

CHAPTER III EXPERIMENTAL



3.1 Materials

3.1.1 Nonionic Surfactants

Two types of nonionic surfactants used in this work were alkyl phenol ethoxylates (APE) and alcohol ethoxylates (AE). The molecular structures of these two surfactants are $(\text{CH}_3)_m-(\text{C}_6\text{H}_4)-(\text{OCH}_2\text{CH}_2)_n \text{OH}$ and $(\text{CH}_3)_m-\text{O}-(\text{OCH}_2\text{CH}_2)_n \text{OH}$ for APE and AE surfactants respectively, where m is numbers of carbon atoms in the alkyl chain and n is numbers of ethylene oxide head groups.

The various numbers of ethylene oxide head groups, n , were used to study the effect of nonionic surfactant head group. For APE surfactants, this work used the homologous series of nonylphenol poly(ethoxyleneoxy) ethanol, $\text{C}_9\text{H}_{19}-\text{(C}_6\text{H}_4)-(\text{OCH}_2\text{CH}_2)_n\text{OH}$. The numbers of ethylene oxide, n , per mole of nonylphenol selected for this study were 3, 5 and 7 moles (C_9PhE_n ; $n = 3, 5$ and 7) with their trade names of Igepal CO-430, Teric N5 and Igepal CO-610 for n equal to 3, 5 and 7, respectively. These surfactants were received from Rhone-Poulenc Co., Ltd. (New Jersey, USA), excepted C_9PhE_5 , which was received from Huntsman Corporation Australia Pty Ltd. (Ascot Vale, Australia).

The C_{12-15} detergent alcohol condensed with various numbers of ethylene oxide, $\text{C}_{12}\text{H}_{25}-\text{O}-(\text{OCH}_2\text{CH}_2)_n \text{OH}$, were used to study the effect of nonionic surfactant hydrophilic parts as well. The numbers of ethylene oxide, n , selected for this part were 3, 6 and 7 moles (C_{12}E_n ; $n = 3, 6$ and 7) with trade names of Teric 12A3, Teric 12A6 and Rhodasurf LA-7 for n equal to 3, 6 and 7, respectively. The former two surfactants, C_{12}E_3 and C_{12}E_6 , were received from Huntsman Corporation Australia Pty Ltd. (Ascot Vale, Australia) while C_{12}E_7 was from Rhone-Poulenc Co.,Ltd. (New Jersey, USA).

To study the effect of alkyl chain length of nonionic surfactant tail groups, the various numbers of carbon atoms at the alkyl chain, m , of both APE and AE surfactants were used. For APE surfactants, the various numbers of carbon atoms at the alkyl chain, m , of alkylphenol poly(ethoxyleneoxy) ethanol with an

average 7 moles of ethylene oxide per mole of alkylphenol, $(\text{CH}_3)_m\text{-(C}_6\text{H}_4\text{)-(OCH}_2\text{CH}_2)_7\text{OH}$, were used. The numbers of carbon atom in the alkyl tail group, m , were 8, 9 and 12 (C_mPhE_7 ; $m = 8, 9$ and 12) with their trade names of Igepal CA-620, Igepal CO-610 and Sulfonic DDP-7 for m equal to 8, 9 and 12, respectively. Both Igepal CA-620 and Igepal CO-610 were received from Rhone-Poulenc Co., Ltd. (New Jersey, USA) while Sulfonic DDP-7 was received from Huntsman Corporation Australia Pty Ltd. (Ascot Vale, Australia).

For the study of effect of alkyl chain length of AE surfactants, the various numbers of carbon atoms at the alkyl chain, m , alcohol detergents condensed with 6 moles of ethylene oxides, $(\text{CH}_3)_m\text{-O-(OCH}_2\text{CH}_2)_7\text{OH}$ were used. The numbers of carbon atoms at the alkyl chain, m , were 9, 12 and 17 (C_mE_6 ; $m = 9, 12$ and 17) with their commercial names of Teric 9A6, Teric 12A 6 and Teric 17A6 for m equal to 9, 12 and 17, respectively. All of these surfactants were received from Huntsman Corporation Australia Pty Ltd. (Ascot Vale, Australia). All surfactants were used as received without further purification.

3.1.2 Toluene

Analytical reagent grade toluene with 99.5 % purity was used as received which was obtained from Lab-Scan Analytical Sciences (Bangkok, Thailand).

3.1.3 Water

The deionized water was used in this study.

3.2 Experimental Methods

3.2.1 The Cloud Point Temperature Determination

The cloud point temperature was determined at one weight percentage of nonionic surfactant. One gram of nonionic surfactant was prepared in the 250 mL volumetric flask; then mixed with 100 ml distilled water. After the solution was well mixed, the solution was pipetted into a 15 mL test tube. The solution in the test tube with a thermometer was then placed in a 250 mL beaker containing purified water.

By using a hot plate, the water was gradually heated and hence causing the solution temperature increased. When temperature was high enough, the solution gradually formed coacervate particles. The hot plate was then removed while the solution was placed in an icebox instead. After the solution temperature had been decreased, the coacervate particles merged together to form a single phase again. The cloud point temperature was taken as the temperature at which the last coacervate particle disappeared.

3.2.2 The Cloud Point Extraction Procedures

The aqueous solution of toluene and nonionic surfactant were respectively prepared at the initial concentrations of 100 ppm and 70 mM for all systems. Nonionic surfactants used in this work were the homologous series of both APE and AE surfactants with variations of alkyl chain length and number of ethylene oxide. In order to investigate the effect of alkyl chain length, the various alkyl chain length (m) at constant of ethylene oxide numbers were utilized. For APE surfactants, the numbers of carbon atoms in the alkyl chain of 8, 9 and 12 with the average number of ethylene oxide equal to 7 were used ($C_m\text{PhE}_7$; $m = 8, 9$ and 12). The AE surfactants at constant of 6 moles of ethylene oxide group with various numbers of carbon atoms of 9, 12 and 17 ($C_m\text{E}_6$; $m = 9, 12$ and 17). Moreover, in order to examine the effect of number of ethylene oxide group, the variation of ethylene oxide numbers (n) with constant alkyl chain length were used. At constant number of carbon atoms equal to 9, the various ethylene oxide numbers of 3, 5 and 7 ($C_9\text{PhE}_n$; $n = 3, 5$ and 7) were used for APE surfactants study. For AE surfactants, the numbers of ethylene oxide of 3, 6 and 7 with the constant numbers of carbon atoms of 12 ($C_{12}\text{E}_n$; $n = 3, 6$ and 7). were employed.

After mixed solution was prepared, they were kept in 22 mL vials and sealed with rubber septa coated with PTFE to prevent the toluene leakage. Then, the solutions was placed in the water bath at studied temperatures, which were 30, 40, 50 and 60 °C for APE surfactants and 60, 70 and 80 °C for AE surfactants. At temperature above the cloud point, the solution gradually separated into dilute phase and coacervate phase. This phase separation took approximately 2 days to reach equilibrium. The equilibrium time in this work was identified when there were no

change in either phase height or concentration of surfactant in the dilute phase. After the phase separation reached equilibrium, the concentrations of surfactant and toluene 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 Total Organic Carbon Analyzer (Model: TOC_5000A, Shimadzu). In the mean time, toluene concentrations in both two phases were measured by using Gas Chromatograph with flame ionization detector (AutoSystem GC ARNEL, Perkin Elmer). For the Supelcowax 10 column with the ultra-pure nitrogen flow rate of 20 mL/min and oven temperature of 250 °C, toluene concentration can be detected at time equals to 1.18 min. Since toluene has a high volatility, the static headspace sampling (Headspace Sampler, HS 40, Perkin Elmer) must be used as a sample injection technique. The setting temperature conditions of headspace sampler were 100 °C for sample temperature, 110 °C for needle temperature and 110 °C of transfer temperature. In addition, the sampler must be fixed at the pressurization time of 0.5 min, injection time of 0.1 min, withdrawal time of 0.2 min, thermostat time of 15 min and GC cycle time of 2.3 min. The N₂ gas was also used in the sampler with the pressure of 160 kPa.

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

3.2.3 Equilibrium Parameters Calculation

After the phase separation reached the equilibrium, the determination of extraction performance must be calculated. The extraction efficiencies are proposed as following.

3.2.3.1 *Toluene removal percentage*

The concentrations of toluene in two phases were determined to calculate the amount of toluene removal, which is defined as follow.

$$\% \text{ Toluene removal} = \frac{\text{Weight of toluene in coacervate phase}}{\text{Total weight of toluene}} \times 100 \quad (3.1)$$

3.2.3.2 *Coacervate phase fractional volume*

The phase volumes in each phase were obtained by measuring the phase height. Then, calculation of the phase volume into a coacervate phase fractional volume was performed as following.

$$\text{Fractional coacervate phase volume} = \frac{\text{coacervate phase volume}}{\text{total volume}} \quad (3.2)$$

3.2.3.3 *Surfactant partition ratio*

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

$$\text{Surfactant partition ratio} = \frac{[\text{surfac tan t}]_{\text{co}}}{[\text{surfac tan t}]_{\text{di}}} \quad (3.3)$$

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

3.2.3.4 *Toluene partition ratio*

The toluene partition ratio was performed as the separation efficiency, which is defined as follow

$$\text{Toluene partition ratio} = \frac{[\text{toluene}]_{\text{co}}}{[\text{toluene}]_{\text{di}}} \quad (3.4)$$

where $[\text{toluene}]_{\text{co}}$ is the concentration of toluene in coacervate phase and $[\text{toluene}]_{\text{di}}$ is the concentration of toluene in dilute phase.