

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Nonionic Surfactants

The homologous series of alcohol ethoxylate (AE) were selected to be a nonionic surfactant to study the effect of molecular structure of surfactant on the cloud point extraction efficiency by the variation of number of ethylene oxide (EO) and number of carbon in the alkyl chain. The molecular structure of AE was $(\text{CH}_3)_m\text{-O-(OCH}_2\text{CH}_2)_n\text{OH}$, where m represents the number of carbon atoms in alkyl chain and n represents the number of ethylene oxide in head group. Properties of a series of AE studied are shown in Table 3.1.

3.1.2 Organic Solutes

There were two types of organic solute used in this work, which were phenol ($\text{C}_6\text{H}_5\text{OH}$) 99.5% purity from Penreac Sintesis Company and *p*-cresol ($\text{CH}_3\text{C}_6\text{H}_4\text{OH}$) 99% purity from Aldrich Company, to study the effect of hydrophobicity of solute. Table 3.2 shows the properties of phenol and *p*-cresol.

3.1.3 Electrolyte

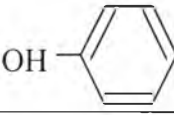
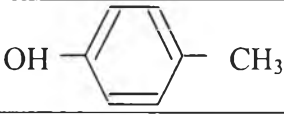
Sodium chloride (NaCl) 99% purity from Lab-Scan Company was utilized as an electrolyte in this work.

Table 3.1 Properties of the nonionic surfactants studied

Trade Name	Company	Structure	EO (<i>n</i>)	C (<i>m</i>)	HLB
Surfonic L24-5	Huntsman	C ₁₂ EO ₅	5	12-14*	10.6
Surfonic L24-7	Huntsman	C ₁₂ EO ₇	7	12-14*	11.9
Surfonic L24-7.1	Huntsman	C ₁₂ EO _{7.1}	7.1	12-14*	12.3
Surfonic L24-9	Huntsman	C ₁₂ EO ₉	9	12-14*	13.0
Surfonic L24-12	Huntsman	C ₁₂ EO ₁₂	12	12-14*	14.4
Surfonic TDA5	Huntsman	C ₁₃ EO ₅	5	13	10.5
Surfonic TDA6	Huntsman	C ₁₃ EO ₆	6	13	11.4
Surfonic TDA8	Huntsman	C ₁₃ EO ₈	8	13	12.8
Surfonic TDA9	Huntsman	C ₁₃ EO ₉	9	13	13.3
Surfonic TDA11	Huntsman	C ₁₃ EO ₁₁	11	13	14.2
Surfonic L12-8	Huntsman	C ₁₁ EO ₈	8	10-12*	13.6
Surfonic DDA8	Huntsman	C ₁₂ EO ₈	8	12	13.0
Neodol 91-5E	Shell	C ₉₋₁₁ EO ₅	5	9-11*	11.6
Neodol 91-6E	Shell	C ₉₋₁₁ EO ₆	6	9-11*	12.5
Neodol 91-8	Shell	C ₉₋₁₁ EO ₈	8	9-11*	13.7
Neodol 1-9	Shell	C ₁₁ EO ₉	9	11	13.9
Neodol 25-9	Shell	C ₁₂₋₁₅ EO ₉	9	12-15*	13.2

* Commercial surfactants do not possess exact numbers of carbon atoms in alkyl chain.

Table 3.2 Physical and chemical properties of phenol and *p*-cresol (chemical land21.com)

Properties	Phenol	<i>p</i> -Cresol
Molecular Structure		
Physical State	Clear to light pink crystals.	Clear to slightly amber semi solid, phenolic odor
Melting Point (°C)	41-43	33-34
Boiling Point (°C)	181	195-205
Specific Gravity	1.07	1.02-1.03
Solubility in Water	8 g/100 ml	23 g/l
Vapor Density	3.2	3.72
Auto-ignition (°C)	N.A.	550
Flash Point (°C)	7.9	86-87
Stability	Stable under ordinary conditions.	Stable under ordinary conditions.

3.2 Experimental

3.2.1 Cloud Point Determination

Cloud point of the homologous series of nonionic surfactant solution with an organic solute at the initial condition was determined at each concentration of electrolyte. Transfer the prepared solution in the test tube with a thermometer and then place it in the isothermal water bath. The solution was gradually heated until the turbidity behavior was observed, then the test tube of turbid solution was taken up to allow the temperature to gradually drop until the clear solution was gained. At the temperature that the turbidity behavior occurred, coacervate particles start to form and as the temperature decreased the solution was clear again, coacervate particles were merged together to form a single phase. The cloud point temperature

was taken as the temperature at which the last coacervate particle disappeared and the solution became clear again, which was the same temperature as the temperature that the turbidity behavior was obtained.

3.2.2 Cloud Point Extraction Procedure

The waste solution was homogeneously prepared by mixing nonionic surfactant, organic solute, and distilled water with or without electrolyte. The initial conditions were 100 ppm for organic solute and 70 mM for nonionic surfactant.

3.2.2.1 *Effect of Number of Ethylene Oxide Group*

To examine the effect of number of ethylene oxide group, the variation of ethylene oxide numbers (n) with constant alkyl chain length were utilized. At constant number of carbon atoms 13, the number of ethylene oxide at 5, 6, 8, 9, and 11 ($C_{13}EO_n$; $n = 5, 6, 8, 9, \text{ and } 11$) were varied.

In CPE, there were still many factors affecting cloud point which were addition of electrolyte, operating temperature, and the hydrophobicity of organic solute. To study the effect of electrolyte, variations of NaCl concentration to 0, 0.4 and 0.8 M were selected. Operating temperatures had very strong effects on the cloud point extraction. To study this effect, variations of operating temperature to 60, 70, and, 80 °C were selected. For the effect of hydrophobicity of solute, two types of organic solutes were selected which are phenol and *p*-cresol. In this experiment, effects of these factors on the molecular structure were also notified.

3.2.2.2 *Effect of Alkyl Chain Length*

To investigate the effect of alkyl chain length (m), the various alkyl chain lengths at constant ethylene oxide numbers were utilized. At the constant number of ethylene oxide head group of 9, at number of carbon in alkyl chain was varied to 9-11, 12, 12-14, 13 (C_mEO_9 ; $m = 9-11, 12, 12-14, \text{ and } 13$).

Effects of addition of electrolyte, operating temperature, and hydrophobicity of solute on the effect of number of ethylene oxide group on the cloud point extraction were also studied in the same conditions as they have already been mentioned.

After mixed solutions were prepared, they were filled in special designed glass bottles (about 95 ml) and sealed with rubber septa coated with PTFE to prevent the leakage. The solutions were placed in a circulating water bath system at studied temperatures until phase separation reached equilibrium. The equilibrium time in this work was identified when there were no changes in either phase height or concentration of surfactant in the dilute phase. At temperatures above the cloud point, the solutions gradually separated into coacervate and dilute phases. After the phase separation reached equilibrium, the concentrations of surfactant and organic solute in both two phases were analyzed to calculate the extraction efficiency.

The concentrations of surfactant in both coacervate and dilute phases were measured by using a Total Organic Carbon Analyzer (Mode: TOC_VcSH, Shimadzu). The concentrations of organic solutes, phenol and p-cresol, in both coacervate and dilute phases were measured by using a UV Visible Spectrophotometer at the wavelengths of 270 nm for phenol and 277 nm for p-cresol. A High Performance Liquid Chromatography (HPLC) with a UV detector was also utilized for the dispersed nonionic surfactants by using of acetonitrile and water (40:60) as mobile phases.

In order to determine the surfactant and organic solute concentrations in both two phases, the external standard quantitative calibrations must be obtained. The calculations of surfactant and organic solute material balances were performed to ensure that there were no surfactant and organic solute losses more than 10%.

3.2.3 Equilibrium Parameter Calculations

After the phase separation reached the equilibrium, the determination of extraction performance could be achieved. The extraction efficiencies were proposed as five important definitions which are coacervate fractional volume, surfactant partition ratio, organic solute partition ratio, surfactant extraction percentage, and organic solute extraction percentage could be defined as follows:

1. Coacervate Fractional Volume

Volumes of both coacervate and dilute phases were obtained by measuring the phase height of the solution. The phase volume into a coacervate phase fractional volume was determined as:

$$\text{Coacervate Fractional Volume} = \frac{\text{Coacervate Volume}}{\text{Total Volume}} = \frac{\text{Coacervate Height}}{\text{Total Height}}$$

2. Surfactant Partition Ratio

The concentrations of surfactant in two phases were computed to perform the separation ability in terms of surfactant partition ratio, which can be obtained by the following equation:

$$\text{Surfactant Partition Ratio} = \frac{[\text{Surfactant}]_{\text{coa}}}{[\text{Surfactant}]_{\text{dil}}}$$

where $[\text{Surfactant}]_{\text{coa}}$ is the concentration of surfactant in coacervate phase and $[\text{Surfactant}]_{\text{dil}}$ is the concentration of surfactant in dilute phase.

3. Organic Solute Partition Ratio

The organic solute partition ratio was performed as the separation efficiency, which is defined as:

$$\text{Organic Solute Partition Ratio} = \frac{[\text{Organic Solute}]_{\text{coa}}}{[\text{Organic Solute}]_{\text{dil}}}$$

where $[\text{Organic Solute}]_{\text{coa}}$ is the concentration of organic solute in coacervate phase and $[\text{Organic Solute}]_{\text{dil}}$ is the concentration of organic solute in dilute phase

4. Surfactant Extraction Percentage

The concentrations of surfactant in two phases were determined to calculate the amount of surfactant extracted, which is defined as:

$$\text{Percentage of Surfactant Extraction} = \frac{\text{Weight of Surfactant in Coacervate Phase}}{\text{Total Weight of Surfactant}} \times 100$$

5. Organic Solute Extraction Percentage

The concentrations of organic solute in two phases were determined to calculate the amount of organic solute removal, which is defined as:

$$\begin{aligned} \text{Percentage of Organic Solute Extraction} \\ = \frac{\text{Weight of Organic Solute in Coacervate Phase}}{\text{Total Weight of Organic Solute}} \times 100 \end{aligned}$$