

CHAPTER IV RESULTS AND DISCUSSION

In this work, the extraction performances are represented in the terms of the coacervate phase fractional volume, surfactant partition ratio and toluene partition ratio as shown in the experimental section. The extraction efficiency is showed to be higher when the coacervate phase fractional volume is decreased. Moreover, the increment of either surfactant partition ratio or toluene partition ratio also shows the greater extraction efficiency. Furthermore, the amount of extracted toluene is calculated in the term of the toluene removal percentage. The original extraction data for this thesis are presented in the Appendix.

4.1 The Cloud Point Temperature Determination

The cloud point temperatures of one weight percentage of nonionic surfactant solutions were determined by observing the temperature at which the turbidity of solution disappears. The cloud point temperatures of nonionic surfactants are reported in Table 4.1. Unexpectedly, some of the results show that the cloud point temperatures did not agree with the surfactant structure. From the previous literatures (Gu and Sjoblom, 1992; Huibers *et. al.*, 1997), the cloud point temperatures increase with increasing the ethylene oxide group but decrease with increasing the alkyl chain length. The disagreement between the cloud point temperature and surfactant structure is probably due to the distribution of ethylene oxide group of surfactants. Since these surfactants are commercial grades, the variation of ethylene oxide group may occur. In addition, the impurity containing in the surfactants may affect the cloud point temperature as well.

Surfactant	Cloud point temperature (°C)
APE surfactants:	
C ₉ PhE ₃	>0
C ₉ PhE ₅	57
C ₉ PhE ₇	27
C ₈ PhE ₇	22
C ₁₂ PhE ₇	59
AE surfactants:	
$C_{12}E_{3}$	25
C ₁₂ E ₆	78
C ₁₂ E ₇	55
C ₉ E ₆	50
C ₁₇ E ₆	74

 Table 4.1 The cloud point temperatures of nonionic surfactants.

4.2 Effect of Cloud Point Temperature on the Cloud Point Extraction

The effect of cloud point temperature on the extraction efficiency of APE and AE surfactants is shown in Figures 4.1- 4.6. The coacervate phase fractional volume is increased with increasing the cloud point temperatures as shown in Figure 4.1 and Figure 4.2 for APE and AE surfactants respectively. Consequently, the surfactant and toluene partition ratios are decreased with increasing the cloud point temperatures as represented in Figures 4.3 - 4.6. From these results, it can be concluded that surfactant with lower cloud point gives the higher extraction performance. This can be explained by that greater dehydration of surfactants for lower cloud point compared with the surfactants with higher cloud point at the same operating temperature.



Figure 4.1 Effect of cloud point temperature on the coacervate phase fractional volume at various operating temperatures for APE surfactants.



Figure 4.2 Effect of cloud point temperature on the coacervate phase fractional volume at various operating temperatures for AE surfactants



Figure 4.3 Effect of cloud point temperature on the surfactant partition ratio at various operating temperatures for APE surfactants.



Figure 4.4 Effect of cloud point temperature on the surfactant partition ratio at various operating temperatures for AE surfactants



Figure 4.5 Effect of cloud point temperature on the toluene partition ratio at various operating temperatures for APE surfactants.



Figure 4.6 Effect of cloud point temperature on the toluene partition ratio at various operating temperatures for AE surfactants.

4.3 Effect of Operating Temperature on the Cloud Point Extraction

The temperature study was carried out at 30, 40, 50 and 60 °C for APE surfactants and 60, 70 and 80 °C for AE surfactants. As shown in Figure 4.7 and Figure 4.8, the coacervate phase fractional volume decreases with increasing the operating temperature. Figures 4.9 - 4.12 indicate that both surfactant and toluene concentrations in the coacervate phase increase with increasing operating temperature. Consequently, both surfactant and toluene partition ratios are increased. Therefore, the cloud point extraction efficiency is increased as the operating temperature is elevated. This can be explained by that the dehydration of ethylene oxide head group of nonionic surfactant is easily occurred at lower temperature. On the other hand, there are more hydrogen bonds breaking between the hydrophilic head groups and water molecules at higher temperature. This dehydration of hydrophilic head groups causes the increasing in the intermicellar attraction and, hence making the coacervate phase more concentrated with lesser the volume. Although it can be concluded that raising temperature enhances the extraction performance, the system can not be heated to the upper critical temperature. At the upper critical temperature, the nonionic surfactant solution does not form the separated phases. Moreover, the heating energy must be considered to compromise the operating cost.



Figure 4.7 Effect of operating temperature on coacervate phase fractional volume for APE surfactants.



Figure 4.8 Effect of operating temperature on coacervate phase fractional volume for AE surfactants.



Figure 4.9 Effect of operating temperature on surfactant partition ratio for APE surfactants.



Figure 4.10 Effect of operating temperature on surfactant partition ratio for AE surfactants.



Figure 4.11 Effect of operating temperature on toluene partition ratio for APE surfactants.



Figure 4.12 Effect of operating temperature on toluene partition ratio for AE surfactants.

4.4 Effect of Alkyl Phenol Ethoxylate and Alcohol Ethoxylate Surfactants

The toluene removals of APE and AE surfactants are shown in Figure 4.13 and 4.14. It was found that more than 80% and 70% of toluene can be removed into the coacervate phase for APE and AE surfactants respectively. This can be concluded that both APE and AE surfactants can be used to successfully extract toluene from wastewater. However, using APE surfactants gives the higher amount of extracted toluene compared to AE surfactants. APE surfactants do not offer only the higher amount of toluene removal but also the lower the operating temperature. Nevertheless, the using of APE surfactants may cause an environmental problem because they are difficult to biodegrade (Mackey, 1987). In addition, AE surfactants have lower viscosities when compare with those of APE surfactants, thus AE surfactants may be easily apply in the continuous processes. It is also important to note that densities of AE surfactants are normally lower than the aqueous solution, therefore the coacervate phases are formed as the upper phase. The APE densities are usually higher than the aqueous solution; hence the coacervate phases are formed as the lower phase.



Figure 4.13 The weight percentage of toluene removal for APE surfactants.



Figure 4.14 The weight percentage of toluene removal for AE surfactants.

4.5 Effect of Alkyl Chain Length on the Cloud Point Extraction

The effect of numbers of carbon atom in alkyl chain (*m*) was done at constant number of ethylene oxide groups (*n*) with various carbon chain lengths. This work used APE surfactants of constant 7 moles of ethoxylates (n = 7) with numbers of carbon atoms equals to 8 and 9 (m = 8 and 9), which were C₈PhE₇ and C₉PhE₇. For AE surfactants, 6 moles of ethylene oxide (n = 6) with numbers of carbon atoms equals to 9 and 17 (m = 9 and 17) were used, which can be represented as C₉E₆ and C₁₇E₆. Unfortunately, the effect of alkyl chain length of AE surfactants could be observed only at 80 °C because the phase separation of C₁₇E₆ did not occur at lower operating temperatures.

Figure 4.15 and Figure 4.16 show that the coacervate phase fractional volume increases with increasing the alkyl carbon chain length increases. Thus, the surfactant and toluene partition ratios are decreased as illustrated in Figures 4.9 - 4.12. From these results, it seems that the surfactants with higher numbers of carbon atoms in the alkyl chain provide the lower extraction efficiencies. However, these experimental results are contrast to the previous literatures (Gu and Sjoblom, 1992;

Huibers *et. al.*, 1997). From these reports, surfactants with longer alkyl chain length have lower cloud point temperature than surfactants with shorter alkyl chain. Therefore, the surfactant with larger amount of carbon atoms or higher hydrophobic should give a lesser coacervate phase volume. Moreover, surfactant and toluene partition ratios should be increased as a consequence of decreasing of coacervate phase fractional volume. The explanation of these unexpected results is possibly due to the distributions of number of ethylene oxide numbers in the hydrophobic group. As a result, their cloud point temperatures were not correspond to the surfactant structures. Subsequently, the ethoxylate deviation may cause an impact not only on the cloud point temperature but extraction performance as well.



Figure 4.15 Effect of numbers of carbon atoms in alkyl chain on the coacervate phase fractional volume for C_8PhE_7 and C_9PhE_7 surfactants.



Figure 4.16 Effect of numbers of carbon atoms in alkyl chain on the coacervate phase fractional volume for C_9E_6 and $C_{17}E_6$ surfactants at operating temperature of 80 °C.



Figure 4.17 Effect of numbers of carbon atoms in alkyl chain on the surfactant partition ratio for C_8PhE_7 and C_9PhE_7 surfactants.



Figure 4.18 Effect of numbers of carbon atoms in alkyl chain on the surfactant partition ratio for C_9E_6 and $C_{17}E_6$ surfactants at operating temperature of 80 °C.



Figure 4.19 Effect of numbers of carbon atoms in alkyl chain on the toluene partition ratio for C_8PhE_7 and C_9PhE_7 surfactants.



Figure 4.20 Effect of numbers of carbon atoms in alkyl chain on the toluene partition ratio for C_9E_6 and $C_{17}E_6$ surfactants at operating temperature of 80 °C.

4.6 Effect of the Number of Ethylene Oxide Group on the Cloud Point Extraction

The effect of number of ethylene oxide group (n) was observed at constant alkyl chain length (m) with various numbers of ethoxylates. For APE surfactants, constant number of carbon atoms equals to 9 (m = 9) with various numbers of ethoxylates equals to 3 and 7 (C₉PhE₃ and C₉PhE₇) were used. The AE surfactants with constant number of carbon atoms equals to 12 (m = 12) with various numbers of ethoxylates equals to 3 and 7 (C₁₂E₃ and C₁₂E₇) were used.

From Figures 4.21 - 4.26, it can be concluded that surfactants with less numbers of ethylene oxide groups show higher extraction efficiency than those surfactants with more numbers of ethylene oxide groups. On the other hand, the efficiency of cloud point extraction can be enhanced by decreasing numbers of ethylene oxide groups. The explanation of these results is that there are more difficult to dehydrate ethylene oxide groups for the higher degree of hydrophilic head groups at the same temperature. On the other hand, surfactants with lower numbers of ethylene oxide group require only a small amount of energy to dehydrate. Thus, the coacervate phase fractional volume is increased whereas surfactant and toluene partition ratios are decreased.



Figure 4.21 Effect of numbers of ethylene oxide group on the coacervate phase fractional volume for C_9PhE_3 and C_9PhE_7 surfactants.



Figure 4.22 Effect of numbers of ethylene oxide group on the coacervate phase fractional volume for $C_{12}E_3$ and $C_{12}E_7$ surfactants.



Figure 4.23 Effect of numbers of ethylene oxide group on the surfactant partition ratio for C_9PhE_3 and C_9PhE_7 surfactants.



Figure 4.24 Effect of numbers of ethylene oxide group on the surfactant partition ratio for $C_{12}E_3$ and $C_{12}E_7$ surfactants.



Figure 4.25 Effect of numbers of ethylene oxide group on the toluene partition ratio for C_9PhE_3 and C_9PhE_7 surfactants.



Figure 4.26 Effect of numbers of ethylene oxide group on the toluene partition ratio for $C_{12}E_3$ and $C_{12}E_7$ surfactants.