

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Equilibrium Phase Behavior

The experimental data for the phase behavior studies, and relative volume of water and oil, are given in Appendix A. The results are described below.

4.1.1 Effect of Electrolyte and Surfactant Concentrations

The phase diagram in the surfactant-electrolyte concentration plane of the microemulsion systems with equal volumes of SDS in brine solution and oil solution (octanoic acid and hexane), and the weight ratio of surfactant to octanoic acid equal to 40 : 60 and temperature at 25°C is shown in Figure 4.1. The phase volume was visually observed for several days (at least 2 weeks) with no volume change before it was recorded.

At low SDS concentrations (less than 4.61% wt) and increasing NaCl concentration, the inversion from Winsor type I to type II is observed. At low electrolyte concentration, the surfactant, being more hydrophilic, has partitioned into the water phase and type I bluish microemulsion appears. Gel formation is also observed in the excess oil phase. At high NaCl concentrations, the surfactant system is over optimized and the surfactant resides in the oil phase which bluish translucent microemulsion (type II system) is present. It is noted that Winsor III is not clearly seen (milky phase), but the middle phase is noticed from the change of the phase volume when increase surfactant concentration. The middle phase regions of Winson type III spanned only a fairly narrow salinity range (less than 0.03% NaCl). At high SDS (above 4.61%) and increasing electrolyte concentrations, the

progression of phase Winsor I-Winsor IV-Winsor II occurs. A bluish translucent solution is observed near the phase transition between Winsor I and Winsor IV, but bluish milky phase (not a liquid crystal phase) in the intermediate region of the Winsor IV microemulsion. The gel formation is observed in the excess oil phase.

4.1.2 Effect of Temperature

Figure 4.2 shows the phase diagram of microemulsion system equilibrated at 35°C in comparison with that of at 25°C. The results show the decrease in equilibrium time and gel formation with increasing the equilibration temperature. At low SDS concentrations (below 3.74%), the phase becomes Winsor I for almost the whole range of NaCl concentrations. Winsor III shows clear and bluish phase. At high SDS concentrations (above 3.74%) and various NaCl concentrations, the phase progression of Winsor I-Winsor IV-Winsor II occurs. The result shows that the Winsor IV microemulsion forms at slightly lower surfactant concentration when the system is equilibrated at higher temperature. Thus, the whole phase shifts to higher salt requirement indicating that the composition of micellar solution is changed, and thus hydrophilicity of surfactant increases. As it was reported by Bourrel and Schechter (1988) and Kahlweit (1995) that at fixed oil and surfactant, increase of temperature decreases tendency to form liquid crystalline mesophase and increases solubility of electrolyte and surfactant in the aqueous phase. As a result, the amount of salt required for traversing the phase region increases.

4.1.3 Effect of Equilibrium Time

Figure 4.3 shows a comparison of the phase behavior of the microemulsion systems obtained at 2 weeks and 2 months equilibration times. The results of the two-month period indicate the progression of phase

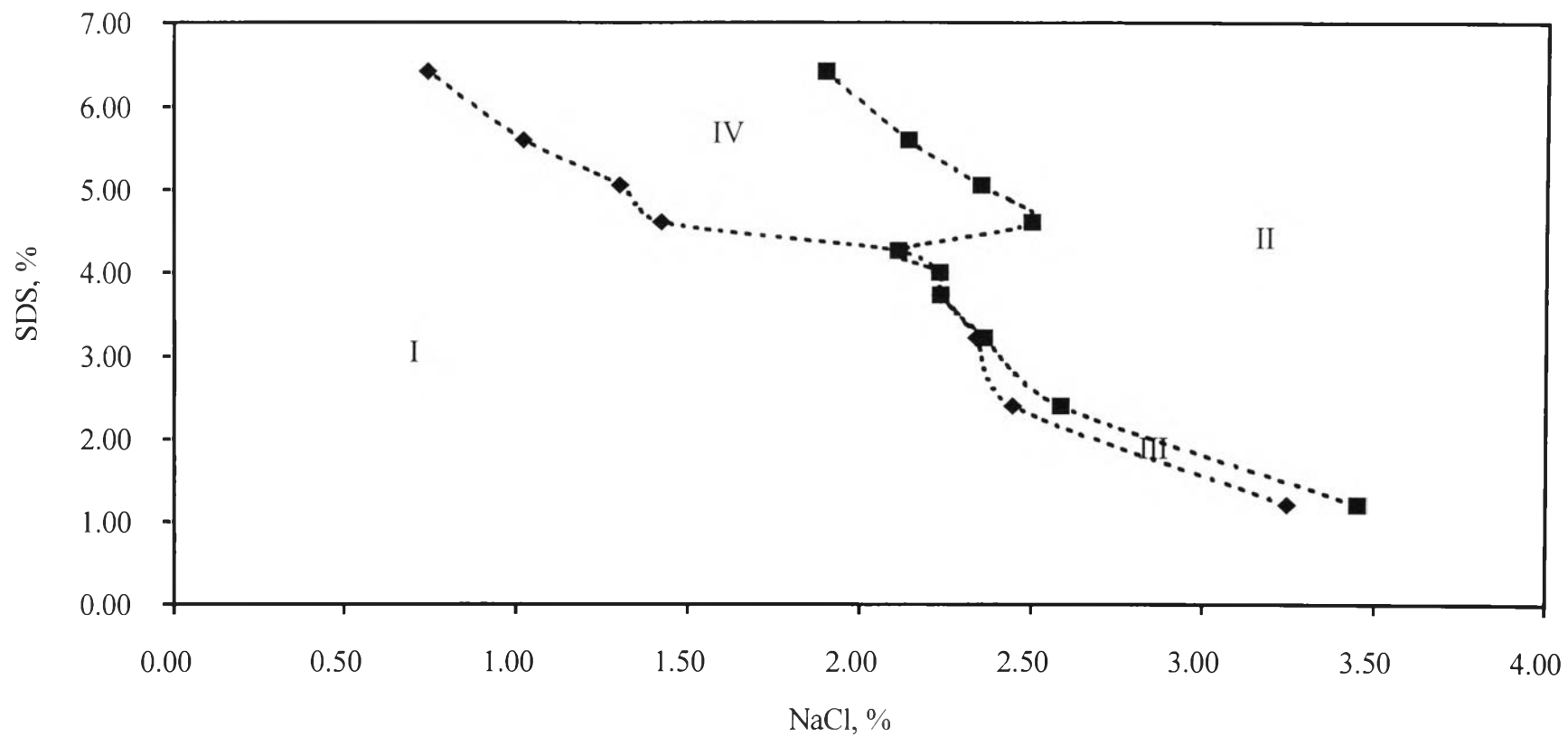


Figure 4.1 Phase diagram of the microemulsion system containing hexane, SDS, NaCl and octanoic acid cosurfactant. The microemulsion solution were equilibrated at 25 °C for 2 weeks.

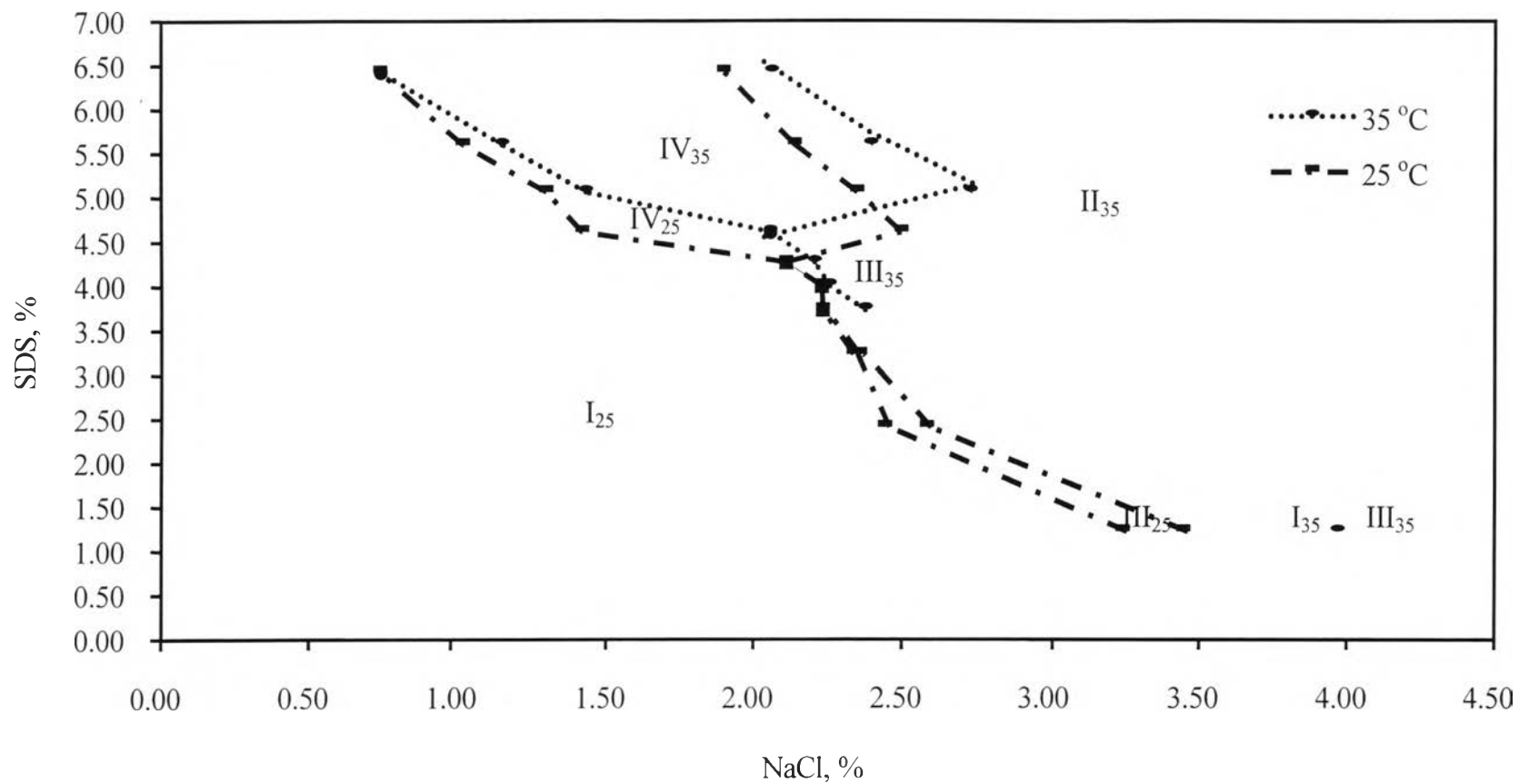


Figure 4.2 Phase behavior of microemulsion system , containing hexane, SDS, NaCl and octanoic acid. The microemulsions solutions were equilibrated at two different temperatures, 25 °C and 35 °C, respectively.

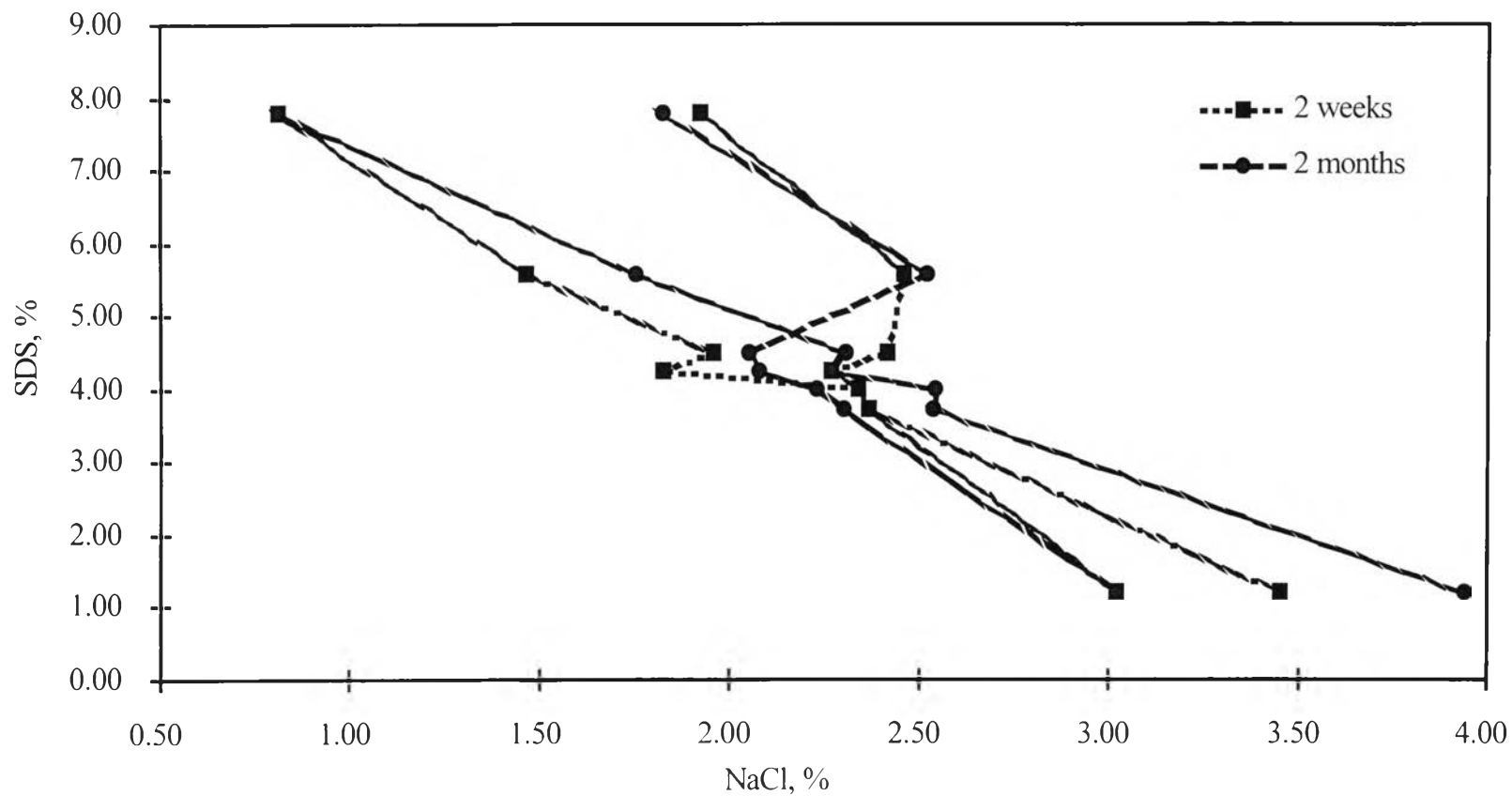


Figure 4.3 Phase diagram of SDS/hexane/octanoic acid system equilibrated at 25 °C at two different times, 2 weeks and 2 months, respectively.

equilibria of Winsor I-Winsor III-Winsor II observed at low SDS concentrations (below 4.53%). The bluish milky phase of Winsor III is clearly seen and the phase transition is slightly shifted to higher electrolyte concentrations. The formation of Winsor IV is observed at slightly higher surfactant concentrations (above 4.53% SDS). These results agree well with those reported by Bourrel and Schecter (1988), in which the phase behavior of the system containing liquid crystalline can be altered, if equilibrated at long time. Furthermore, the time required is dependent of additive used.

4.2 Physicochemical Properties

4.2.1 Solubilization

Solubilization parameters SP_o and SP_w data are given in Appendix B.

4.2.1.1 Effect of Electrolyte and Surfactant Concentrations

The point of intersection (SP^*) of the solubilization parameter curves of oil and water inside the middle phase region indicates the equal amount of oil and water solubilized at the optimum salinity (S^*). At this point, minimum amount of the surfactant is required to produce a single phase, type IV microemulsion as illustrated in Figure 4.4 for different SDS concentrations. The results indicate that the optimum solubilization parameter increases with increasing surfactant concentration and reaches the maximum values at 4.27% SDS where the optimal salinity is 2.09% NaCl.

4.2.1.2 Effect of Temperature

Table 4.1 shows a comparison of solubilization of microemulsion systems at 25 °C and 35 °C. The results show that the optimum solubilization parameters for higher temperature are similar to those obtained at lower temperature.

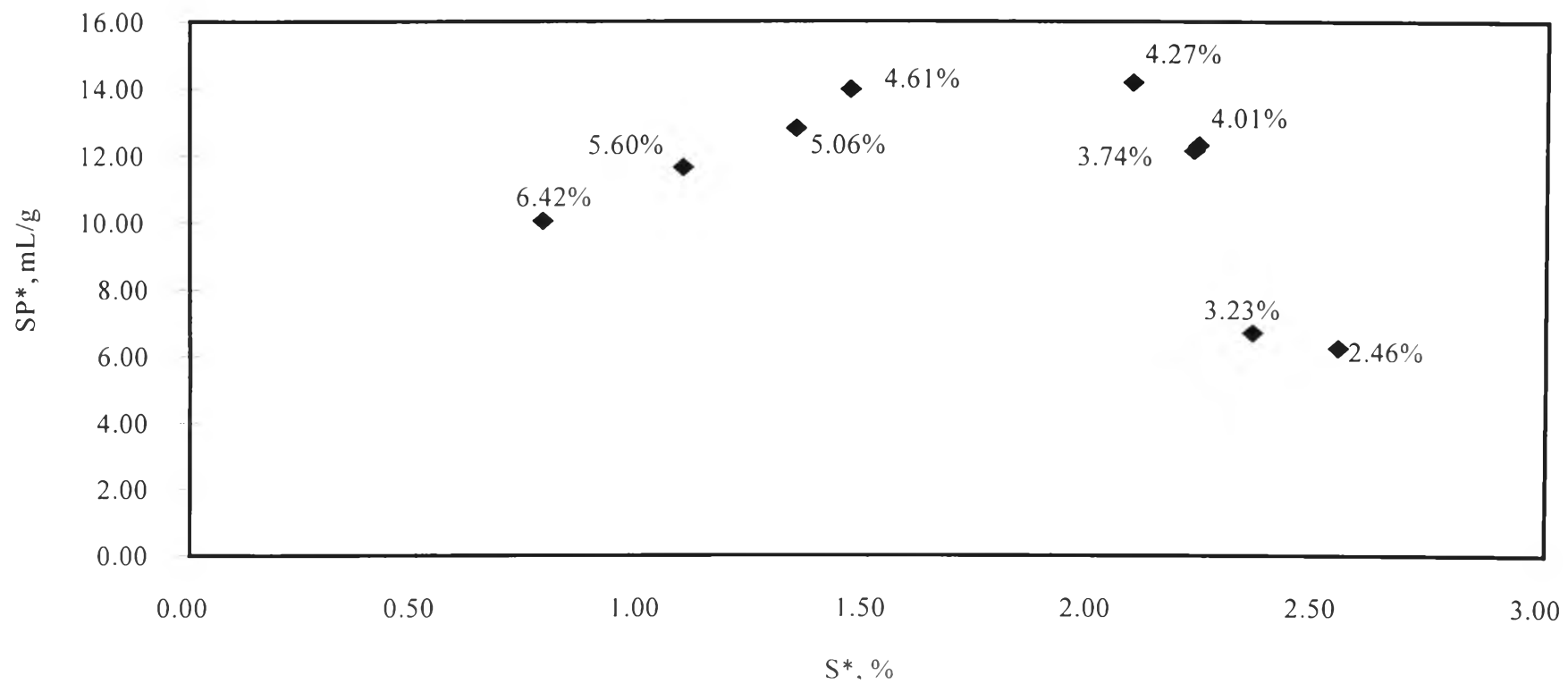


Figure 4.4 Optimum solubilization parameters of system containing the hexane, SDS, NaCl and octanoic acid at 25 °C and 2 weeks equilibration.

It indicates that an increase in the system temperature increases the area occupied per surfactant molecule (SDS) and thus, decreasing the interactions per unit area of interface. This is due to hydrophobic effect, i.e., increasing temperature will increase the movement of water molecules in the presence of a hydrocarbon or any nonpolar compound which reduces the adsorption driving force and solvency, correspondingly. As a consequence, the optimum solubilization is expected to decrease. However Aarra (1999) reported that the optimal salinity in electrolyte systems seemed to be independent of the temperature.

Table 4.1 Optimum salinity (S^*) and optimum solubilization parameter (SP^*) for microemulsion system containing hexane, octanoic acid and NaCl at 25 °C and 35 °C.

SDS (%)	25 °C		35 °C	
	SP* (mL/g)	S* (%)	SP* (mL/g)	S* (%)
1.22	N/A	N/A	N/A	N/A
2.46	6.30	2.54	N/A	N/A
3.23	6.71	2.35	N/A	N/A
3.74	12.31	2.23	13.05	2.38
4.01	12.15	2.22	N/A	N/A
4.27	14.18	2.09	N/A	N/A
4.61	13.97	1.46	12.79	2.51
5.06	12.81	1.34	12.81	1.46
5.60	11.64	1.09	12.22	1.22
6.42	10.05	0.78	10.05	0.78

N/A: not available

4.2.1.3 Effect of Equilibrium Time

When the equilibrium time was increased from 2 weeks to 2 months to observe the solubilization of n-hexane in the micellar phase, the SP* and S* values were not obviously changed (as shown in Table 4.2). This clearly shows that the microemulsion system reaches equilibrium within 2 weeks.

Table 4.2 Optimum salinity (S*) and optimum solubilization parameter (SP*) at optimum for microemulsion for system equilibrated for 2 weeks and 2 months and temperature at 25 °C.

SDS (%)	2 weeks		2 months	
	SP* (mL/g)	S* (%)	SP* (mL/g)	S* (%)
1.22	NA	NA	NA	NA
3.74	11.34	2.37	12.83	2.28
4.01	10.28	2.34	4.92	2.33
4.27	15.22	1.89	10.07	2.06
4.53	13.39	2.02	12.14	2.21
5.60	11.42	1.73	11.53	1.79
7.81	8.12	0.85	8.12	0.85

4.2.2 Interfacial Tension

The experimental data for the interfacial tension are given in Appendix F.

The interfacial tension of microemulsion systems of three different SDS concentrations, (3.74%, 4.27% and 4.53%) were measured as a function of salinity and reported in Figure 4.5. The interfacial tension between oil and micellar phases (γ_{om}) is calculated from $\gamma_{ow} \leq \gamma_{om} + \gamma_{mw}$, where w, m, o represents water, micellar and oil phases, respectively. As the salinity of the

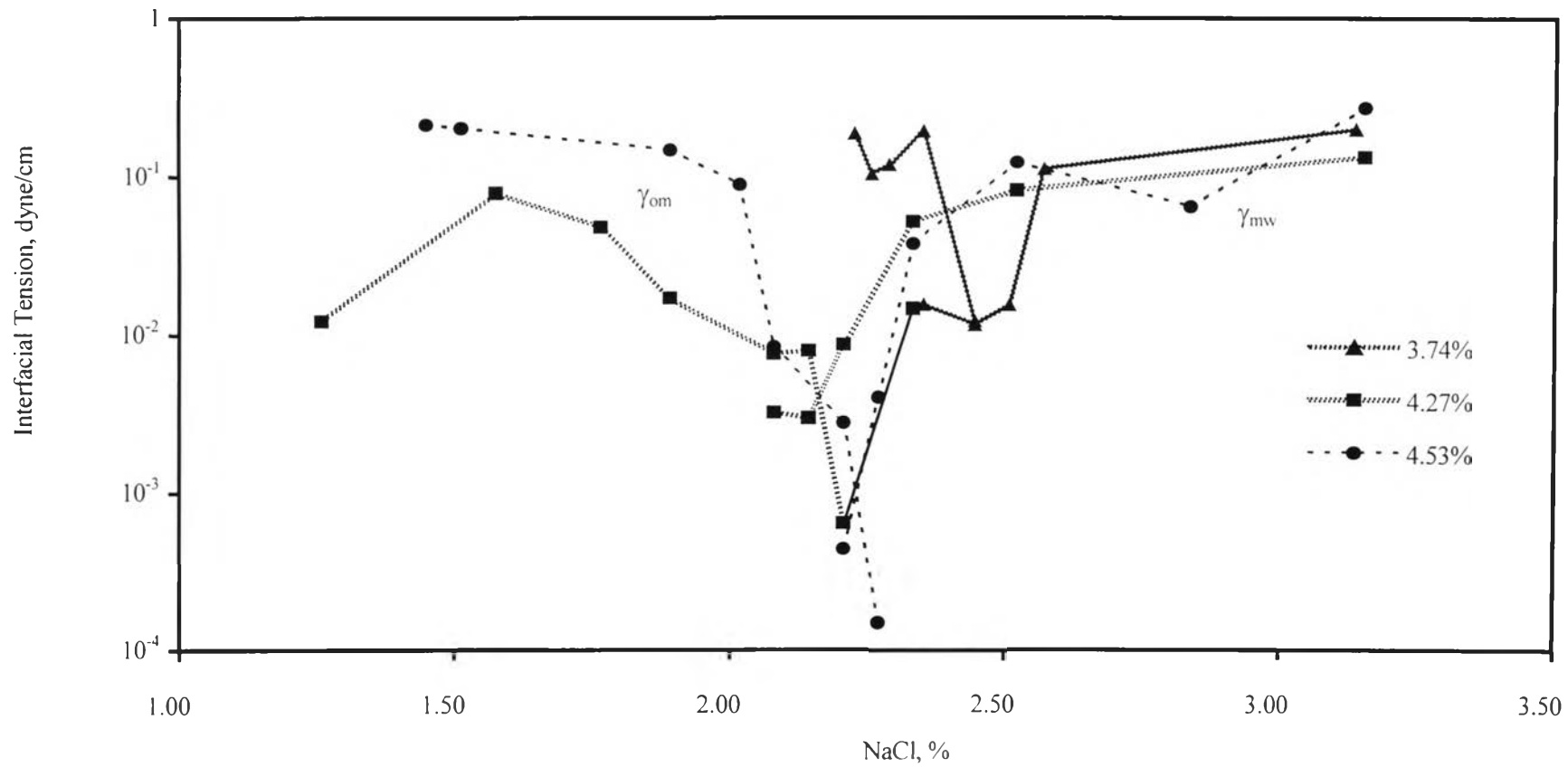


Figure 4.5 Interfacial tension of microemulsion type III for three different SDS concentrations. The system consists of SDS, hexane, octanoic acid and NaCl and constant temperature at 25 °C.

system increases, the interfacial tension γ_{om} between excess oil and micellar solutions decreases, whereas the γ_{mw} between micellar and excess aqueous solutions increases. The plots show interfacial tension minimum occurring at the intersection of the γ_{mo} and γ_{mw} lines which is in the middle phase regions. The intersection point is designated as optimum salinity, S^* , for NaCl and where the value $\gamma_{om} = \gamma_{mw}$ is γ^* . The results also show that as the SDS concentration increases, the interfacial tension minimum decreases and the ultralow interfacial tension values in the order of 10^{-3} dyne/cm can be obtained at the optimum solubilization parameter values shown in Table 4.3.

Table 4.3 Interfacial tension of microemulsion systems equilibrated for 2 months.

SDS (%)	IFT (dyne/cm)	S^* (%)	S^* (%) from solubilization measurement
3.74 %	11.80×10^{-3}	2.46	2.28
4.27%	5.10×10^{-3}	2.17	2.11
4.53%	1.84×10^{-3}	2.24	2.13

Figure 4.6 shows the interfacial tension (a) and the solubilization parameter (b) of the systems with 4.53% SDS as a function of electrolyte concentration (%NaCl). The results show the correlation existing between the amount of oil (or water) solubilized in the surfactant phase and the interfacial tension which it is displayed against the excess oil (or water) phase. The higher the degree of the solubilization, the lower the interfacial tensions (as shown in Table 4.3). At the optimum salinity (S^*), the interfacial tension $\gamma_{om} = \gamma_{mw}$. Comparison of the optimum salinity values obtained from both measurements in Table 4.3 show good agreement.

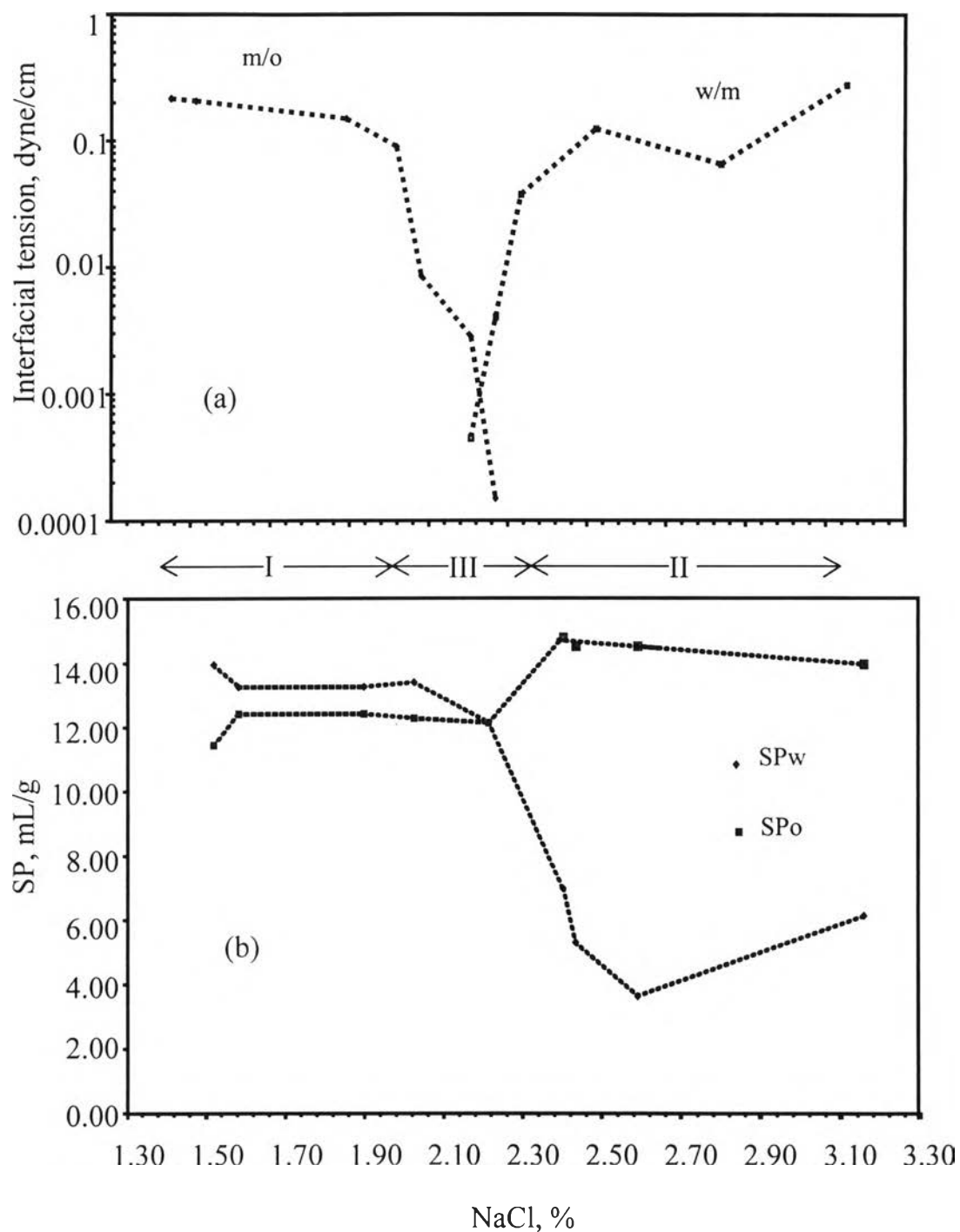


Figure 4.6 Interfacial tension (a) and solubilization parameter (b) as a function of salinity at constant temperature of 25 °C for the mixture of 4.53% SDS, hexane, NaCl and octanoic acid.

4.2.3 Electrical Conductivity

Conductivities of microemulsion systems with different SDS concentrations as a function of electrolyte concentration (NaCl) are shown in Figure 4.7. As surfactant concentration increases, the electrical conductivity decreases. High conductivity values occur at low electrolyte concentrations (microemulsion of type I region) and low conductivity values occur at high salt concentrations (Winsor II region). In the intermediate salt concentration region (middle phase region of Winsor III microemulsion), the conductivities of the systems increase sharply and then decrease rapidly. Thus, the conductivity varies from high to low values corresponding to the inversion from water to oil continuity as the system undergoes a I-III-II transformation. Figure 4.8 shows the changes of electrical conductivity (a) and the water and the oil contents in microemulsions (b) with salinity. In Winsor I microemulsion phase, the conductivity and the corresponding relative volume change slightly. Upon reaching the phase (I-III) transition, the conductivity and the relative volume rise to their maximum values in the middle phase region, then gradually decrease as approaching the phase (III-II) transition, and eventually decreases slightly in Winsor II microemulsion. It is noticed that the maximum conductivity value in the middle phase region occurs at electrolyte concentration which corresponds to the specific salinity of NaCl. The electrical conductivity of microemulsion is used to reveal the structure of micellar phase. Thus Winsor I systems tend to retain a conductivity characteristic the aqueous phase. On the other hand, Winsor II systems are expected to reflect an electrical conductivity characteristic of oil. Winsor III systems yield intermediate behavior.

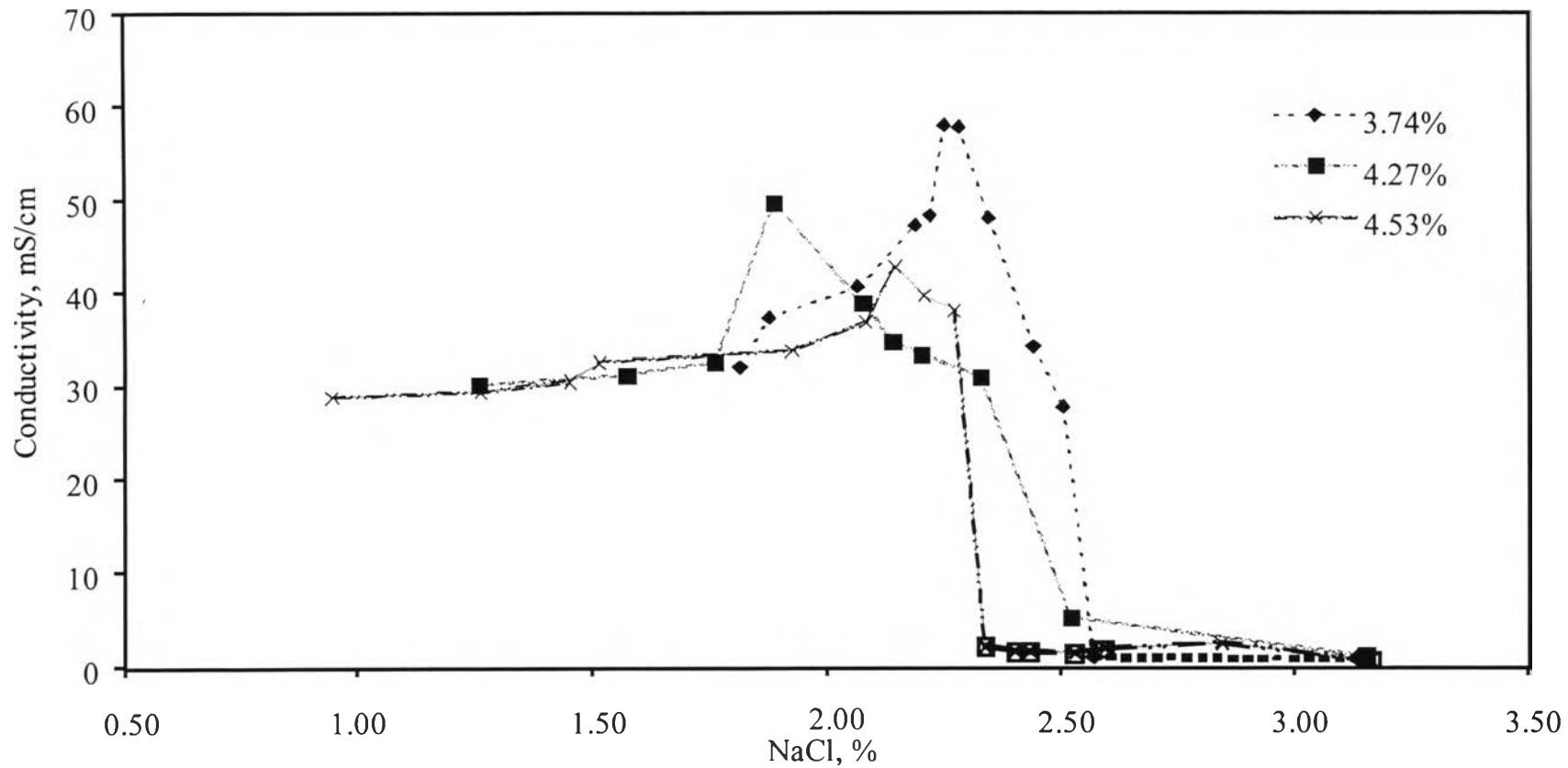


Figure 4.7 Electrical conductivity as a function of salinity and constant temperature at 25 °C for mixture of electrolyte, hexane, octanoic acid and SDS system. The SDS concentrations studied are 3.74%, 4.27%, and 4.53 %, respectively.

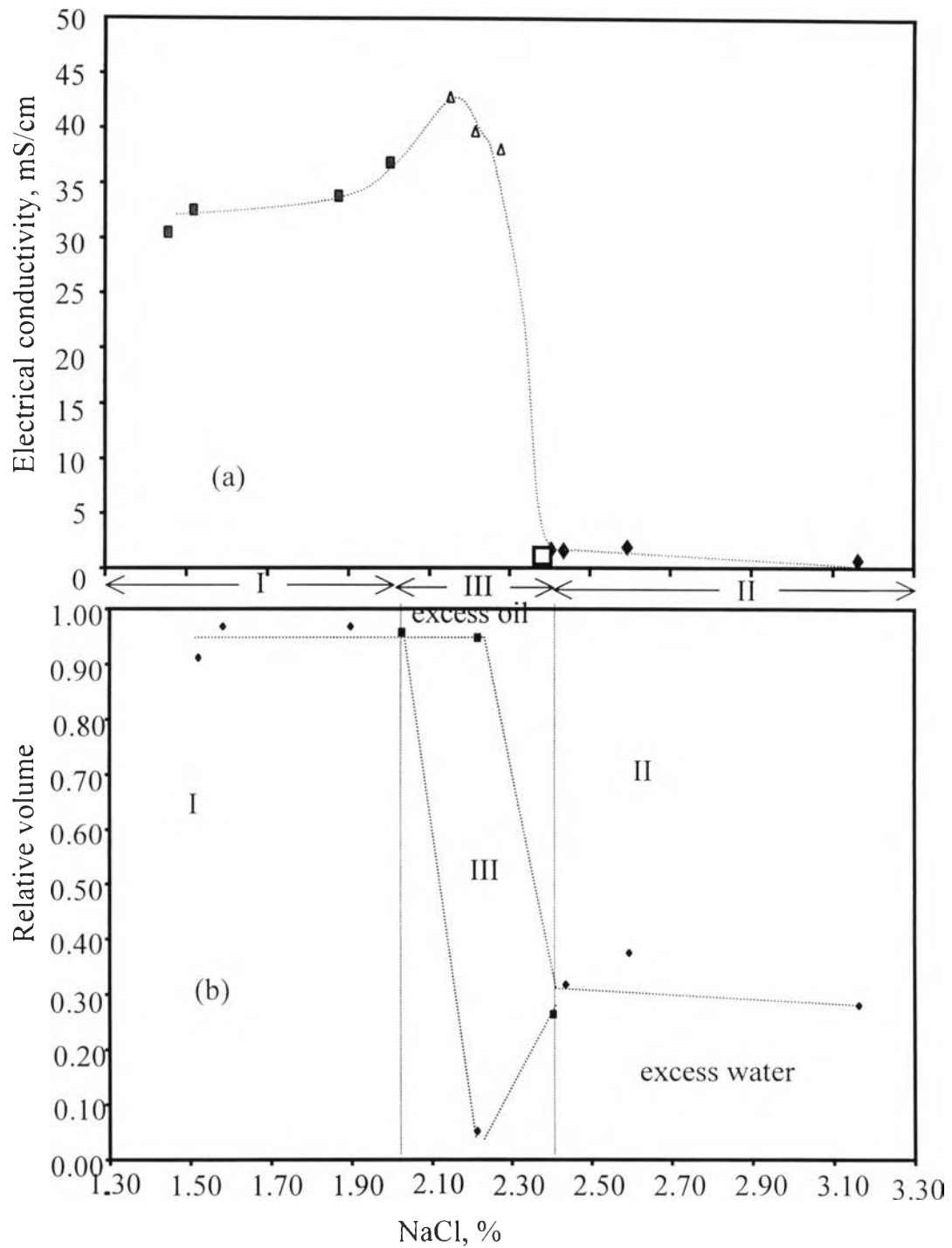


Figure 4.8 The effect of salinity on the conductivity (a) and relative volume of water, oil and surfactant phases (b) for the system of 4.53% SDS, hexane, NaCl and octanoic acid at 25°C.