

CHAPTER IV

RESULTS AND DISCUSSION

In this work, CPE performances were reported in terms of coacervate phase fractional volume, surfactant partition ratio, organic solute partition ratio, percentage of surfactant extraction, and percentage of organic solute extraction as defined in the experimental section. The value of coacervate fractional volume should be low because this makes coacervate phase easy to be removed for further remediation or recovery.

Surfactant concentrations were reported in mM, while organic solute concentrations were in ppm because wastewater pollutant concentrations were often designated in these weight-based units. The initial conditions were 70 mM for surfactant and 100-ppm for organic solutes.

4.1 Cloud Point Determination

The cloud point of 70 mM nonionic surfactant solutions was determined by observing the temperature at which the turbidity of solution disappeared. The concentrations of NaCl were varied to 0, 0.4 0.8 M. Table 4.1 summaries the cloud points of the nonionic surfactants used at various concentrations of NaCl.

Table 4.1 Cloud points of the nonionic surfactants used at 0, 0.4, and 0.8M NaCl

Surfactant Trade Name	Structure	Cloud Point (°C)		
		0M NaCl	0.4M NaCl	0.8M NaCl
Surfonic L24-5	C ₁₂ EO ₅	35.0	29.0	24.2
Surfonic L24-7	C ₁₂ EO ₇	49.0	44.3	39.0
Surfonic L24-7.1	C ₁₂ EO _{7.1}	57.0	N.A.	39.5
Surfonic L24-9	C ₁₂ EO ₉	73.0	66.8	58.5
Surfonic L24-12	C ₁₂ EO ₁₂	>90	89.0	78.5
Surfonic TDA5	C ₁₃ EO ₅	34.5	29.5	24.2
Surfonic TDA6	C ₁₃ EO ₆	38.0	32.0	26.0
Surfonic TDA8	C ₁₃ EO ₈	41.5	37.0	30.0
Surfonic TDA9	C ₁₃ EO ₉	54.8	48.3	40.5
Surfonic TDA11	C ₁₃ EO ₁₁	72.0	65.0	57.5
Surfonic L12-8	C ₁₁ EO ₈	78.8	71.0	63.0
Surfonic DDA8	C ₁₂ EO ₈	51.0	45.5	38.0
Neodol 91-5E	C ₉₋₁₁ EO ₅	35.5	30.0	24.5
Neodol 91-6E	C ₉₋₁₁ EO ₆	54.0	47.0	41.0
Neodol 91-8	C ₉₋₁₁ EO ₈	82.0	72.5	65.5
Neodol 25-9	C _{12.5} EO ₉	80.0	71.0	64.0
Neodol 1-9	C ₁₁ EO ₉	72.0	63.0	57.0

Figures 4.1 and 4.2 show the cloud points of the constant number of carbons in alkyl chain with varied numbers of ethylene oxide and of the constant number of ethylene oxide with varied numbers of carbons in alkyl chain, respectively at 0.8 M NaCl.

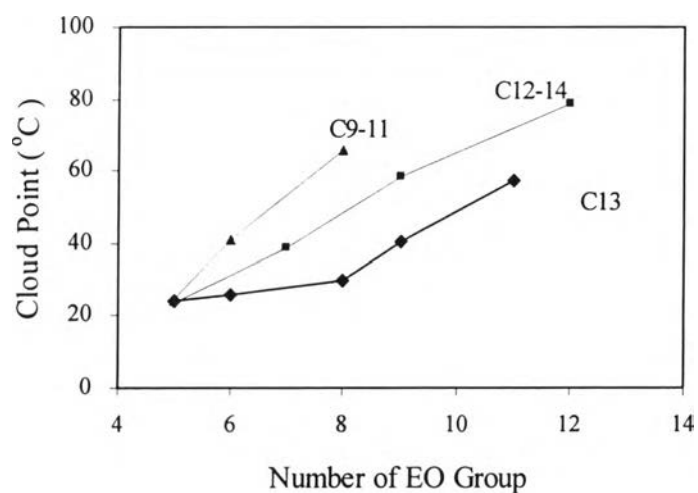


Figure 4.1 Cloud point temperatures of the constant number of carbon in the alkyl chain with varied numbers of ethylene oxide at 0.8M NaCl.

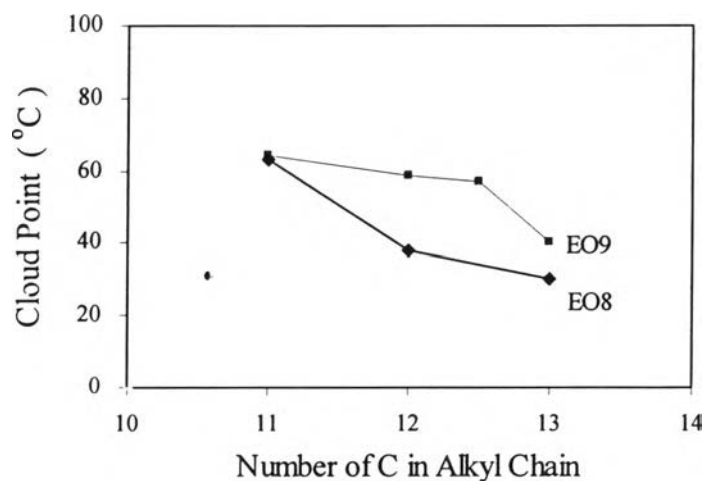


Figure 4.2 Cloud point temperatures of the constant number of ethylene oxide with varied numbers of C in alkyl chain at 0.8M NaCl.

The results showed that the cloud point of alcohol ethoxylate increased as the number of ethylene oxide increased. This is because the higher numbers of ethylene oxide consume the higher energy to dehydrate water molecules from the polar head groups. On the other hand, the cloud point decreased as the number of carbons in alkyl chain increased because the longer the alkyl chain, the lower the micelle-water interface area. The results for the cloud points of 0.4M and 0M of NaCl are shown in Figures 4.3 to 4.6, respectively.

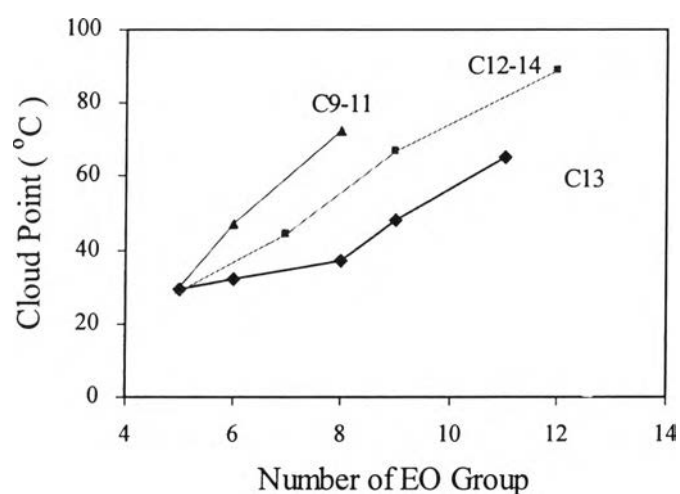


Figure 4.3 Cloud point temperatures of the constant number of carbon in the alkyl chain with varied numbers of ethylene oxide at 0.4M NaCl.

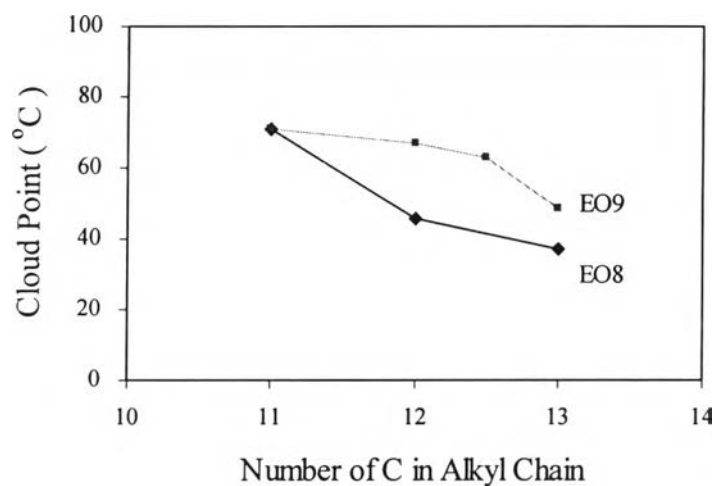


Figure 4.4 Cloud point temperatures of the constant number of ethylene oxide with varied numbers of C in alkyl chain at 0.4M NaCl.

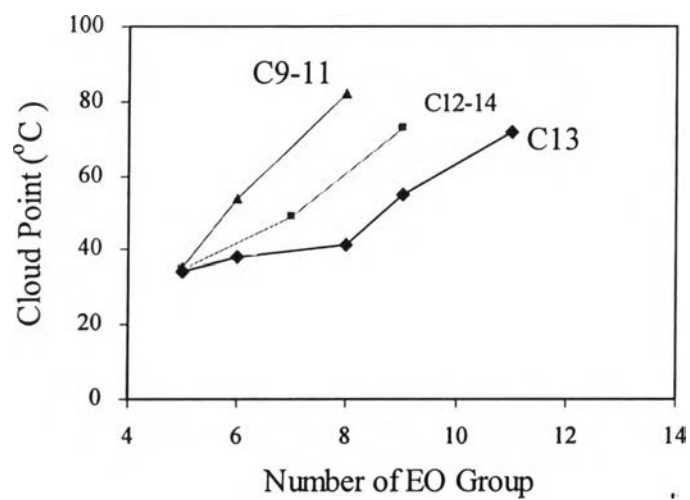


Figure 4.5 Cloud point temperatures of the constant number of carbons in the alkyl chain with varied numbers of ethylene oxide at 0M NaCl.

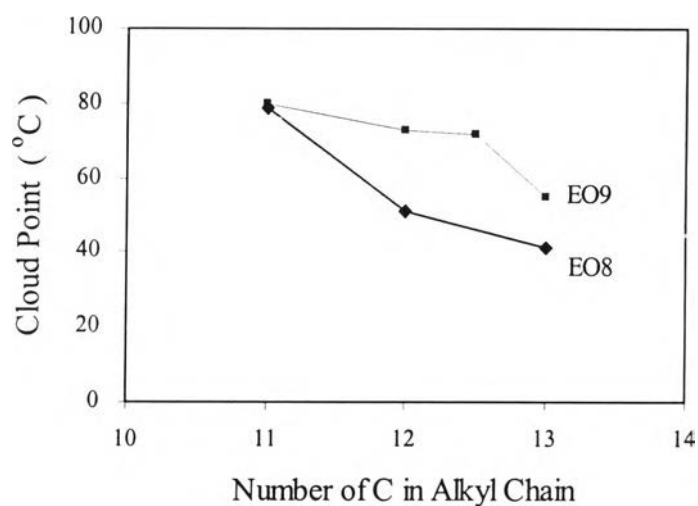


Figure 4.6 Cloud point temperatures of the constant number of ethylene oxide with varied numbers of C in alkyl chain at 0M NaCl.

The results also showed the same trend for 0.8M NaCl. The results can confirm that molecular structure of the nonionic surfactant affected cloud point as mentioned in the literature review.

4.2 Effect of Number of Ethylene Oxide Group on Cloud Point Extraction

The effect of number of ethylene oxide group (n) was observed at constant alkyl chain length (m) with various numbers of ethylene oxides. This work used AE surfactant at constant number of carbon atoms of 13 ($m = 13$) which are TDA5, TDA6, TDA8, TDA9, and TDA11. In these homologous series, the number of ethylene oxide was equal to 5, 6, 8, 9, and 11 ($n = 5, 6, 8, 9, \text{ and } 11$) whose molecular structures were $C_{13}EO_5$, $C_{13}EO_6$, $C_{13}EO_8$, $C_{13}EO_9$, and $C_{13}EO_{11}$, respectively.

The results for phenol and *p*-cresol at the conditions of 0M NaCl and operating temperature at 80 °C showed that as the number of ethylene oxide groups increased coacervate phase fractional volumes increased as shown in Figure 4.7.

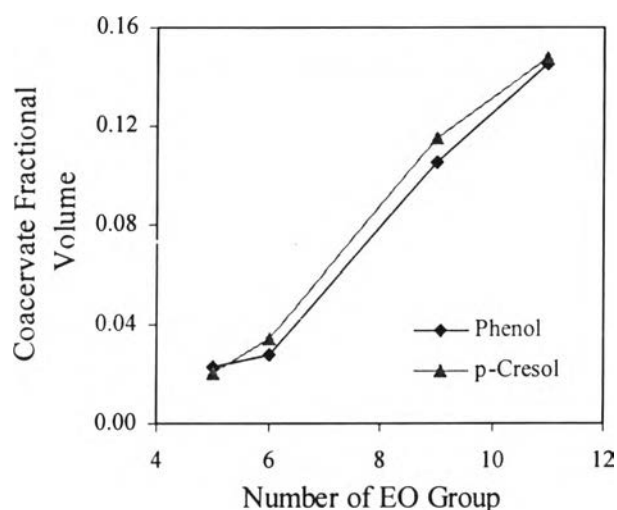


Figure 4.7 Coacervate fractional volumes of the constant number of carbon 13 atoms alcohol ethoxylate at 0M NaCl and 80 °C.

As the number of ethylene oxide increased, coacervate fractional volumes increased because an increasing in EO groups resulted in increasing the cloud point which, in turn, could enable water molecules difficult to dehydrate from the polar head group of surfactant micelles in the coacervate phase. The results also showed that the increment of coacervate fractional volume of the two different solutes was almost the same; therefore, the molecular structure of organic solutes has an insignificant effect on coacervate fractional volume.

Surfactant partition ratios of these series are presented in Figure 4.8.

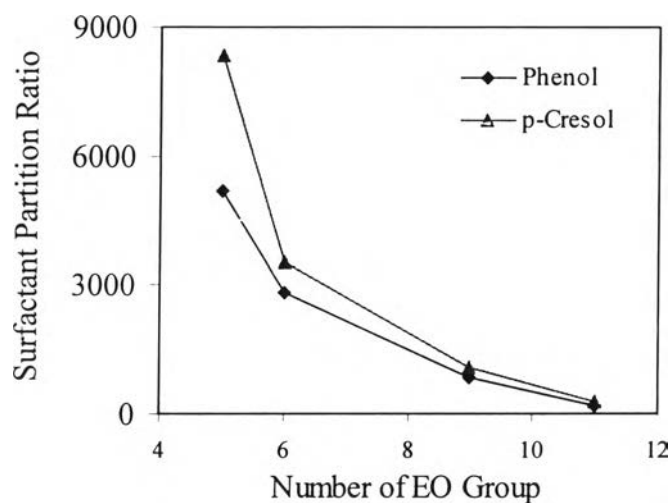


Figure 4.8 Surfactant partition ratios of the constant number of carbon 13 atoms alcohol ethoxylate at 0M NaCl and 80 °C.

As the number of ethylene oxide increased, surfactant partition ratios of both phenol and p-cresol decreased. This is because the larger volume of coacervate phase contains the higher amount of water molecules. The result also showed that surfactant partition ratios of the two different solutes decreased in a similar manner. This can be implied that the molecular structure of organic solutes has a slight effect on surfactant partition ratio.

Since an organic solute tended to solubilize in rich surfactant micelles formed in the coacervate phase, organic solute partition ratios also decreased as the number of ethylene oxide groups increased as shown in Figure 4.9.

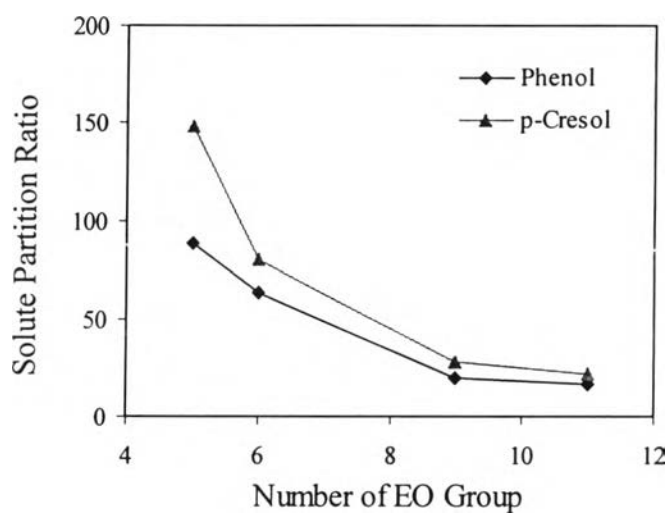


Figure 4.9 Solute partition ratios of the constant number of carbon 13 atoms alcohol ethoxylate at 0M NaCl and 80 °C.

To investigate the extraction efficiency, the extraction percentages of surfactant and organic solutes were calculated as shown in Figures 4.10 and 4.11.

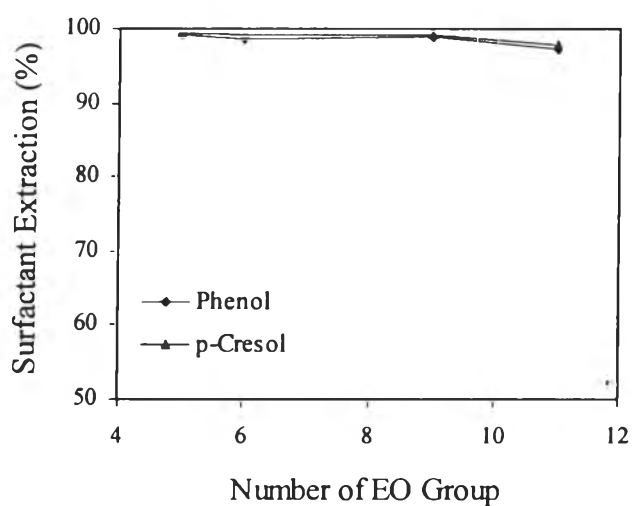


Figure 4.10 Percentage of surfactant extraction of the constant number of carbon 13 atoms alcohol ethoxylate at 0M NaCl and 80 °C.

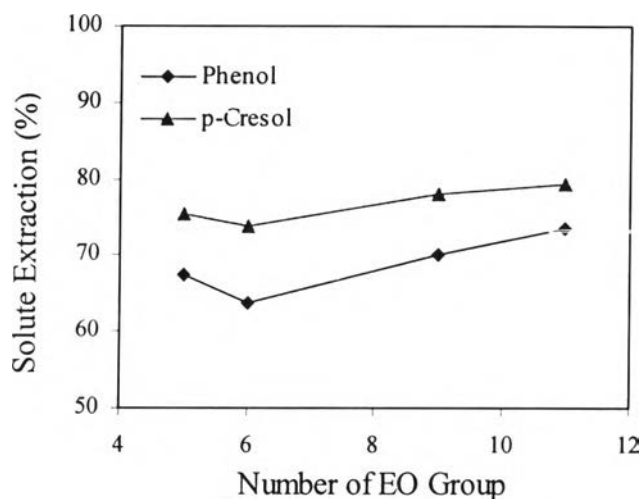


Figure 4.11 Percentage of organic solute extraction of the constant number of carbon 13 atoms alcohol ethoxylate at 0M NaCl and 80 °C.

Figure 4.10 shows that surfactant extraction percentages are almost 100% for both solutes. The number of ethylene oxide groups has only very slight effect at its higher number.

4.3 Effect of Alkyl Chain Length on Cloud Point Extraction

The effect of carbon atoms in alkyl chain (m) was observed at constant number of ethylene oxide head group (n) with various carbon chain lengths. This work used AE surfactants at constant ethylene oxide group of 9 ($n = 9$) which were Neodol 1-9, Surfonic L24-9, Neodol 25-9, and Surfonic TDA9. In these homologous series, the number of carbon atoms in the alkyl chain was equal to 11, 12-14, 12-15, and 13 ($m = 11, 12-14, 12-15,$ and 13) whose structures were $C_{12-14}EO_9$, $C_{12-15}EO_9$, and $C_{13}EO_8$ respectively.

At operating temperature of 80 °C, the results for 0M NaCl at constant EO group of 9 showed that as the number of carbon atoms in alkyl chain increased, coacervate fractional volumes decreased as shown in Figure 4.12.

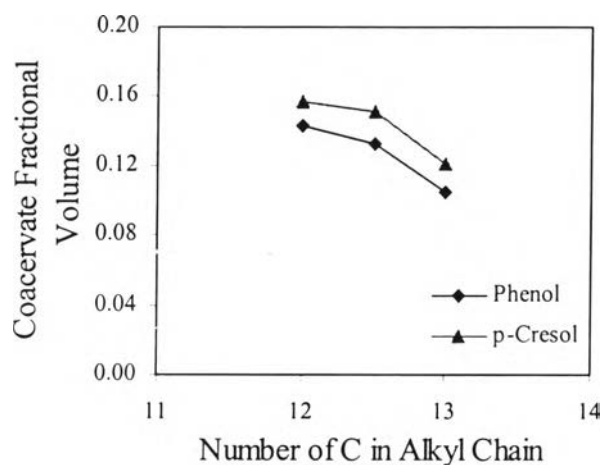


Figure 4.12 Coacervate fractional volumes of the constant 9 ethylene oxide alcohol ethoxylate at 0M NaCl and 80 °C.

This is because an increase in C atom resulted in decreasing the cloud point which, in turn, could enable water molecules easy to dehydrate from the polar head group of surfactant micelles in the coacervate phase. It should be noted that the result obtained from the C atom effect was opposite to that obtained from EO group effect.

After investigating the concentration of surfactant in the coacervate phase, surfactant partition ratios of phenol and *p*-cresol are shown in Figure 4.13.

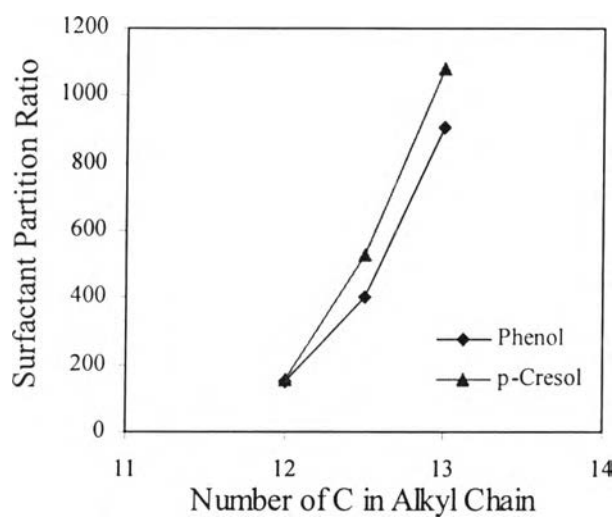


Figure 4.13 Surfactant partition ratios of the constant 9 moles ethylene oxide alcohol ethoxylate at 0M NaCl and 80 °C.

As the number of carbon atoms increased, surfactant partition ratios for both phenol and *p*-cresol also increased. This can be similarly explained as mentioned in Section 4.2. Similar to the surfactant partition ratio, organic solute partition ratio increased as shown in Figure 4.14.

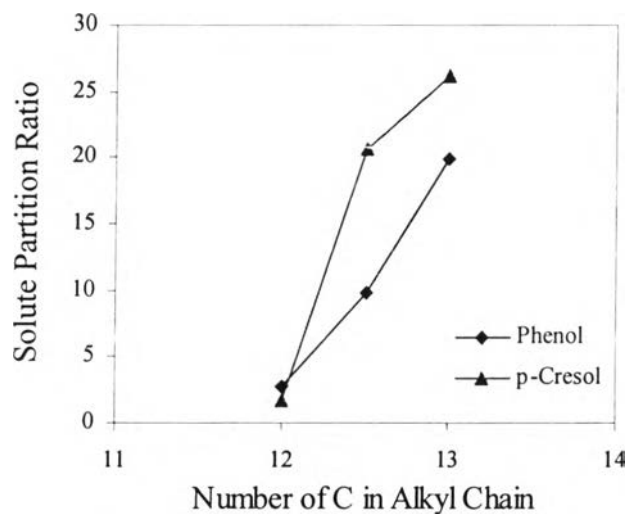


Figure 4.14 Organic solute partition ratios of the constant 9 moles ethylene oxide alcohol ethoxylate at 0M NaCl and 80 °C.

The percentages of surfactant extraction and organic solute extraction are shown in Figures 4.15 and 4.16.

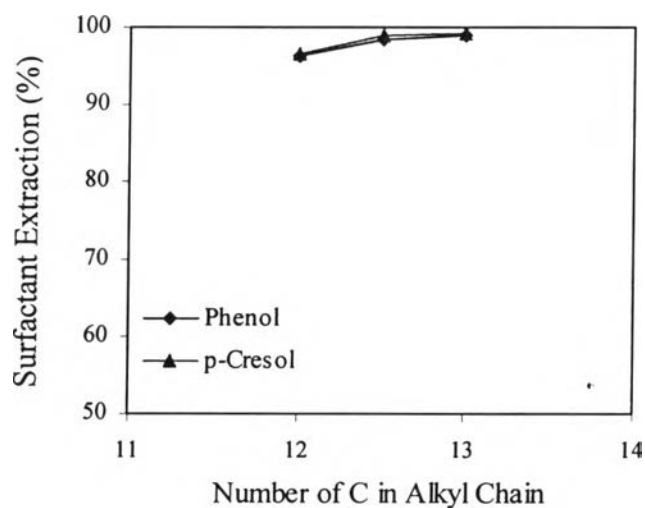


Figure 4.15 Percentage of surfactant extraction of the constant 9 moles ethylene oxide alcohol ethoxylate at 0M NaCl and 80 °C.

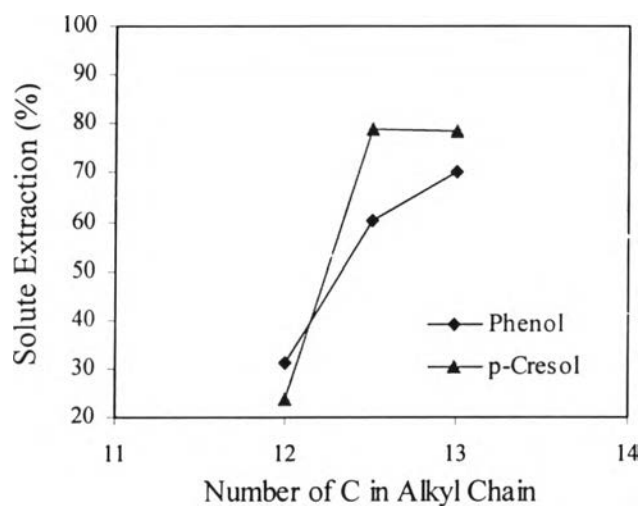


Figure 4.16 Percentage of organic solute extraction of the constant 9 moles ethylene oxide alcohol ethoxylate at 0M NaCl and 80 °C.

As can be seen, the percentages of both surfactant and organic solute extractions increased as the number of carbon atoms in alkyl chain increased indicating that the surfactant containing a high number of C atoms in alkyl chain could be more extracted. In addition, the organic solutes could also be more extracted by such a surfactant.

The result of percentage of organic solute extraction showed that as the number of carbon atoms in alkyl chain increased, percentage of organic solute extraction also increased because of the decreasing cloud point.

4.4 Effect of Electrolyte on Cloud Point Extraction

The salinity effect on CPE was studied by varying NaCl concentrations to 0, 0.4, and 0.8 M in the prepared solution. Figures 4.17 and 4.18 show the cloud point at different concentrations of NaCl for the constant number of carbon in alkyl chain at 13 atoms series and number of ethylene oxide at 9 moles series, respectively.

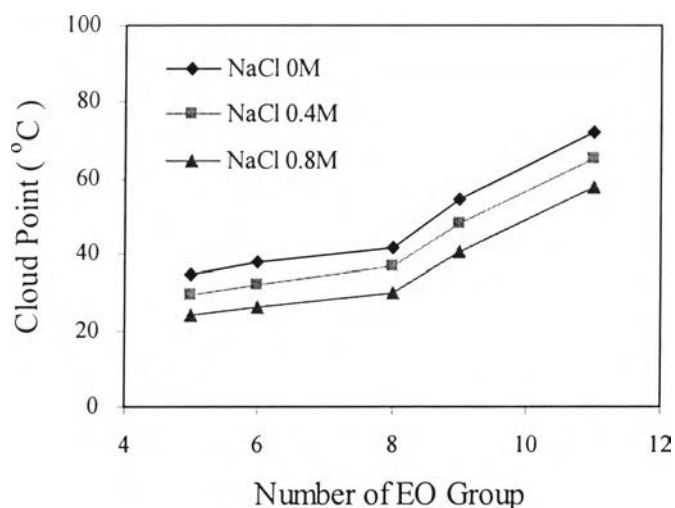


Figure 4.17 Effect of electrolyte on cloud point for the constant number of carbon in alkyl chain at 13 atoms series.

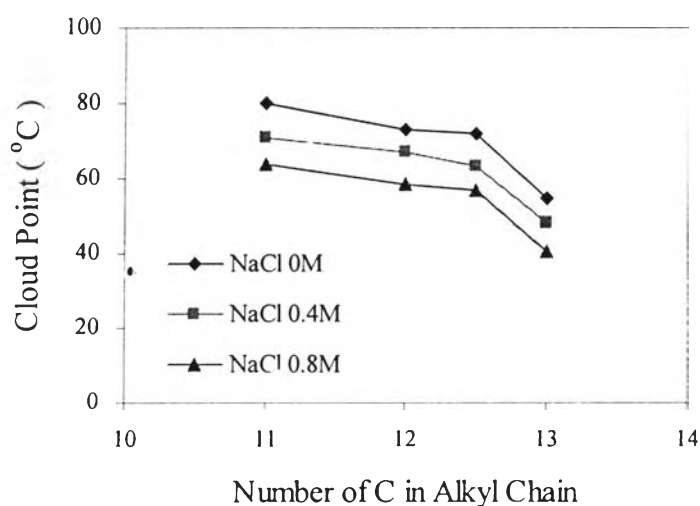


Figure 4.18 Effect of electrolyte on cloud point for the constant number of ethylene oxide at 9 moles series.

Apparently, addition of NaCl resulted in decreasing the cloud points both at a given number of C atoms and a given number of EO groups. Figures 4.19 and 4.20 show *p*-cresol partition ratios and percentage of *p*-cresol extraction for various concentrations of NaCl at 70°C.

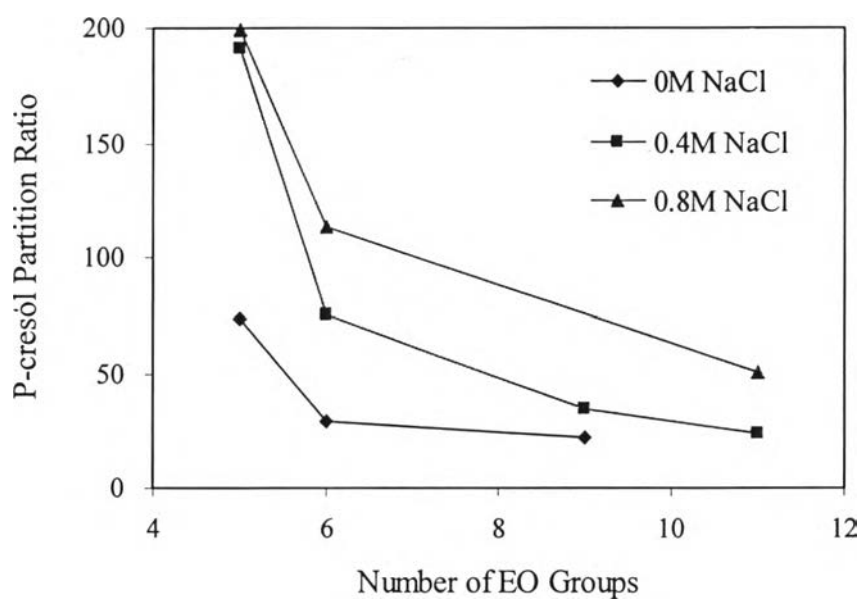


Figure 4.19 *p*-Cresol partition ratios for various concentrations of NaCl at 70°C.

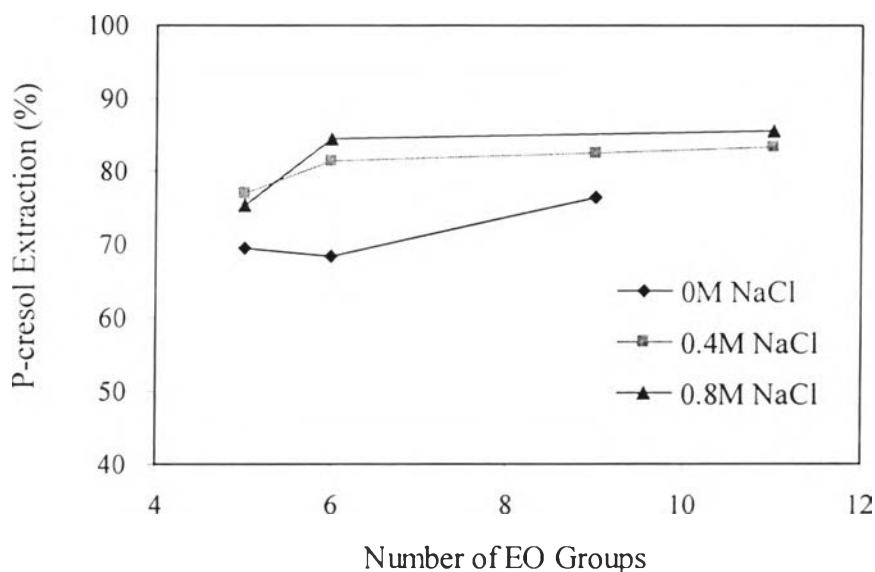


Figure 4.20 Percentage of *p*-cresol extraction for various concentrations of NaCl at 70°C.

The results show that as the concentration of NaCl increases, *p*-cresol partition ratio and percentage of *p*-cresol extraction also increases because of decreasing of cloud point. Figures 4.19 and 4.20 also show that the effect of molecular structure of surfactant was obtained in the same trend.

Addition of NaCl also had another effect which is a coacervate phase shifting effect for the high number of ethylene oxide groups. This effect causes only in long ethylene oxide groups which have high molecular weight. At the lower concentration of NaCl, coacervate phase stays at the bottom of the solution. At the higher concentration of NaCl, coacervate phase stays on the top of the solution. This is because the dilute phase of the higher NaCl concentration has higher density than another phase. Figure 4.21 shows phase separation patterns of both phenol and *p*-cresol at operating temperature of 60 °C.

Salinity Concentration	TDA5	TDA6	TDA8	TDA9	TDA11	L24-9	N25-9
0M NaCl					N.A.	N.A.	N.A.
0.4M NaCl						N.A.	N.A.
0.8M NaCl							

coacervate phase dilute phase , cloudy middle phases

N.A. Not Available

Figure 4.21 Phase separation patterns for different surfactants with various salinity concentrations at operating temperature of 60 °C.

The results in Figure 4.21 showed that at the NaCl concentration of 0.4M, the coacervate phase of Surfonic TDA11 or $C_{13}EO_{11}$ stays at the bottom of the solution. At the higher NaCl concentration of 0.8M, the coacervate phase of TDA11 shifts to the top of the solution. This phase shifting effect is possibly caused by a change in density of the solution in the dilute phase.

Surprisingly, the results of phase separation patterns showed that some surfactants caused thin cloudy middle phases. At 0 M NaCl and 60 °C, TDA8 or $C_{13}EO_8$ had one cloudy middle phase. At 0.4 and 0.8 M NaCl, TDA8 had a quite thick cloudy middle phase and its coacervate phase was also thick and turbid. Phase separation pattern of TDA9 or $C_{13}EO_9$ also yielded the cloudy middle phase at a higher NaCl concentration.

It should be noted that the purposes of this study were not focused on the formation of the cloudy middle phase. However, since the cloudy middle phase contained a relatively large amount of surfactant, the removal of the surfactant from the cloudy middle phase should be considerably concerned.

4.5 Effect of Operating Temperature on Cloud Point Extraction

The experiments were carried out at 60, 70, and 80°C to investigate the effect of operating temperature.

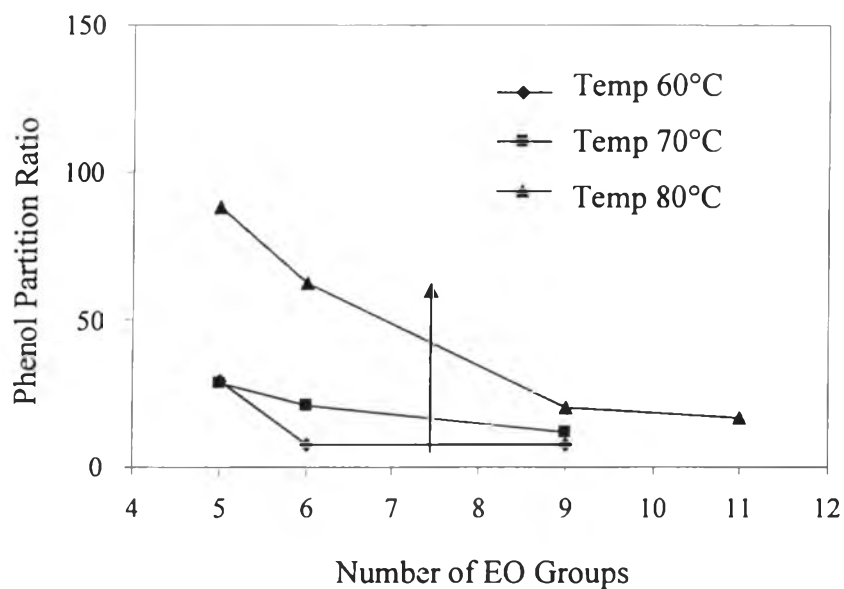


Figure 4.22 Phenol partition ratios at 0M NaCl for various operating temperatures.

Figures 4.22 and 4.23 show phenol partition ratios and coacervate fractional volumes at 0 M NaCl for various operating temperature conditions.

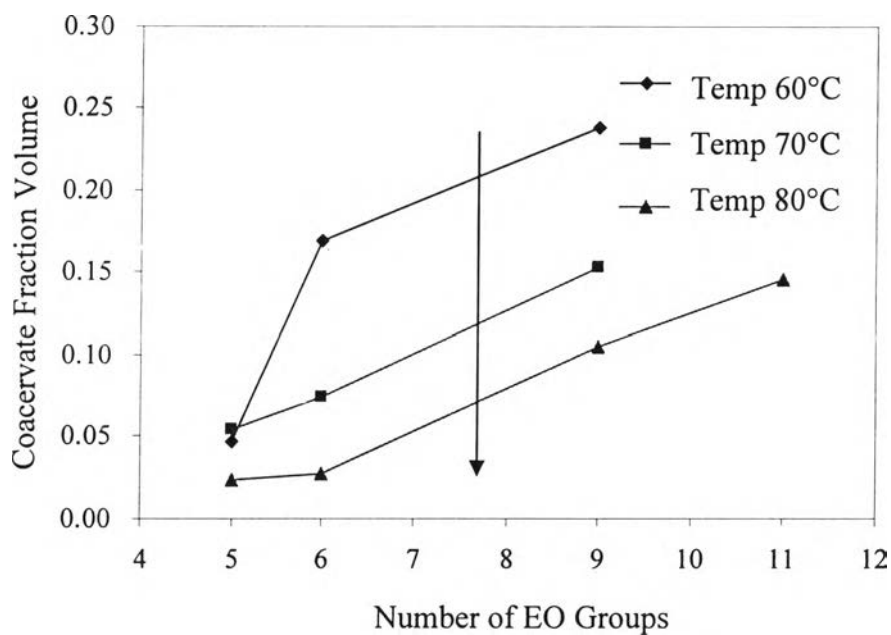


Figure 4.23 Coacervate fractional volumes of phenol at 0M NaCl at various operating temperatures.

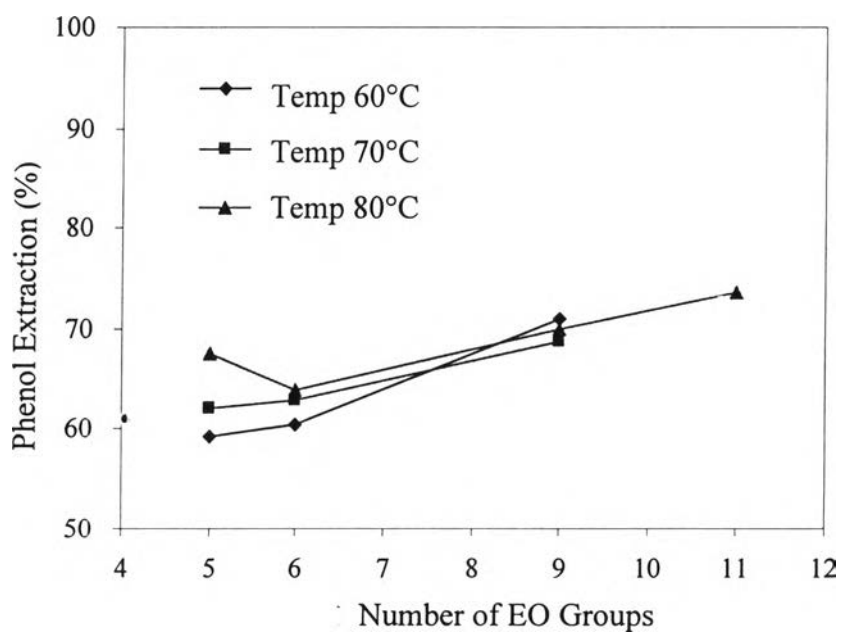


Figure 4.24 Percentage of phenol extraction at 0M NaCl at various operating temperatures.

Percentage of phenol extraction was somewhat unchanged as shown in Figure 4.24. It is clear from the figure that even though the temperature has strong effects on both phenol partition ratio and coacervate fractional volume, the percentage of phenol extraction remained almost unchanged with operating temperatures.

4.6 Effect of Molecular Structure of Organic Solute on Cloud Point Extraction

Phenol and *p*-cresol were selected to investigate the effect of molecular structure on CPE efficiency. Because *p*-cresol has more hydrophobicity than phenol, from the methyl group at the para-position, the higher *p*-cresol solubilization in surfactant was obtained. According to the effects of EO group and C atom in alkyl chain on both solute partition ratio and percentage of solute extraction (Figure 4.9, 4.11, 4.14, and 4.16), *p*-cresol always yielded higher properties than phenol. Although *p*-cresol has higher hydrophobicity than phenol, it is not higher enough to change the solubilized region to the core region of micelles in the coacervate.