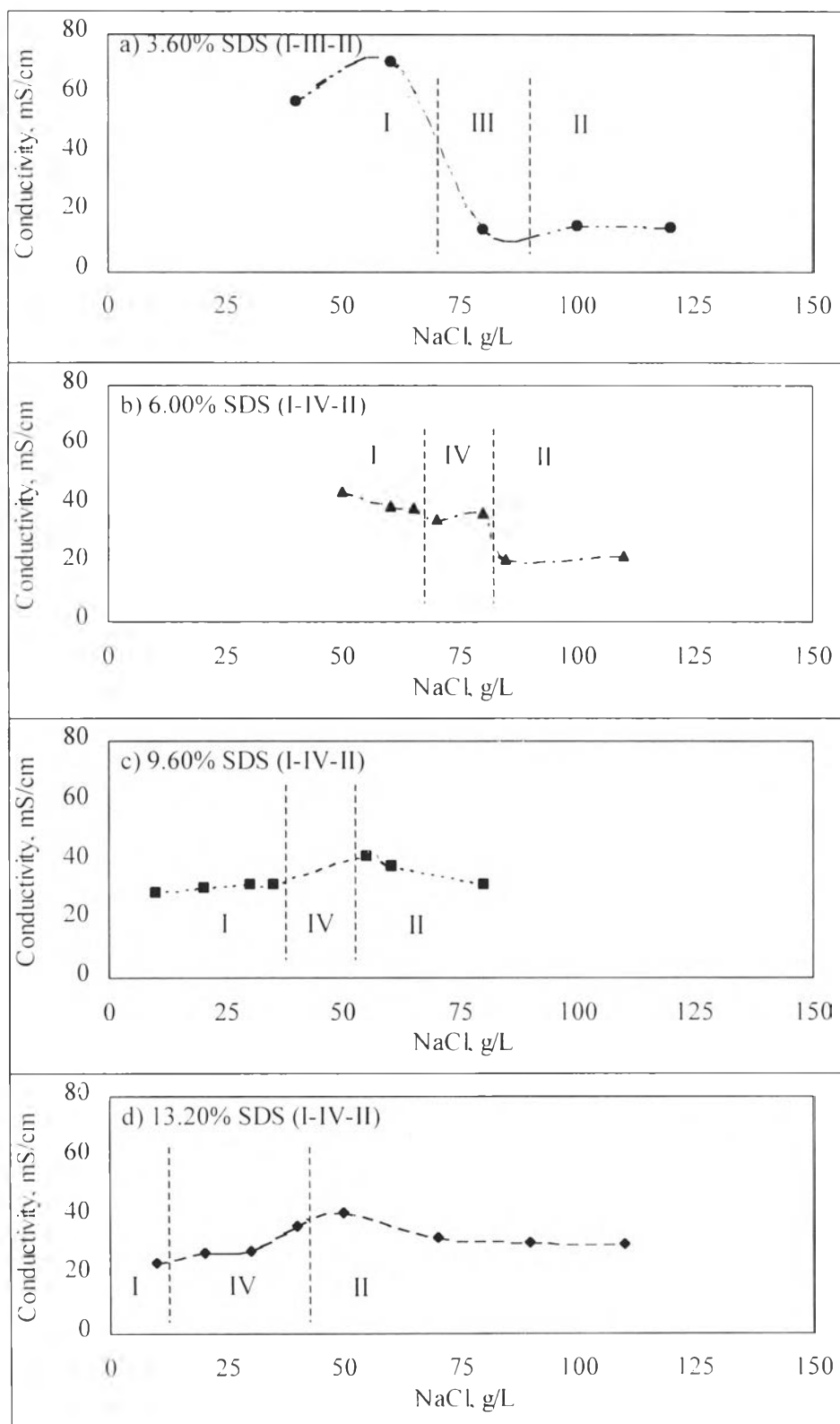


Figure 4.9 The electrical conductivity of the microemulsion systems containing pentanoic acid.

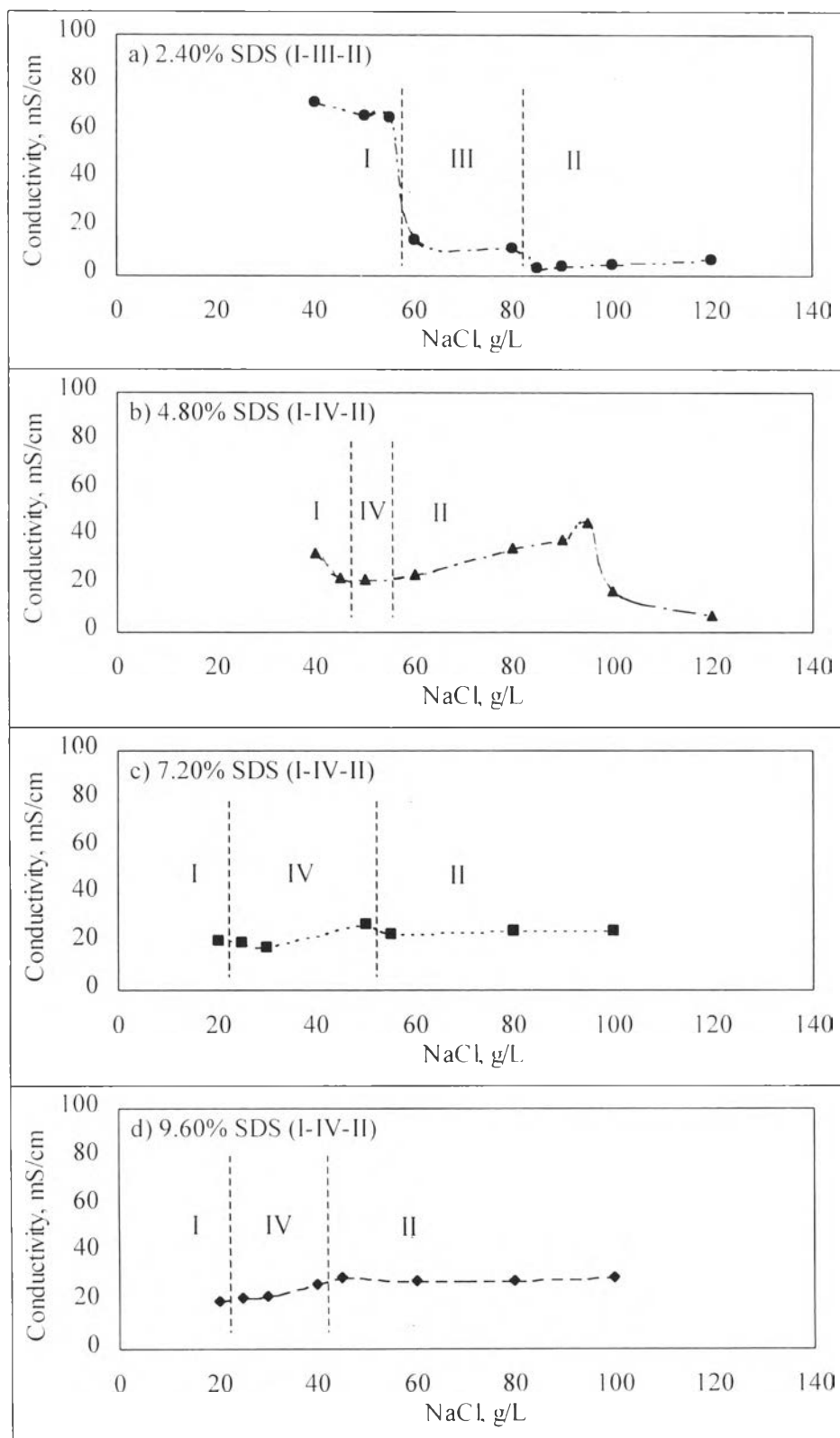


Figure 4.10 The electrical conductivity of the microemulsion systems containing hexanoic acid.

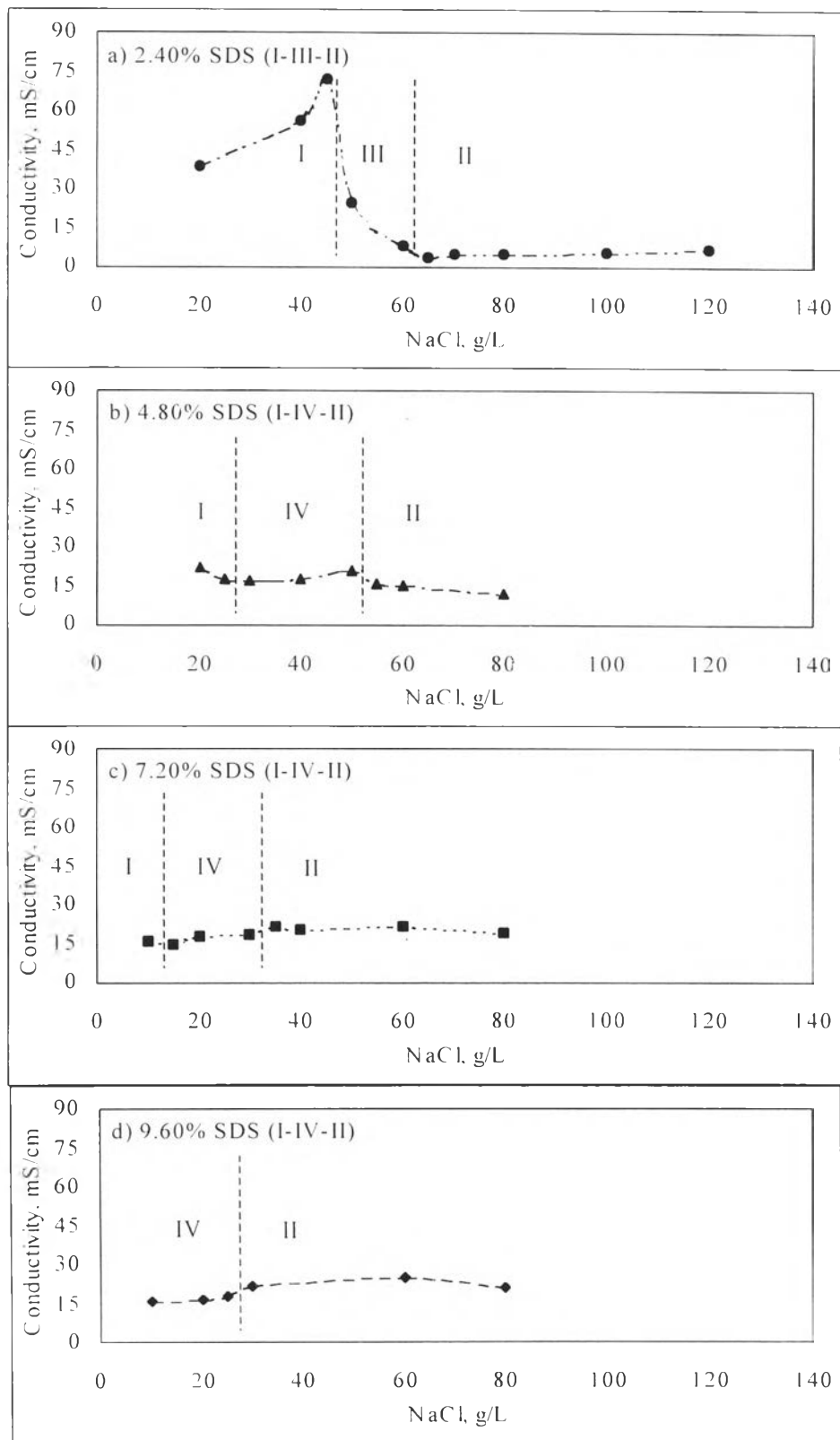


Figure 4.11 The electrical conductivity of the microemulsion systems containing heptanoic acid.

2.4% SDS, when scanning salinity. This variation was due to the gradual change in the proportions of oil relative to water in microemulsion phase (Bourrel and Schechter, 1988a). For the second type, the conductivity of microemulsion first rose due to the increasing salt concentration in the continuous aqueous phase, it then passed through a maximum. The conductivity then dropped as the system became oil continuous. Bourrel and Schechter (1998a) concluded that this maximum in conductivity reflects the high-viscosity Newtonian fluids or even liquid crystals and gels. Kahlweit *et al.* (1995b) reported that a conductivity maximum occurs when adding salt at a fixed temperature because the self-diffusion coefficient of water drops while that of oil increases as it passes through the three-phase region. For the systems that have I-IV-II transition, the conductivity is relatively unchanged because the structure of the micellar phase is only trivially changed (Bourrel and Schechter, 1988a).

4.6 Measurement of Microemulsion Interfacial Tension

Figure 4.12 to Figure 4.16 show the results of IFT measurement at 25°C as a function of salinity. In each SDS concentration, there are two curves of the IFT, IFT of microemulsion phase/excess water phase (γ_{mw}) and IFT of microemulsion phase/excess oil phase (γ_{om}). As the salinity of the system increased, γ_{om} decreased as the system crossed the Winsor I-III transition and γ_{mw} increased as the system crossed the Winsor III-II transition.

The IFT values of these systems were very low, in the magnitude of 10^{-1} to 10^{-4} mN/m. There was no abrupt change of IFT at the I-III and III-II boundaries. Moreover, these two curves intersected inside the three-phase region and the intersection point was regarded as the optimum condition. As SDS concentration increased, the interfacial tension at the optimum condition increased for the systems containing C3-C6 fatty acid and decreased for the

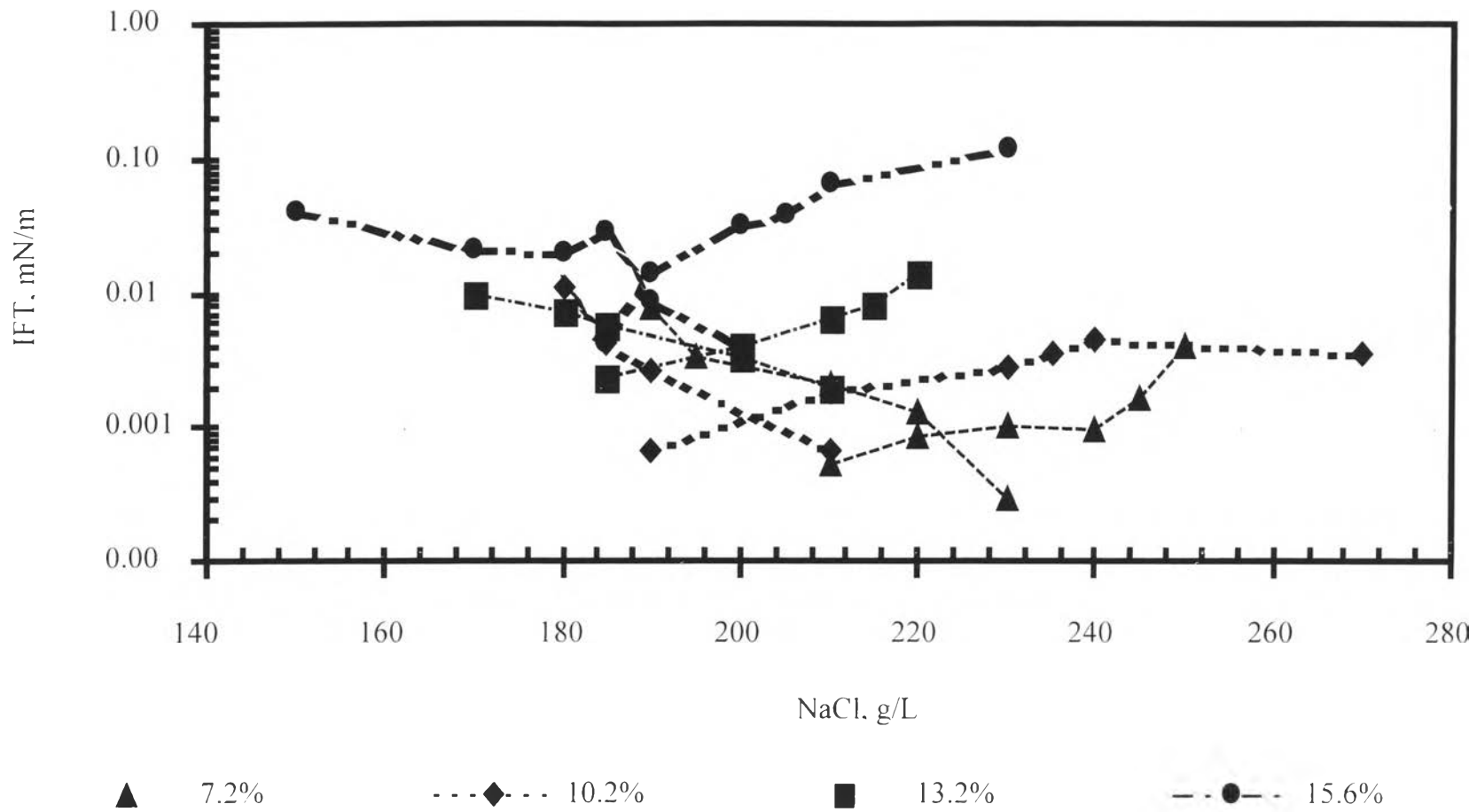


Figure 4.12 The interfacial tension of the microemulsion systems containing propanoic acid.

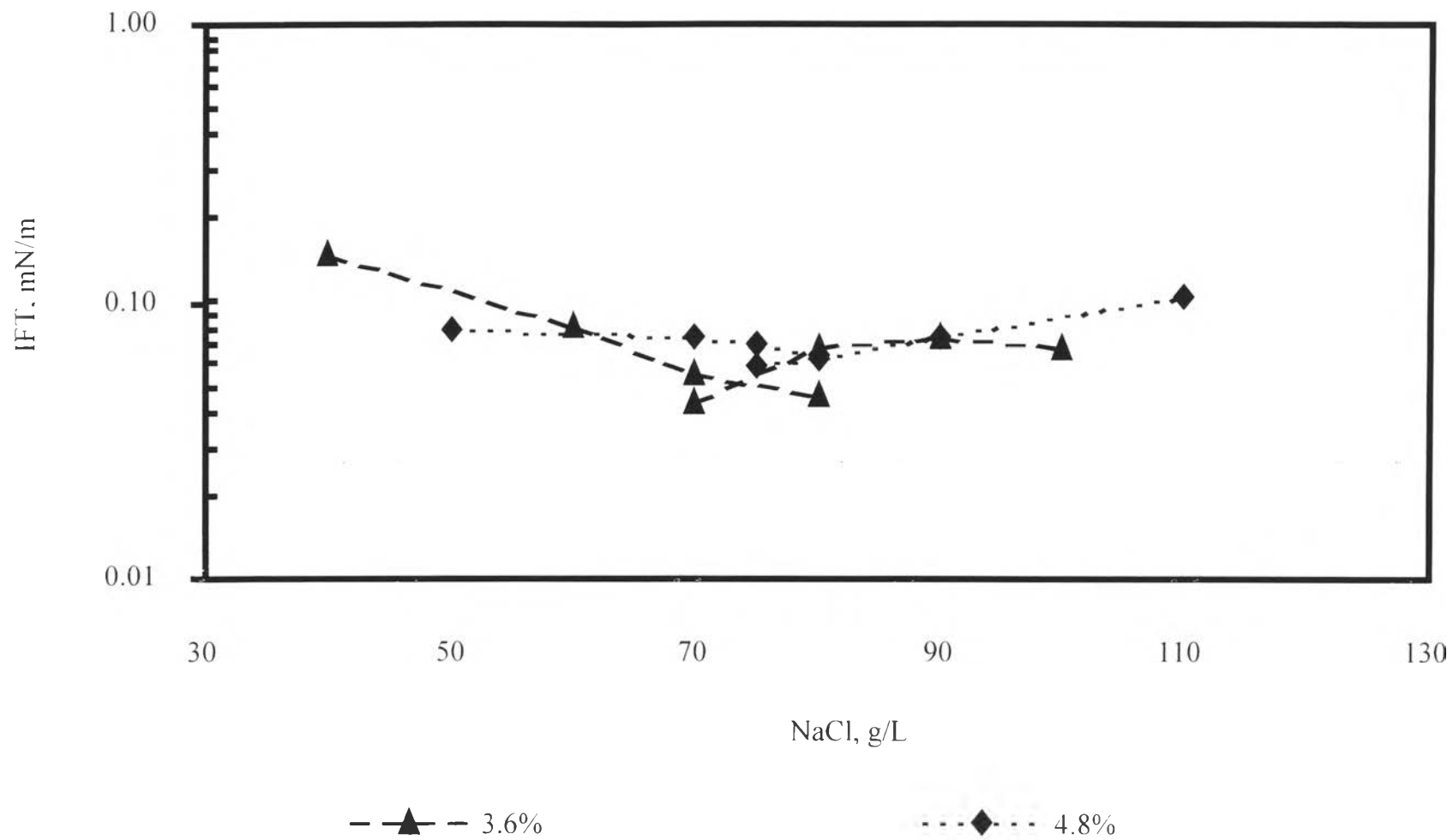


Figure 4.14 The interfacial tension of the microemulsion systems containing pentanoic acid.

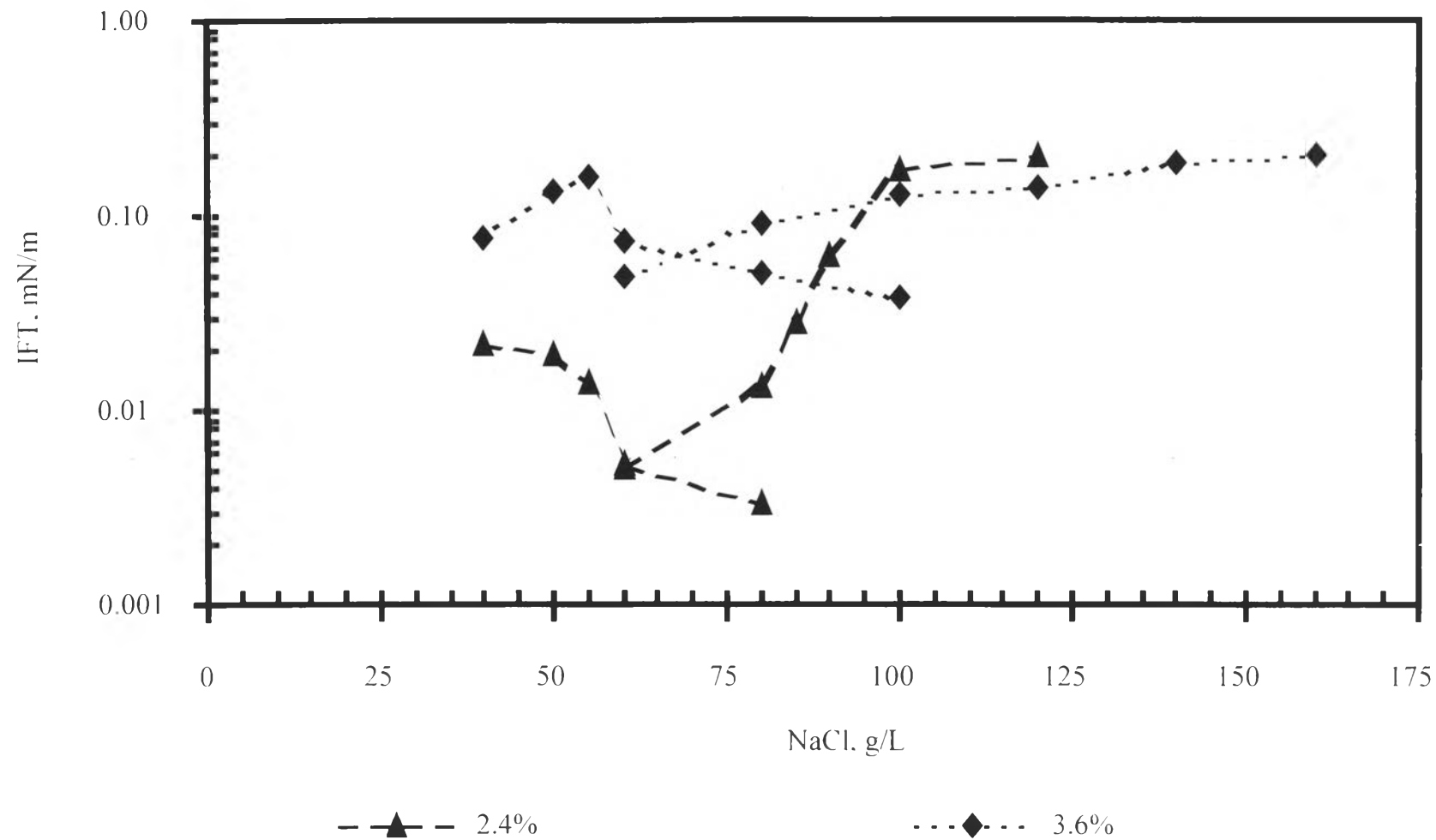


Figure 4.15 The interfacial tension of the microemulsion systems containing hexanoic acid.

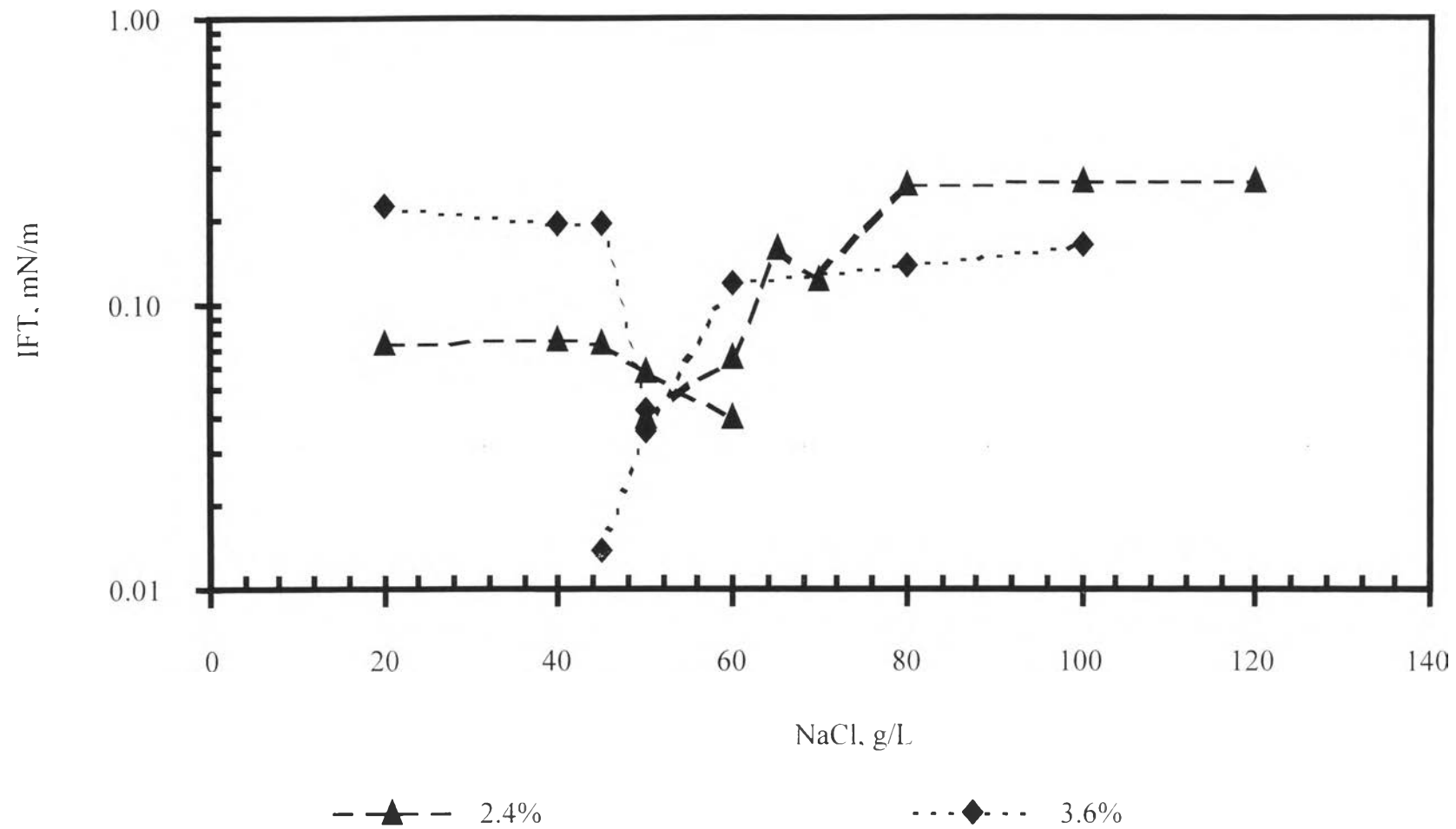


Figure 4.16 The interfacial tension of the microemulsion systems containing heptanoic acid.

heptanoic acid system. These results show good agreement with the results of SP^* from solubilization part (the lower the interfacial tension, the higher the solubilization obtained). Comparing the S^* obtained from solubilization and IFT results at the same condition showed that the values were very similar as shown in Table 4.3. The S^* obtained from IFT results also distinctly decreased as the amount of SDS increased similar to the results obtained from the solubilization part.

Table 4.3 A comparison between the optimum salinity of the microemulsion systems obtained from the solubilization and interfacial tension measurements.

Fatty acid	SDS (%)	IFT* (mN/m)	S* in g/L obtained from	
			Solubilization	IFT
Propanoic acid	7.2	7.5×10^{-4}	222	224
	10.2	1.3×10^{-3}	197	202
	13.2	3.0×10^{-3}	191	195
	15.6	1.4×10^{-2}	184	188
Butanoic acid	4.8	1.8×10^{-3}	138	142
	7.8	2.2×10^{-3}	108	113
	10.8	3.8×10^{-3}	85.8	82
Pentanoic acid	3.6	5.0×10^{-2}	79	75
	4.8	7.0×10^{-2}	82	80
Hexanoic acid	2.4	5.0×10^{-3}	59	60
	3.6	6.0×10^{-2}	65	70
Heptanoic acid	2.4	5.0×10^{-2}	49	55
	3.6	3.5×10^{-2}	43	50