

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Equilibrium Phase Behavior

In this section experimental data for the phase behavior studies, relative volumes of oil and water, are given in Appendix A. The experimental including results, are described below.

4.1.1 The Effect of Hardness and Surfactant Concentration

The microemulsion phase behavior studies were performed in many concentrations of Dowfax8390 solution. Figure 4.1 illustrates the effect of hardness on the phase behavior when the ratio of Dowfax#8390 to octanoic acid is 0.75 and temperature at 24 °C for different surfactant concentrations. At low surfactant concentrations (4.15% - 28.22%), the inversion from Type I to Type III and Type III to Type II occurred when CaCl₂ was continuously added. As the surfactant concentrations increased above 28.22%, the inversion from Type I to Type IV and from Type IV to Type II occurred. As the surfactant concentrations increased, the relative volume of middle phase increased and the relative volume of the two excess phases decreased until, at sufficiently high concentration of surfactant, all the compositions in the mixture were soluble, and the microemulsion became a single phase.

Figure 4.2 shows the Kahlweit fish diagram, the plot of weight percent of (Dowfax#8390 + octanoic acid) related to water and oil, as a function of weight percent of electrolyte. The graph demonstrates the phase behavior of the system, microemulsion Type I, II, III, and IV. The result showed that the width of the three phase region increased as the Dowfax#8390

concentration increased from 4.15% to 20.47%, decreased as the concentration further increased to 33.38%, and eventually the three phase region was replaced by the single phase (Type IV) as the Dowfax8390 concentration continuously increased to 45.61%.

It was observed that the gel formation occurred in the microemulsion Type II at low surfactant concentration below 28.22% and disappeared at high concentration (above 28.22%). Addition of the electrolyte caused a decreasing of the electrical potential on the dispersed (oil) particle and an increasing interaction between the surfactant ions and counter-ions thereby making them less hydrophilic. The charged film in the O/W microemulsion (Type I system) was neutralized and the oil droplets formed a continuous phase. The trapped water is surrounded by an interfacial film that realigns to form irregularly shaped droplets of water stabilized by a rigid, uncharged film. The result is a W/O microemulsion (Type II system) (Schulman, 1940; Rosen, 1988). The divalent counterion of CaCl_2 stabilizes the ionic surfactant better than a monovalent counterion, the amount of electrolyte can be reduced. The association of counterions is highly dependent on the surfactant concentration (Bourrel and Schechter, 1988). At low surfactant concentration, a high electrolyte concentration was needed to produce inversion from a Type III to a Type II system. Calcium ions, which associate with the head group of Dowfax#8390 in the Type II system, also react with octanoic acid, which was soluble in perchloroethylene. In some systems a gel phase was present. At high surfactant concentration, only a low electrolyte concentration was needed to produce inversion from the Type III to Type II system. The amount of calcium ions associating with the head group of Dowfax#8390 in the Type II system was very low. Thereby, calcium ions and octanoic acid reaction did not effect formation of gel in the high surfactant concentration system. It could be

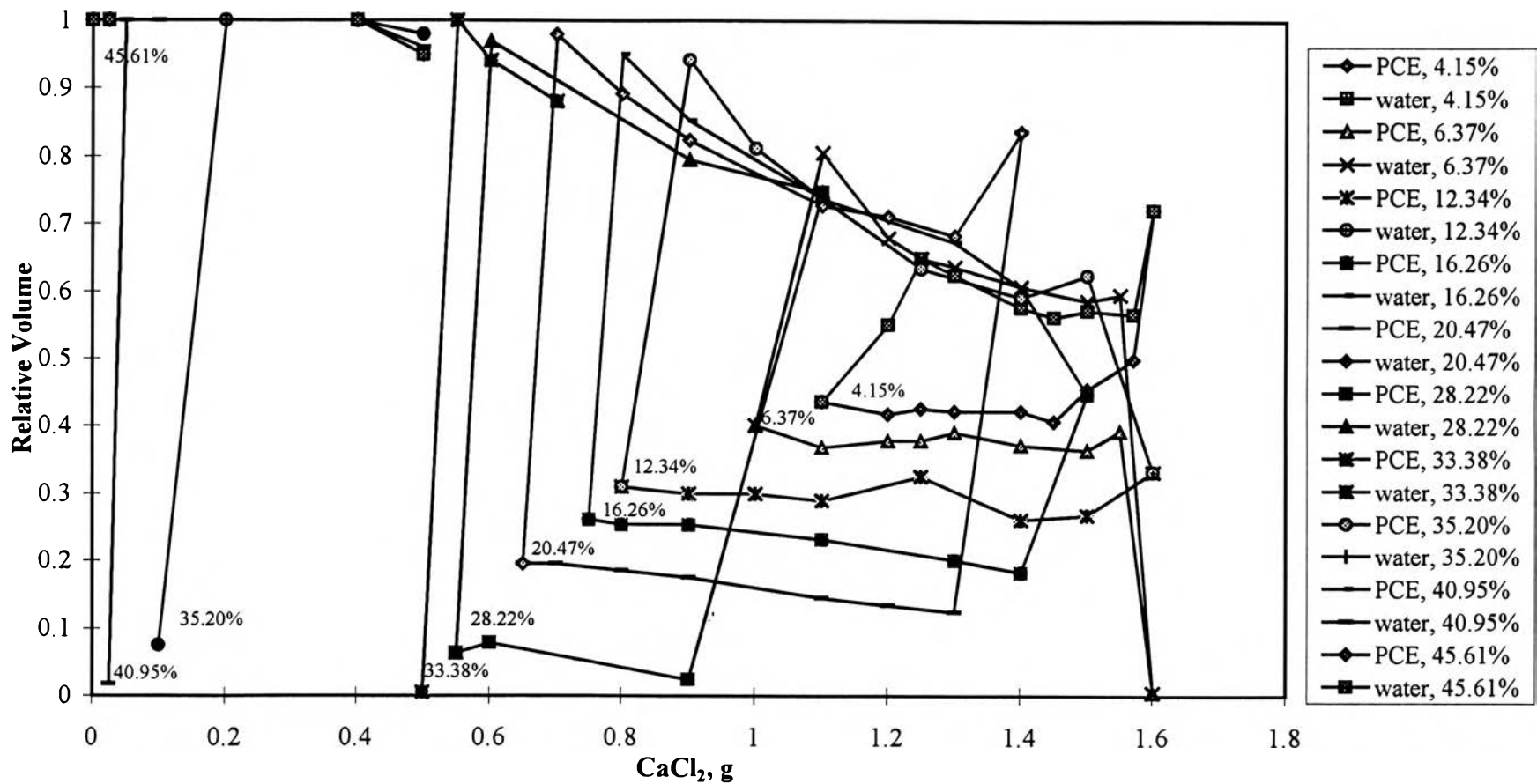


Figure 4.1 Relative Volume of the microemulsion, 4.15%-45.61% (Dowfax#8390 + octanoic acid), R = 0.75, 24 °C.

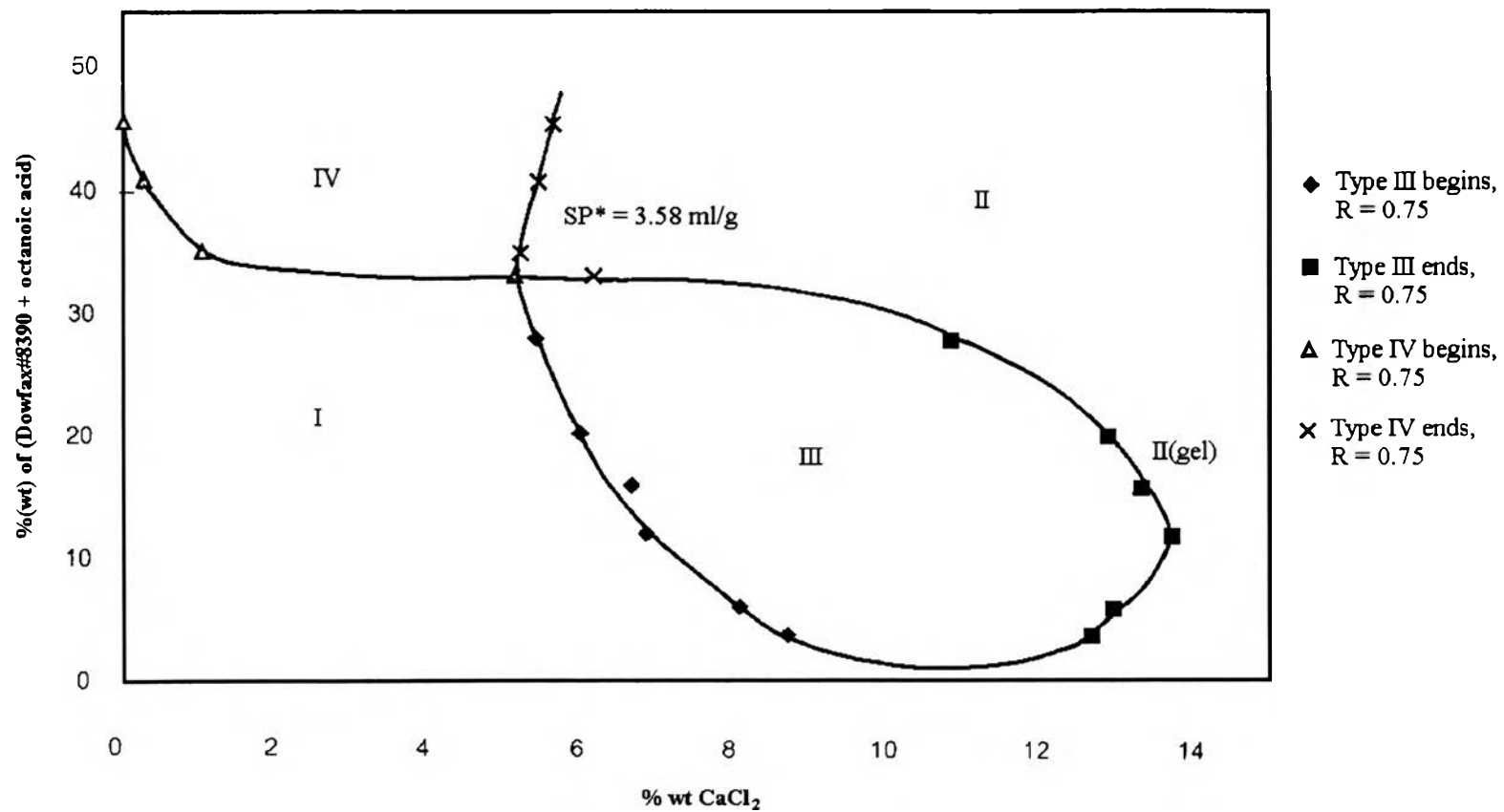


Figure 4.2 Phase diagram of the microemulsion of Dowfax#8390/PCE/octanoic acid, R = 0.75, 24 °C.

concluded that the amount of calcium ions in the Dowfax#8390/PCE/octanoic acid system had an effect on the gel formation in the Type II region.

4.1.2 Co-surfactant Study

Gel formation is an unwanted phenomenon of surfactant in the microemulsion system. The co-surfactant, octanoic acid, was reduced to get rid of the gel phase in the Type II region, so the ratio of Dowfax#8390 to octanoic acid was changed to 1.0 (shown in Figure 4.3). Consequently, the system became less hydrophobic, and required higher electrolyte to salt out or drive the microemulsion to form a middle phase or a single phase microemulsion. It is suggested by Kahlweit (Kahlweit, 1995) that at fixed temperature and oil, the amount of salt required is increased with decreasing lipophilicity of amphiphile. The plots of the weight percent of (Dowfax#8390 + octanoic acid) related to water and PCE against the weight percent of CaCl_2 electrolyte at 24°C , $R = 0.75$ and 1.0 are shown in Figure 4.4. The result showed that the Type III for $R = 1.0$ required a higher weight percent of electrolyte than $R = 0.75$ to begin the middle phase. For example at 12.5(wt)% surfactant the $R = 0.75$ system required 6.8% CaCl_2 , while $R = 1.0$ required 7.5% CaCl_2 . Furthermore, as the weight percent of surfactant increased, the middle phase for $R = 1.0$ became narrower than $R = 0.75$. Gel formation occurred at the surfactant concentration below 21% and 23% for $R = 0.75$ and 1.0 , respectively. Therefore, decreasing co-surfactant caused Type IV formation at lower surfactant concentration and had little effect on gel formation in the Type II region.

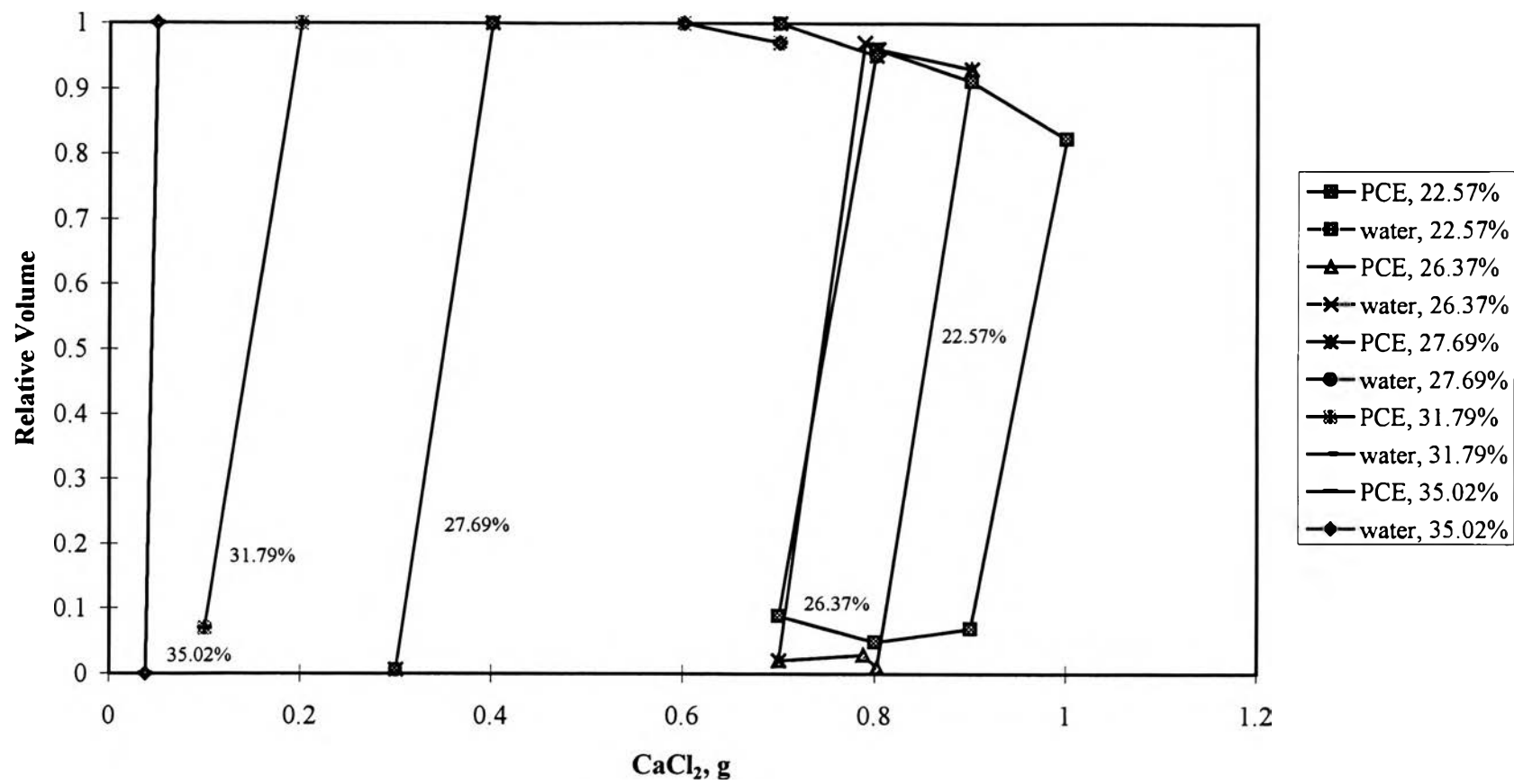


Figure 4.3 Relative Volume of the microemulsion, 22.57%-35.02% (Dowfax#8390 + octanoic acid), $R = 1.0$, $24\text{ }^\circ\text{C}$.

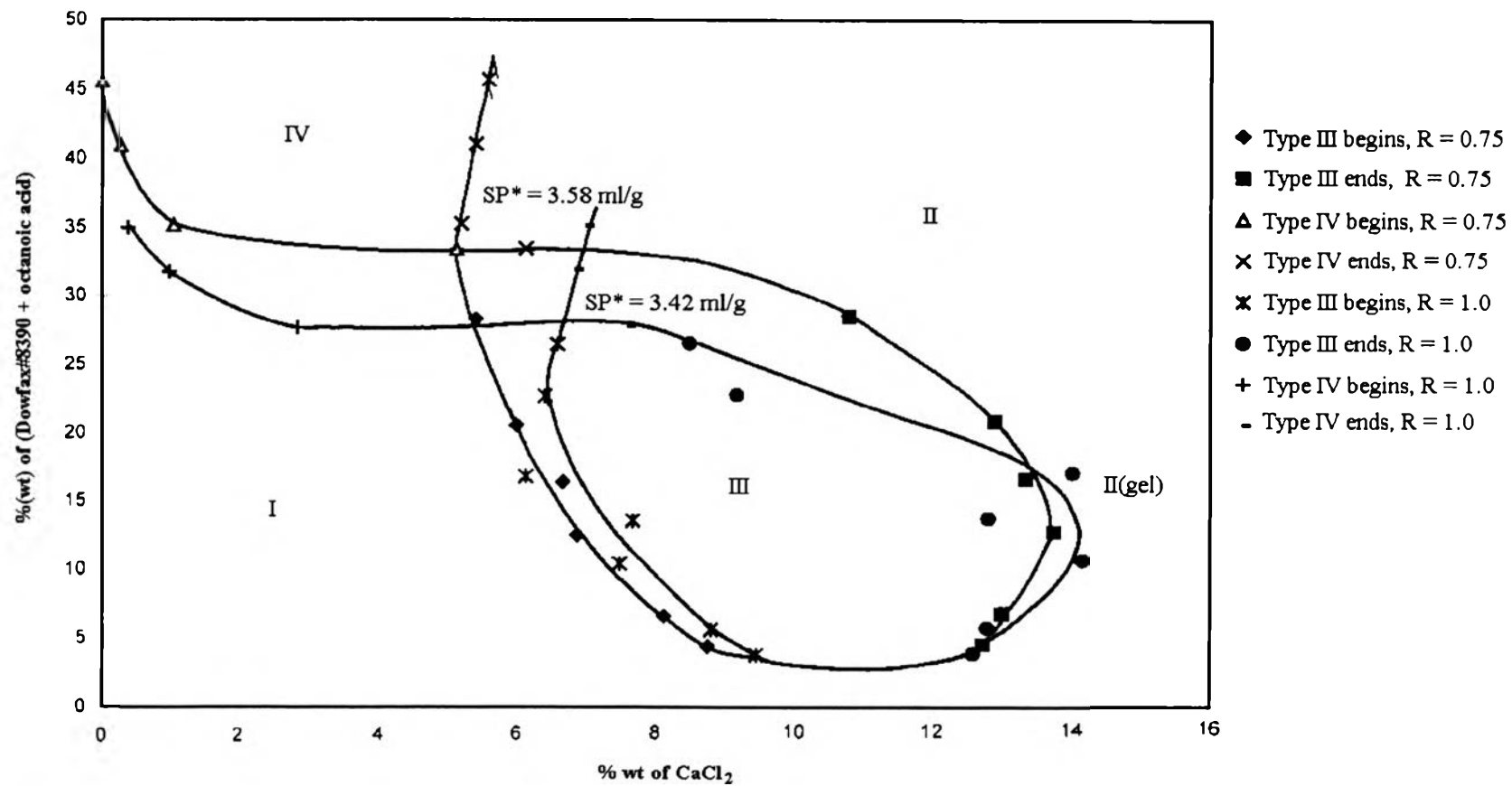


Figure 4.4 Comparison of the phase diagram of $R = 0.75$ with $R = 1.0$ microemulsion, single electrolyte, 24°C .

4.1.3 Mixed Electrolyte Studies

The result from the previous study showed that the decrease of co-surfactant concentration had little effect on elimination of gel formation. The mixed electrolyte was used to get rid of the gel phase in the Type II region. Magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), a highly soluble electrolyte, was mixed with calcium chloride. Figure 4.5 and 4.6 show that the relative volumes of the middle phases are similar to those obtained from the single electrolyte system for both R ratios. It was found that the mixed system needed much higher electrolyte than the single electrolyte system necessary to produce the middle phase or single phase microemulsion for both $R = 0.75$ (shown in Figure 4.7) and $R = 1.0$ (shown in Figure 4.8). The results obtained from the mixed electrolyte systems (Figure 4.9) are the same as the single electrolyte systems (Figure 4.4) for both R ratios.

The formation of gel in the Type II microemulsion still occurred with the mixed electrolyte system. The addition of highly soluble electrolyte shifted the formation of the Type III microemulsion to higher electrolyte concentration.

4.1.4 Temperature Studies

In this study, the temperature were increased from 24 °C to 35 °C and 45 °C to dissolve the gel phase in the Type II region. The relative volumes of middle phase slightly decreased as the temperature was increased to 35 °C, but further change was not significant when the temperature was increased to 45 °C. The phase diagrams of the single electrolyte system at different temperatures, for $R = 0.75$, and 1.0 are shown in Figure 4.10 and 4.11, respectively. In Figure 4.10, increasing the temperature extended the Type III to higher surfactant concentration, for example, at 35% surfactant concentration, Type IV already formed at 24 °C, but the system was still Type

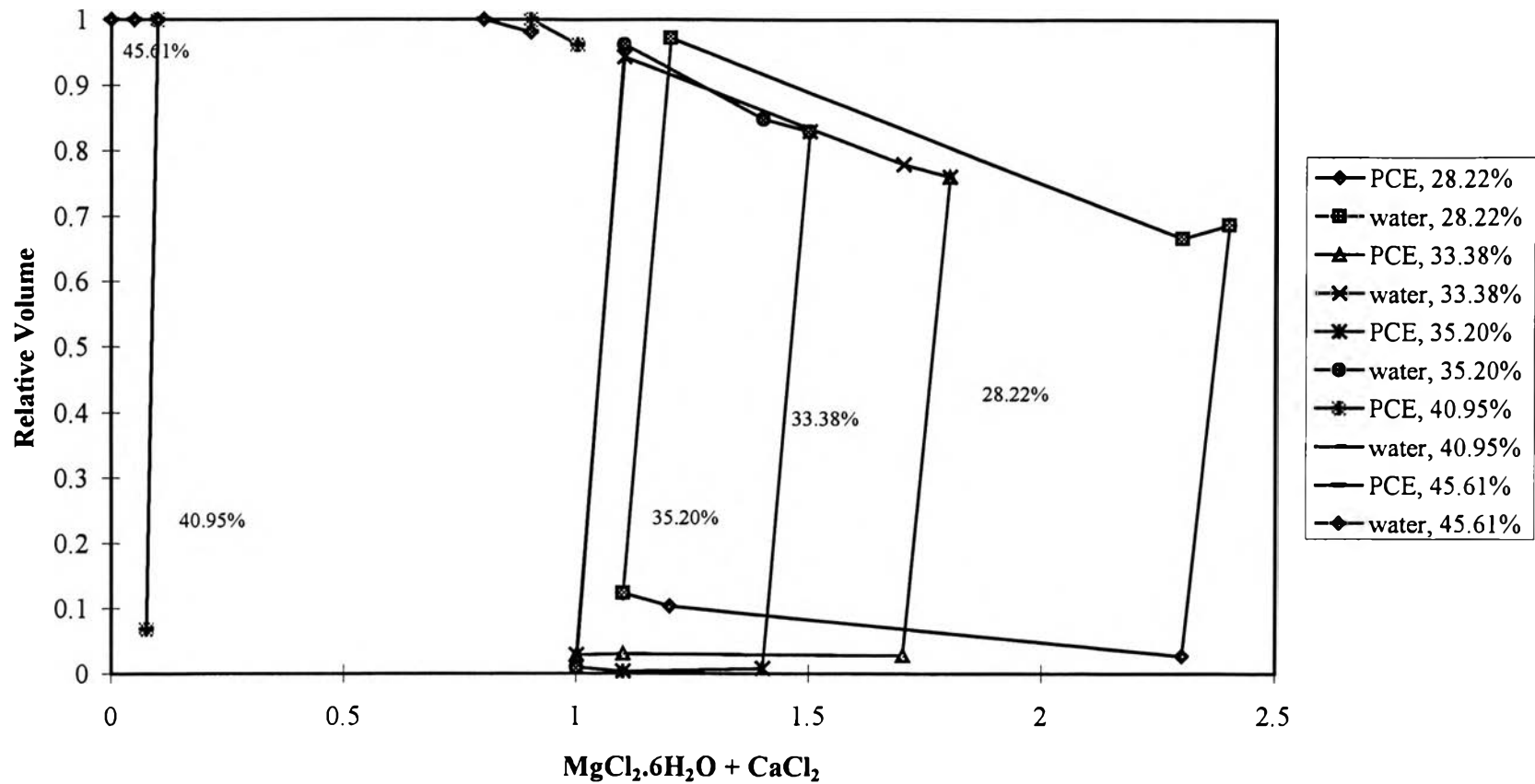


Figure 4.5 Relative Volume of the microemulsion, 28.22%-45.61% (Dowfax#8390 + octanoic acid), R = 0.75, 24 °C.

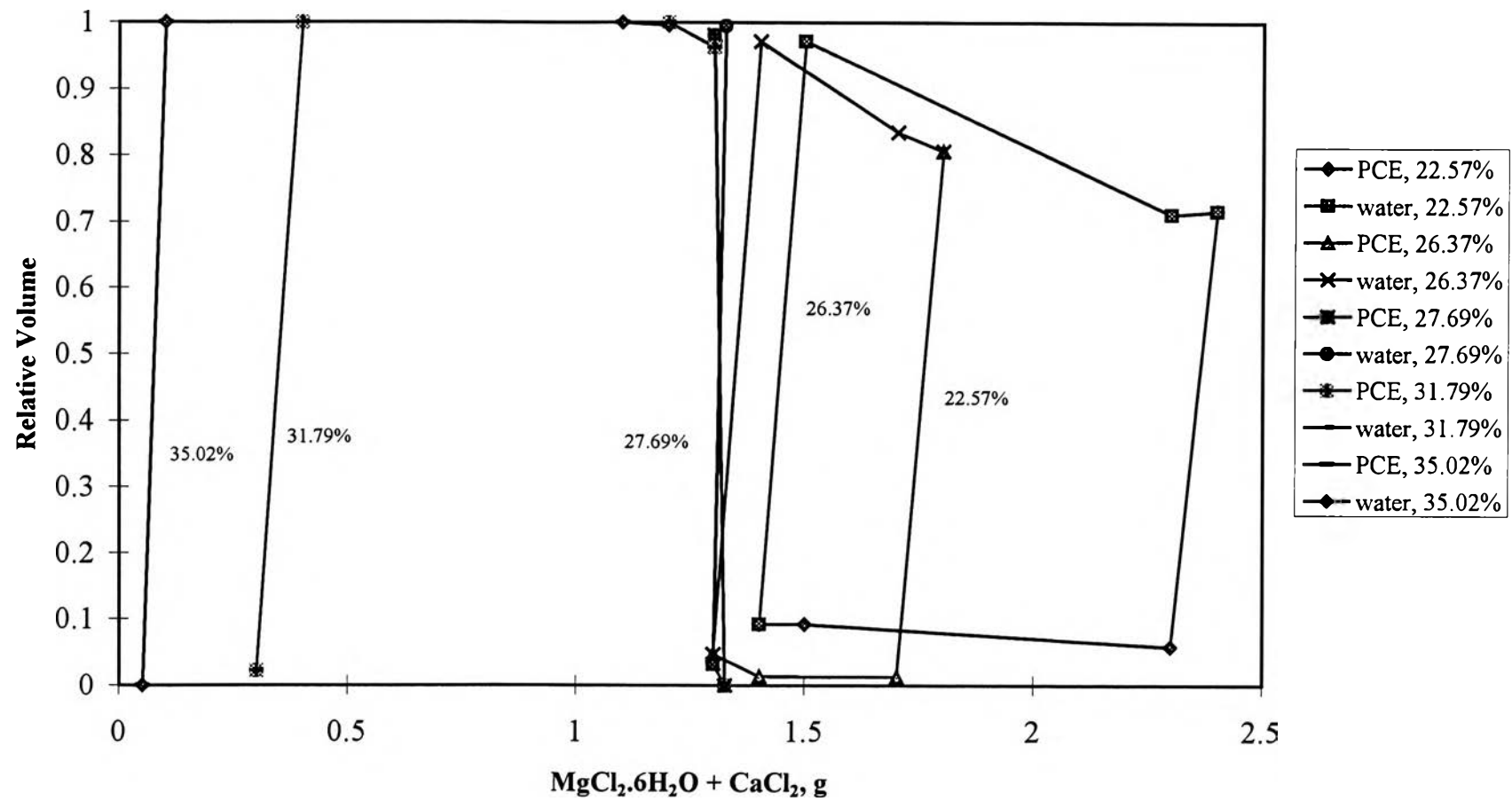


Figure 4.6 Relative Volume of the microemulsion, 22.57%-35.02% (Dowfax#8390 + octanoic acid), $R = 1.0$, $24\text{ }^\circ\text{C}$.

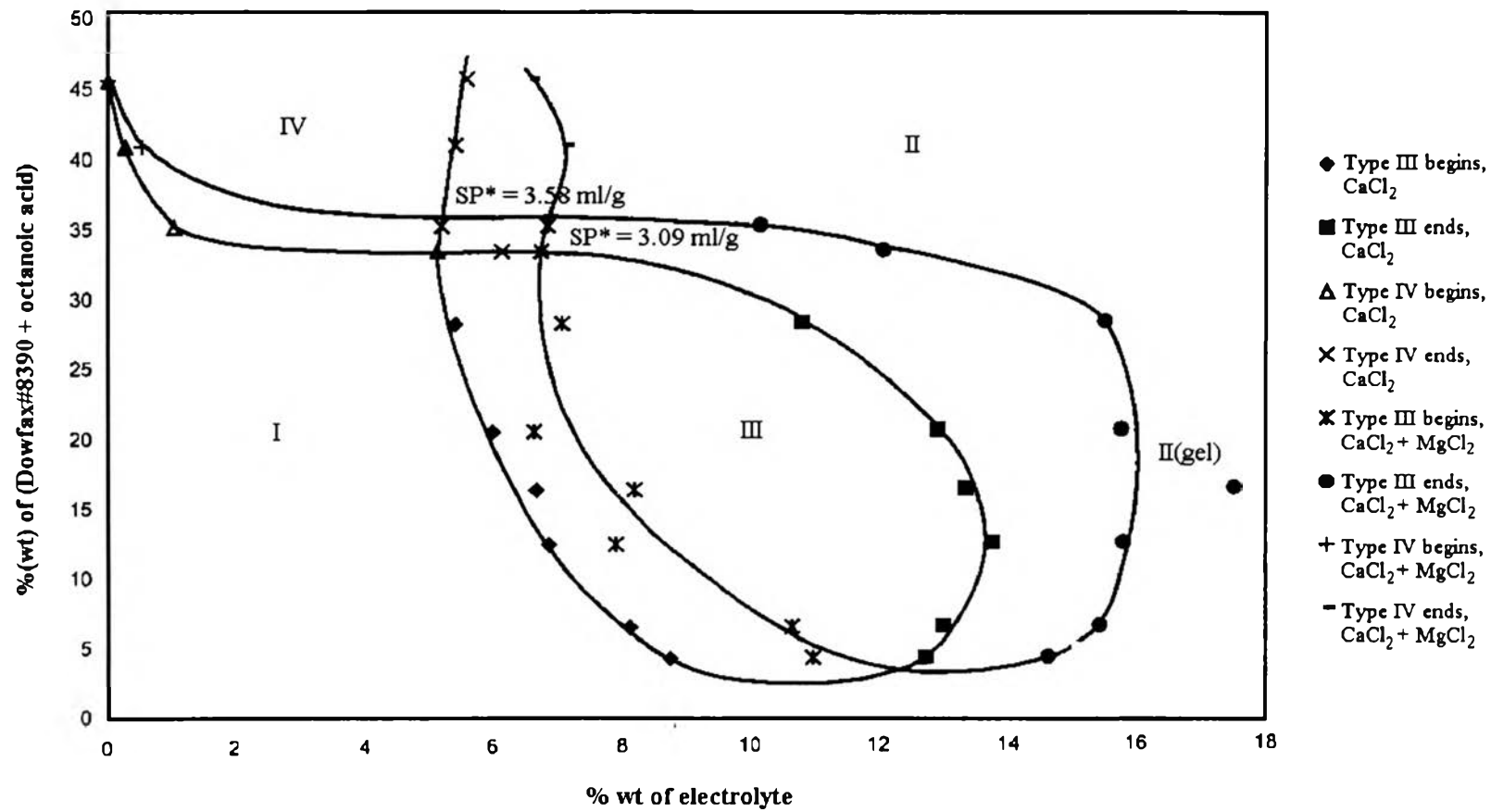


Figure 4.7 Comparison of the phase diagram of CaCl_2 , with $(\text{CaCl}_2 + \text{MgCl}_2)$, $R = 0.75$, 24°C .

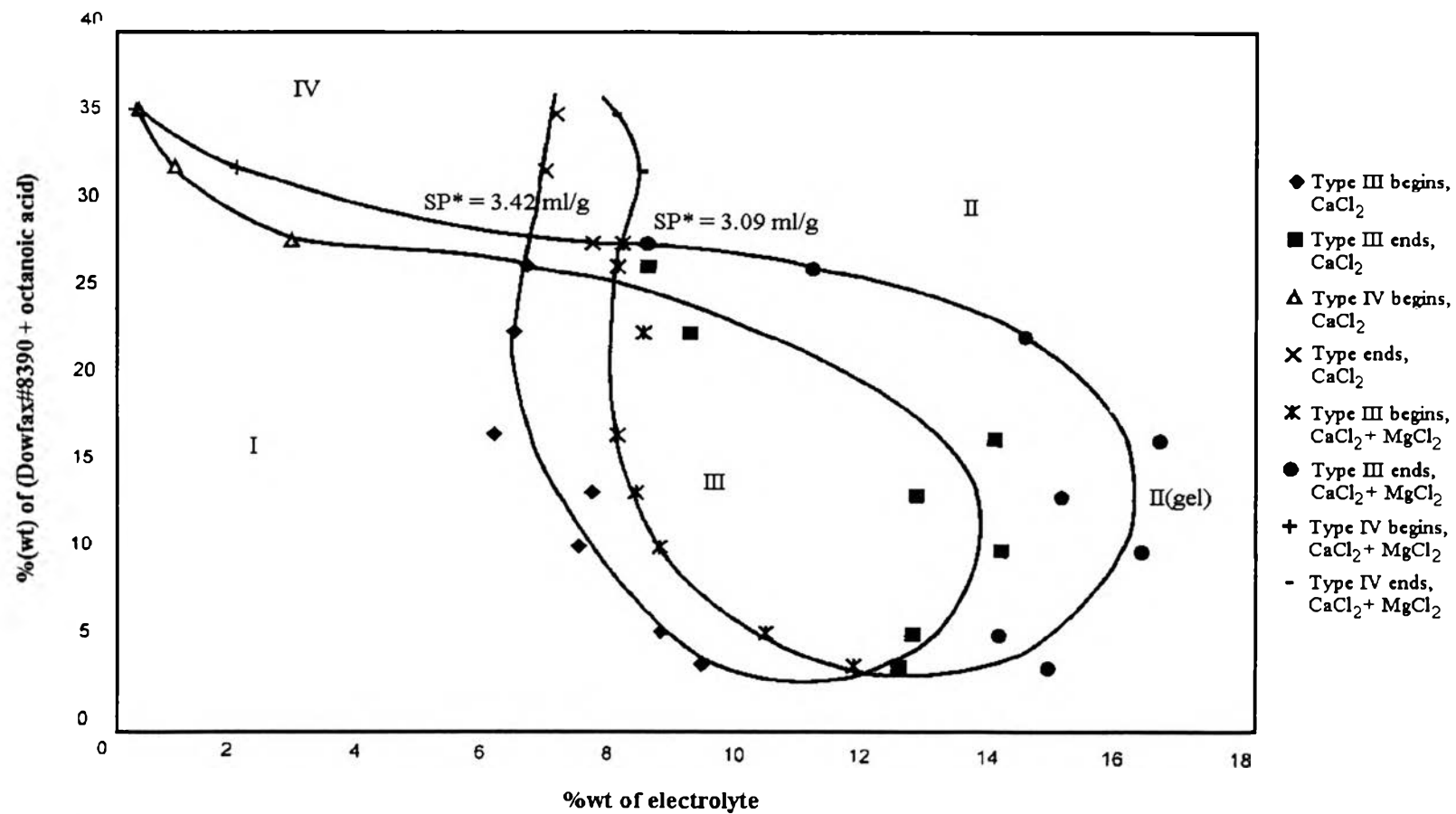


Figure 4.8 Comparison of the phase daigram of CaCl₂ with (CaCl₂ + MgCl₂), R = 1.0, 24 °C.

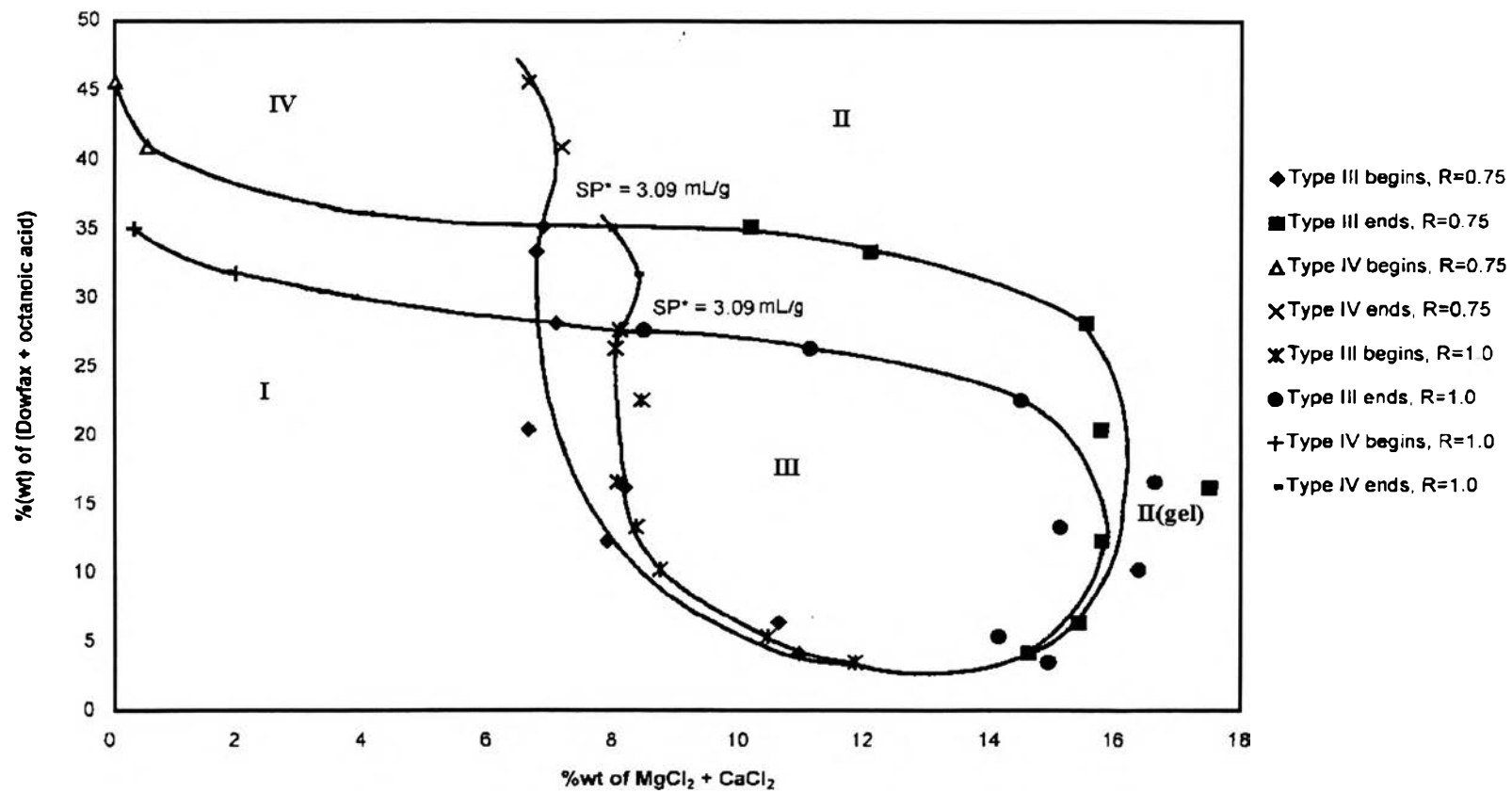
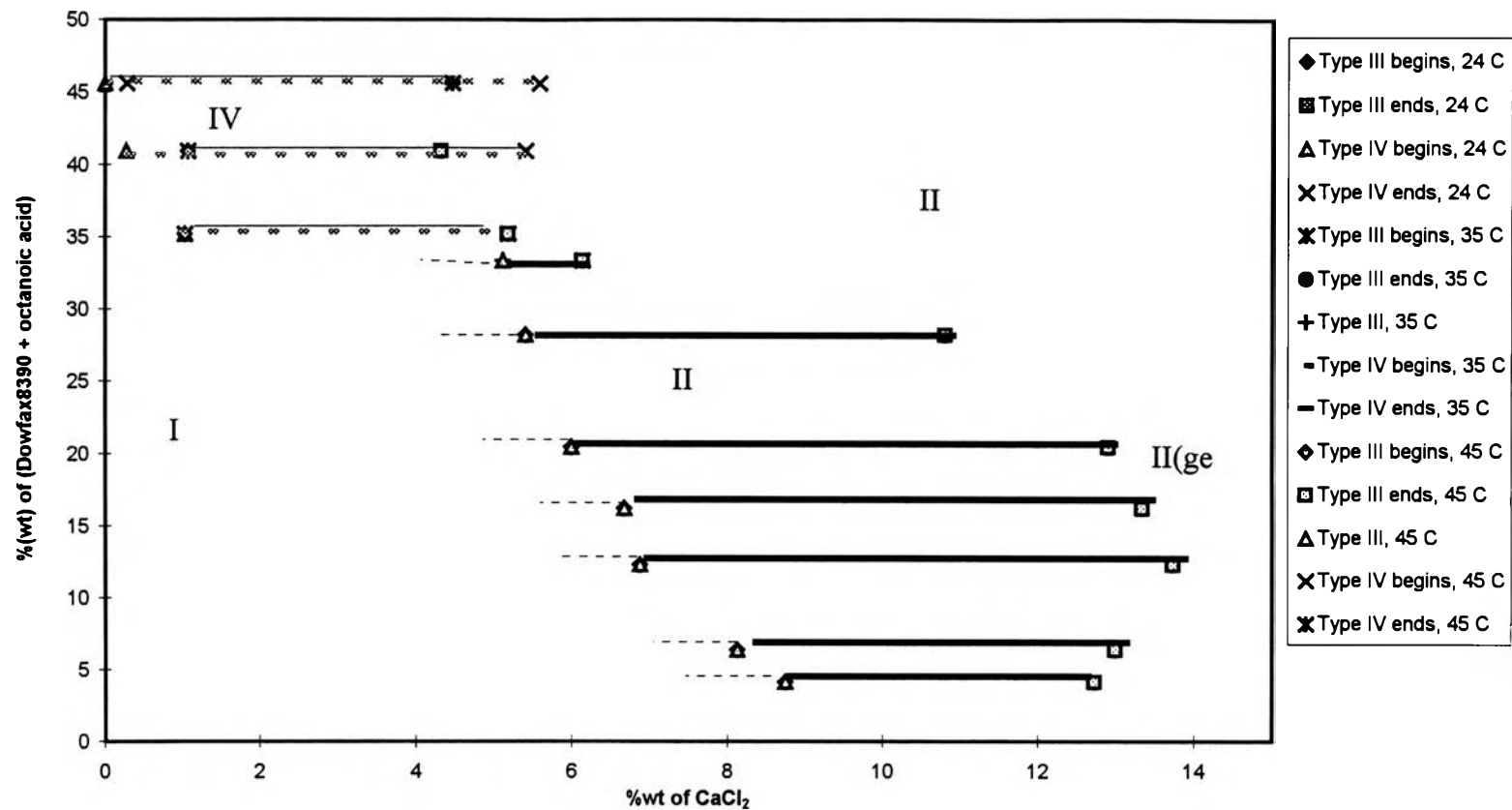


Figure 4.9 Comparison of the phase diagram of $R = 0.75$ with $R = 1.0$ microemulsion, mixed electrolyte, 24°C .



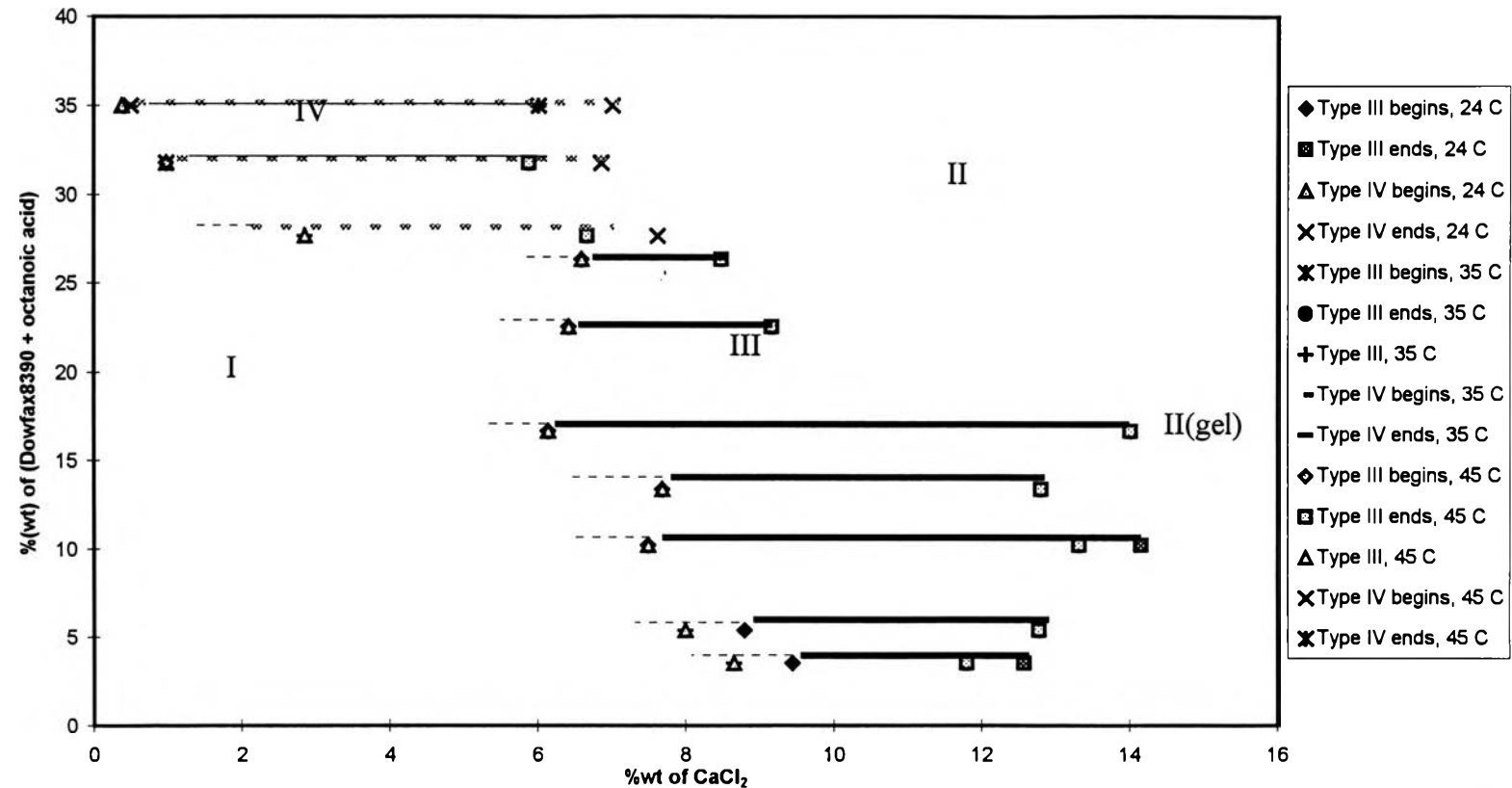
indicates CaCl₂ range for type III at 24 °C - - - indicates expansion of CaCl₂ range for type III at 35 °C and 45 °
 indicates CaCl₂ range for type IV at 24 °C — indicates shrinkage of CaCl₂ range for type IV at 35 °C and 45 °

Figure 4.10 Comparison of the phase diagram of CaCl₂, R = 0.75, 24 °C, 35 °C, 45 °C.

III at 35°C and 45°C. Further increasing the temperature and the surfactant concentration, beyond 35%, the middle phase disappeared and a Type IV occurred at very high concentration (45%), while 24°C showed Type IV at 35% and higher concentration. It was noted that there was discontinuation where the middle phase ended (35%) and Type IV began (45%). Furthermore, at higher temperature and below 35% surfactant concentration, the range of CaCl₂ required to produce the middle phase began at lower %CaCl₂ than at 24°C, but the CaCl₂ range shrank above 35% surfactant concentration. In Figure 4.11, R = 1.0, as the temperature increased, the middle phase ended at 32% and converted to Type IV at higher surfactant concentration, while 24°C showed Type IV at 32% and higher concentration. In addition, at higher temperature, at low surfactant concentration, the range of CaCl₂ which produced middle phase was widened and the middle phase appeared at lower %CaCl₂, but the range shrank at higher surfactant concentration and the middle phase appeared at higher % CaCl₂.

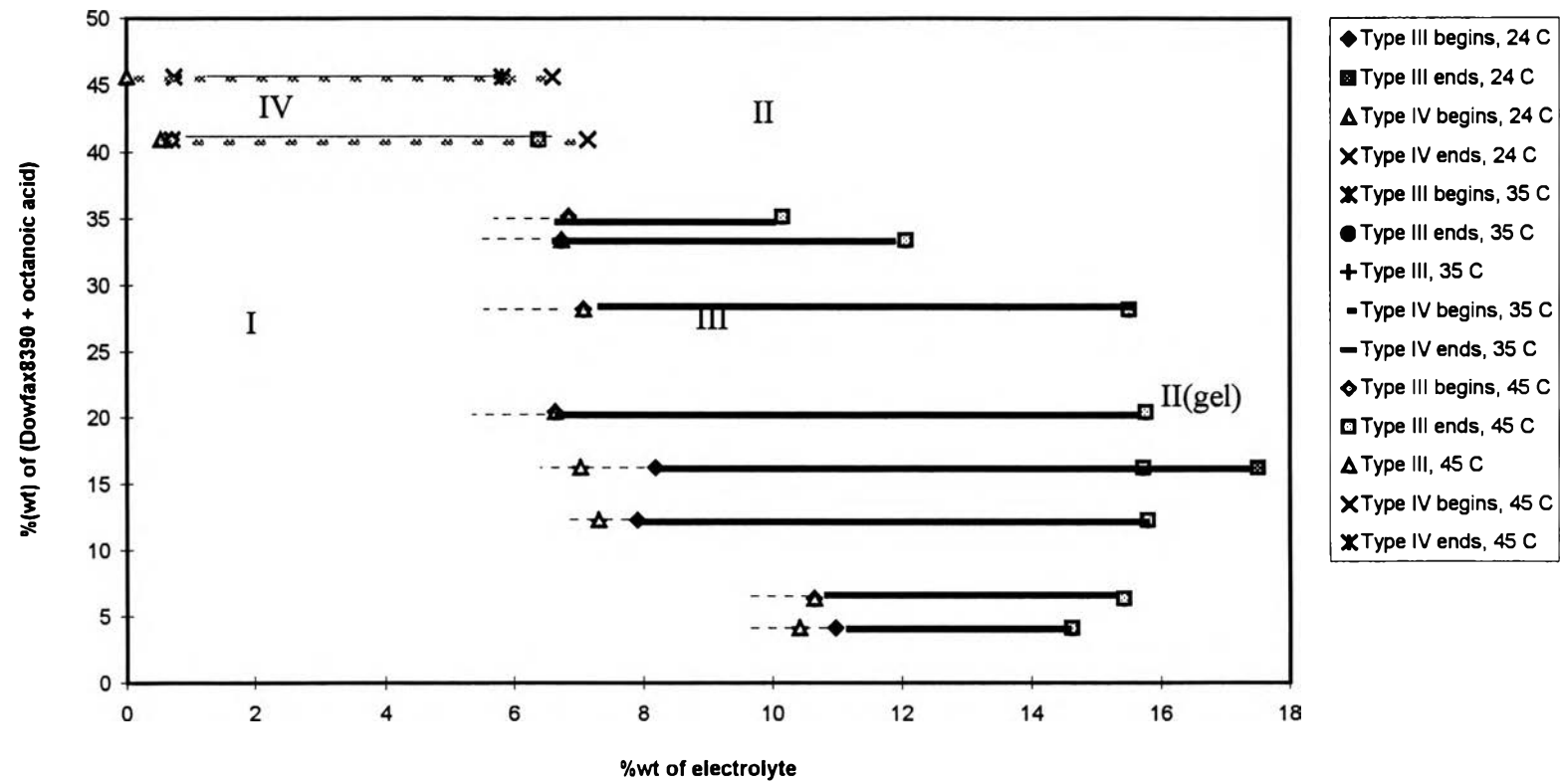
When the mixed electrolyte was used (shown in Figure 4.12 and 4.13), increased temperature showed very similar behavior to the single electrolyte system for both the R ratios. There was Type IV formation at very high surfactant concentration. Similarly, the range of mixed electrolyte produced the same results as the single electrolyte at higher temperature for both R ratios.

The results for both R ratios and both electrolyte systems agreed partly with the Kahlweit recipes. According to the Kahlweit (1995) recipes, at fixed oil and amphiphile, the amount of salt required for traversing the three phase region increases with increasing temperature as shown in Figure 2.7. Two observations are obtained from Figure 2.7. First, the amount of salt necessary to produce microemulsion inversion increases with increasing temperature. Second, the width of the three phase region is widened with increasing temperature. The experimental results could be compared with the



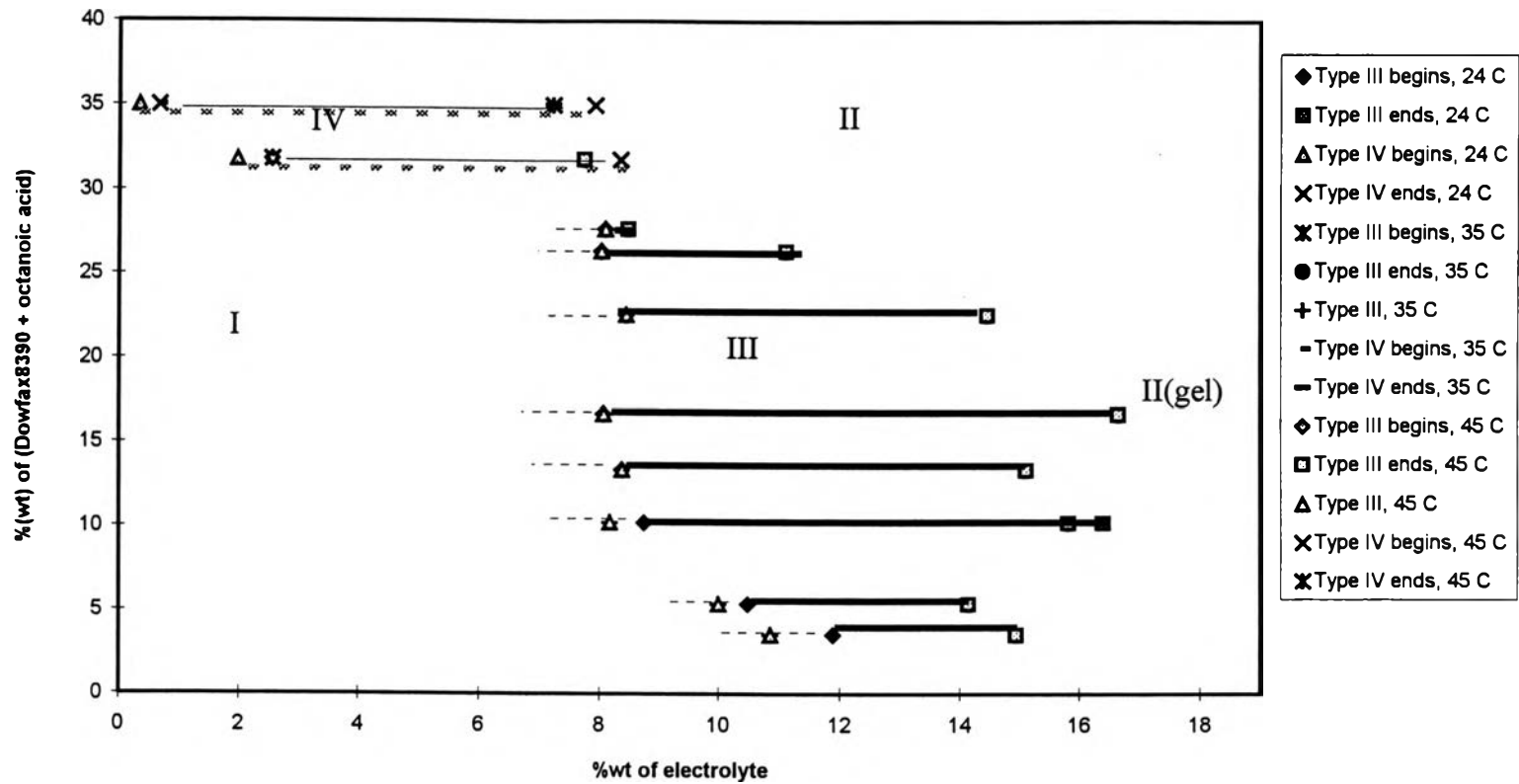
— indicates CaCl₂ range for type III at 24 °C
 ~ ~ indicates CaCl₂ range for type IV at 24 °C
 - - - indicates expansion of CaCl₂ range for type III at 35 °C and 45 °
 — indicates shrinkage of CaCl₂ range for type IV at 35 °C and 45 °

Figure 4.11 Comparison of the phase diagram of CaCl₂, R = 1.0, 24 °C, 35 °C, 45 °C.



— indicates CaCl₂ range for type III at 24 °C
 ~ ~ indicates CaCl₂ range for type IV at 24 °C
 - - - indicates expansion of CaCl₂ range for type III at 35 °C and 45 °
 — indicates shrinkage of CaCl₂ range for type IV at 35 °C and 45 °

Figure 4.12 Comparison of the phase diagram of CaCl₂ + MgCl₂, R = 0.75, 24 °C, 35 °C, 45 °C.



— indicates CaCl_2 range for type III at 24 °C
 - - - indicates expansion of CaCl_2 range for type III at 35 °C and 45 °
 * * indicates CaCl_2 range for type IV at 24 °C
 — indicates shrinkage of CaCl_2 range for type IV at 35 °C and 45 °

Figure 4.13 Comparison of the phase diagram of $\text{CaCl}_2 + \text{MgCl}_2$, $R = 1.0$, 24 °C, 35 °C, 45 °C.

first Kahlweit's consideration that it showed contradiction at low surfactant concentration when the amount of salt necessary to produce middle phase microemulsion decreased with increasing temperature (Figure 4.14). However, at high surfactant concentration, the result agreed in that the amount of salt required to produce the middle phase microemulsion increased with increasing temperature (Figure 4.15). Comparison of the experimental results with Kahlweit's second consideration showed different profiles in that as temperature increased, the width of the three phase region widened for low surfactant concentration but shrank for high surfactant concentration (Figure 4.14 and 4.15).

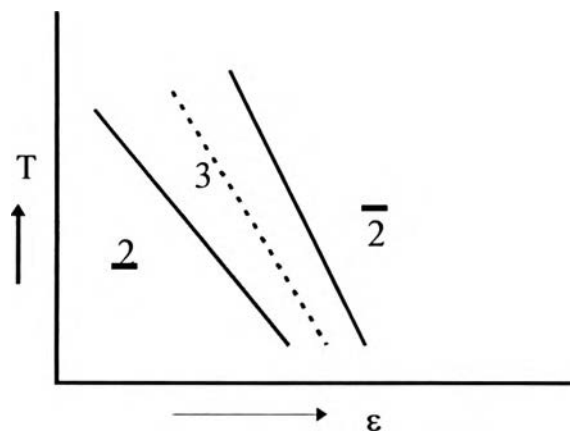


Figure 4.14 Schematic of salting out of low Dowfax#8390 concentration.

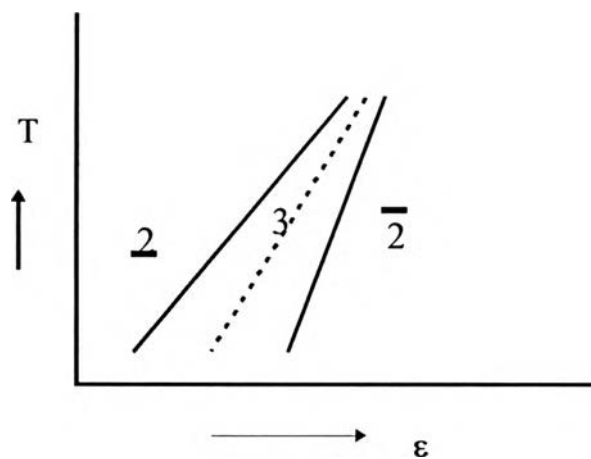


Figure 4.15 Schematic of salting out of high Dowfax#8390 concentration.

4.2 Solubilization

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

4.2.1 The Effect of Surfactant Concentration

The point of intersection (SP^*) of the Solubilization Parameter curves of PCE and water inside the middle phase region, indicating equal amount of the oil and water solubilizing occur at the optimum hardness (s^*). The minimum amount of the surfactant required to produce a single phase, Type IV microemulsion is illustrated in Figure 4.16 for the $R = 0.75$, $CaCl_2$. The results indicated that the optimum Solubilization Parameter increased with increasing surfactant concentration and reached the maximum at 33.38% surfactant. The optimum hardness was 5.62% $CaCl_2$. Further, when increasing the surfactant concentration, the SP^* value decreased. Therefore, for solubilization only, it is not worth it to increase the surfactant concentration beyond the optimum to emulsify both the oil and water.

4.2.2 Effect of Co-surfactant

The effect of octanoic acid at $R = 1.0$ on the solubilization of PCE at $24^\circ C$ was also determined. The plot of the optimum Solubilization Parameters, SP^* , versus optimum hardness for different surfactant concentrations is shown in Figure 4.17, it indicates that the optimum surfactant concentration, solubilizing the most PCE, is 28%. Comparison of the SP^* values for $R = 1.0$ and $R = 0.75$ shows that the reduction of octanoic acid decreased the percent of surfactant at optimum, but also the SP^* value.

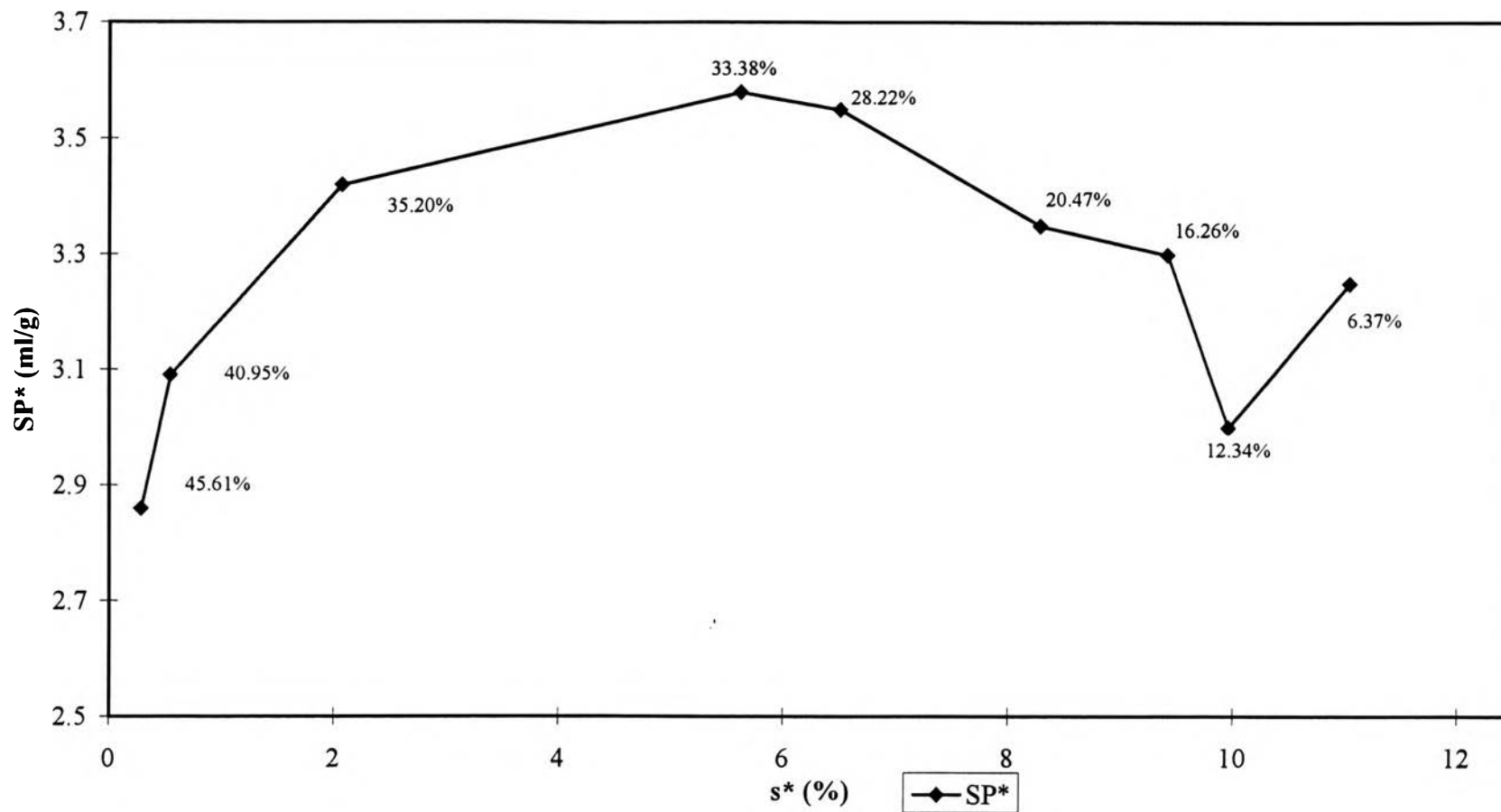


Figure 4.16 Optimum solubilization parameters and optimum hardness, 6.37%-45.61% (Dowfax#8390 + octanoic acid) R = 0.75, 24 °C.

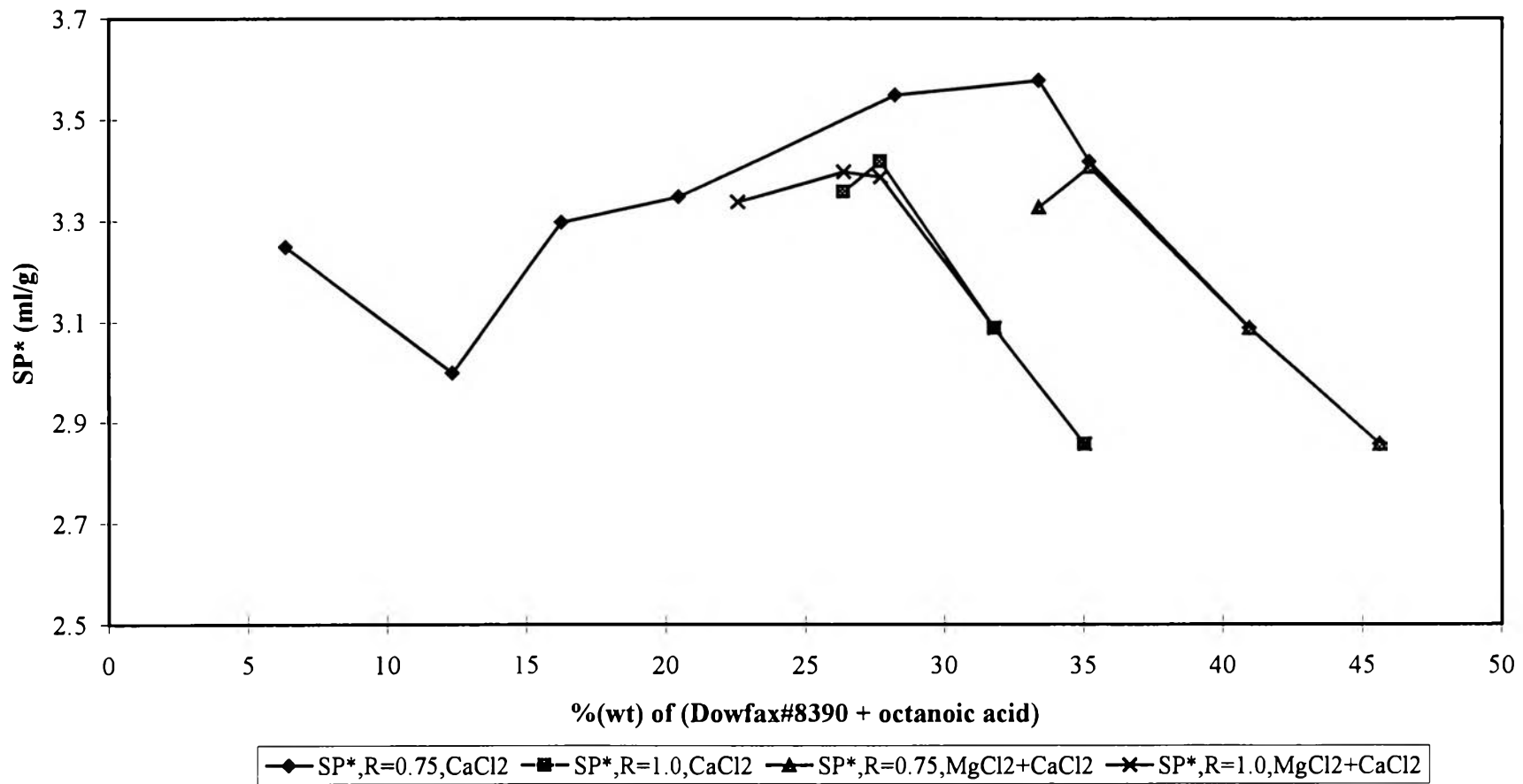


Figure 4.17 Comparison of optimum solubilization parameters of different system.

4.2.3 Effect of Mixed Electrolyte

The effect of magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) on solubilization potential was determined for $R = 0.75$ and 1.0 . The plots of SP^* versus s^* for different surfactant concentrations are shown in Figure 4.17. The results showed that the SP^* values of the mixed electrolyte systems for both R ratios were still in the middle phase region, and showed the single phase at 41% and 32% surfactant concentrations for $R = 0.75$ and 1.0 , respectively. The appropriate SP^* value for $R = 0.75$ should be higher than 36% and lower than 41% surfactant concentrations ($36\% < [\text{surfactant}]^* < 41\%$), and for $R = 1.0$ should be $25\% < [\text{surfactant}]^* < 32\%$. The comparison of the results of the mixed electrolyte with the single electrolyte systems (Table 4.1) indicates that the plots of the mixed electrolyte systems has similar trend to the single electrolyte, but the SP^* values of the former are less than those of the latter system for both R ratios.

4.2.4 Effect of Temperature

The temperature was increased to $35\text{ }^\circ\text{C}$ and $45\text{ }^\circ\text{C}$ to observe the effect on the solubilization potential of PCE in the micellar solution for $R = 0.75$ and 1.0 in both the single and mixed electrolyte systems. As the temperature increased, all the results showed that the SP^* values slightly decreased and electrolyte concentration also decreased. For ionic amphiphiles, as temperature increases, the interaction per unit area of interface decreases because the area occupied per surfactant molecule increases. This is due primarily to a decrease in a restriction of the movement of water molecule in the presence of a hydrocarbon or any apolar compound (hydrophobic effect) which reduces the adsorption driving force and solvency is correspondingly reduced. As a consequence, the solubilization at optimum is expected to decrease (Bourrel and Schechter, 1988).

Table 4.1 Comparison of optimum solubilization parameter, optimum hardness, and optimum Dowfax#8390 concentration, at 24 °C

electrolyte	R	%Dowfax	SP*(ml/g)	s* (%)	Viscosity
CaCl ₂	0.75	33.38	3.58	5.62	High
		40.95	3.09	0.54	Low
	1.0	27.69	3.42	3.80	High
		31.79	3.09	1.47	Low
MgCl ₂ +CaCl ₂	0.75	36%<%Dowfax<41%	3.09<SP* to 3.41	0.71	Low
		40.95	3.09	0.71	Low
	1.0	28%<%Dowfax<32%	3.09<SP* to 3.39	2.57	High
		35.02	2.86	0.66	Low

4.3 Selection of the Optimum System

The phase behavior studies, indicating gel formation and the optimum solubilization potential at each R-ratio and for each electrolyte system, are concluded in Figures 4.4 and 4.7 - 4.9 and in Table 4.1. Gel formation occurred below the optimum surfactant concentration used to produce the most solubilization of PCE in the single phase microemulsion. The optimum solubilization of PCE ($SP^* = 3.58$) for high octanoic acid ($R = 0.75$) required higher surfactant concentration (33.38%) than the low octanoic acid ($R = 1.0$) system (27.69%). However, the percent increase of the SP^* value was 5% while the percent of surfactant increase was 20%, and the percent of hardness decrease was 22%, if one wanted to solubilize PCE at the highest SP^* value.

The selection of the appropriate microemulsion to solubilize PCE depends not only on the appropriate SP^* value but also on the clarity and viscosity of the microemulsion phase. The viscosity of all emulsions was evaluated visually after adding the small amount of electrolyte into the system at which a Type IV occurred. An excess of electrolyte showing as precipitate at the bottom of the tube indicated too much electrolyte was added. Table 4.1 shows that the low viscosity microemulsion ($R = 1.0$, and $CaCl_2$ system) requires a higher surfactant concentration (32%), but has a lower SP^* value. A low viscosity for the microemulsion reduces time and saves pumping cost in a remediation. The optimum system requires a compromise among the surfactant concentration, time (viscosity), and the quantity of PCE solubilized per volume of surfactant injected.