CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Nonionic Surfactants

3.1.1.1 Alcohol Ethoxylate

The homologous series of the polydisperse commercial alcohol ethoxylate (AE, [R-(OCH_2CH_2)$_n$OH]) nonionic surfactants with variation of alkyl chain length (R) and number of ethylene oxide group (n), (trade name Neodol and Surfonic) were contributed by Shell (USA) and Huntsman (USA), respectively. The homogeneous polyoxyethylene nonionic surfactants with variation of alkyl chain length (R) and number of ethylene oxide group (n) (99% purity of single alkyl chain) were purchased from Nikko Chemicals (Tokyo, Japan).

3.1.1.2 Alkylphenol Ethoxylate

A polydisperse commercial branched t-octylphenolpolyethoxylate, $OP(OE)_7$, with an average of 7 moles of ethylene oxide per mole of octylphenol (trade name Triton X-114) was contributed by Dow Chemical Inc. (South Charleston, USA).

3.1.2 Organic Solutes

Reagent grade 99.8% pure toluene, benzene, ethylbenzene, trichloroethylene (TCE), tetrachloroethylene (PCE), phenol, and o-cresol were purchased from Carlo Erba Inc. (Italy). The 1,2-dichloroethane (DCE) was purchased from Labscan Inc. (Ireland) and catechol was purchased from Aldrich chemical company, Inc (USA).

3.1.3 Electrolyte

NaCl (99.9% purity) as electrolyte was purchased from AJAX chemical company (Auburn, Australia).

3.2 Methodology

3.2.1 The Cloud Point Determination

To measure the cloud point of the surfactants, the solution containing surfactant, solute, and electrolyte was transferred to a test tube with a thermometer and then the test tube was placed in an isothermal water bath. The solution was gradually heated until turbidity was observed, then the temperature was gradually dropped until the solution became clear. Turbidity indicates formation of a second liquid phase whose droplets scatter light, so if heating/cooling rates are low enough, the cloud point indicates a thermodynamic phase boundary. In our experiments, the cloud point obtained upon heating was the same as that measured upon cooling, the lack of hysteresis indicating that the equilibrium value is being obtained.

3.2.2 The Cloud Point Extraction Procedures

3.2.2.1 Batch Experiment

Homogeneous aqueous solutions containing nonionic surfactant and solute at specific initial concentrations were prepared and then transferred into several identical vials. To prevent headspace loss, especially for the volatile solute samples, the solution must occupy almost all of the vial volume to avoid overhead vapor volume. Rubber septa coated with polytetrafluoroethylene (PTFE) were used to seal these vials to make sure that no leakage occurred. The vials were placed in an isothermal water bath and phase separation occurred very rapidly because of the density difference between two phases. When equilibrium was reached in about 2 days, which is defined as the time where no further change in coacervate volume is observed, the relative phase volumes of each phase were measured by the solution height. Both coacervate phase and dilute phase were carefully collected and the concentrations of nonionic surfactant and solute in each phase were analyzed. The external standard quantitative calibrations were obtained for the analysis of surfactant and phenol in both phases.

In the study of effect of nonionic surfactant molecular structure on CPE, the concentrations of the AE surfactant and phenol were measured by using a Total Organic Carbon analyzer (TOC-5000A, Shimadzu) and a CE 2000 series UV-spectrophotometer (Cecil Instrument Limited, Cambridge, UK) at 270 nm, respectively.

In the study of effect of structure and concentration of solutes on CPE, the concentrations of $OP(EO)_7$ and the volatile solutes were measured by

using a CE 2000 series UV-spectrophotometer (Cecil Instrument Limited, Cambridge, England) at 224 nm and a gas chromatograph with a flame ionization detector (Agilent Technology, USA), respectively. Due to the high volatility of some solutes, a static headspace autosampler was used for sample injection. The conditions of the gas chromatograph for VOCs determination were as follows: capillary column: HP-5; carrier gas: helium with a flow rate of 15 mL/min; make up gas: ultra pure nitrogen with a flow rate of 30 mL/min; oven temperature: 120 °C isothermal for benzene, toluene, and ethylbenzene and 80 °C isothermal for the chlorinated solutes; injector temperature: 200 °C; and detector temperature: 300 °C. The external standard quantitative calibrations were obtained for the analysis of surfactant and organic solutes in both phases. Closure of the material balance was taken as evidence that leakage of the volatile solute was negligible. The concentration of phenols (catechol, phenol, and o-cresol) was analyzed by the 4-aminoantipyrine colorimetric method with a UV-spectrophotometer at 510 nm. Phenols combine in alkaline solution with 4-aminoantipyrine to produce a stable reddish-brown colored antipyrine dye. The amount of color (absorbance) produced is a function of the concentration of the phenolic material.

3.2.2.2 Continuous Experiment

Apparatus: rotating disc contactor (RDC)

Figure 3.1 shows a schematic of the cloud point extraction pilot unit. A cylindrical column made of Pyrex glass with 29.2 mm ID had an acrylic water jacket with 49.2 mm ID, through which temperature controlled water was circulated. The extractor column had a mixing zone in the middle and settling or empty zones at either end of the column. In order to increase the residence time and decrease the terminal velocity of the raffinate (micellar dilute phase or treated water) and the extract phase (coacervate or micellar rich phase) before leaving at the top and bottom of the column, respectively, the diameter of the settling zone (100 mm ID) needs to be substantially larger than that of the mixing zone (29.2 mm ID). The heights of the settling zone and mixing zone were 150 mm and 700 mm, respectively. In the mixing zone, there were 32 horizontal rotor discs of 17.52 mm in diameter and 1 mm in thickness mounted on a speed adjustable, vertical shaft at the center of the column. In addition, there were 33 annular stator rings with an outer and

inner diameter of 29.2 mm and 20.44 mm, respectively, and 1 mm in thickness. The opening of the stator rings was larger than the rotor disc diameter. The compartment spacing between stators was 22 mm. The rotor discs, stators and shaft were made of 316-stainless steel.

Procedure:

The contaminated feed water containing individual solute as the trace pollutant and the surfactant solution were fed into the extractor countercurrently at defined flow rates regulated by rotameters. Based on the density difference, the heavy surfactant solution was fed into the top, while the light wastewater was fed into the bottom of the extractor. In the column, the coacervate phase was beaten into tiny drops as rotating discs induced shear and these drops settled down to the bottom of the column; while the dilute phase or the treated water was ejected at the top of the column. The feed wastewater and the dilute phase samples were collected every 45 minutes for analysis of the solute concentration. Due to the high volatility of the solute, the solute concentration of the inlet wastewater was closely monitored to ensure that it was unchanged for the entire operating time and that there was no significant loss of the solute by volatilization before feeding into the column. When the system reached steady state, as indicated by the absence of change in solute concentration in the dilute phase with time, samples were collected from the effluent dilute phase and the coacervate phase (see Figure 3.1) to determine the concentrations of nonionic surfactant and solute in order to evaluate the extraction performance of the column. In addition, the flow rate of the dilute phase stream and the coacervate phase stream were determined by measuring the volume of the dilute phase and coacervate phase collected over a measured time interval.

The concentrations of $OP(EO)_7$ and the volatile solutes were measured by using a CE 2000 series UV-spectrophotometer (Cecil Instrument Limited, Cambridge, England) at 224 nm and a gas chromatograph with a flame ionization detector (Agilent Technology, USA), respectively. Due to the high volatility of some solutes, a static headspace autosampler was used for sample injection. The conditions of the gas chromatograph for VOCs determination were as follows: capillary column: HP-5; carrier gas: helium with a flow rate of 15 mL/min;

make up gas: ultra pure nitrogen with a flow rate of 30 mL/min; oven temperature: 120 °C isothermal for benzene, toluene, and ethylbenzene and 80 °C isothermal for the chlorinated solutes; injector temperature: 200 °C; and detector temperature: 300 °C. The external standard quantitative calibrations were obtained for the analysis of surfactant and organic solutes in both phases. Closure of the material balance was taken as evidence that leakage of the volatile solute was negligible. The concentration of phenols was analyzed by the 4-aminoantipyrine colorimetric method with a UV-spectrophotometer at 510 nm. Phenols combine in alkaline solution with 4-aminoantipyrine to produce a stable reddish-brown colored antipyrine dye. The amount of color (absorbance) produced is a function of the concentration of the phenolic material.

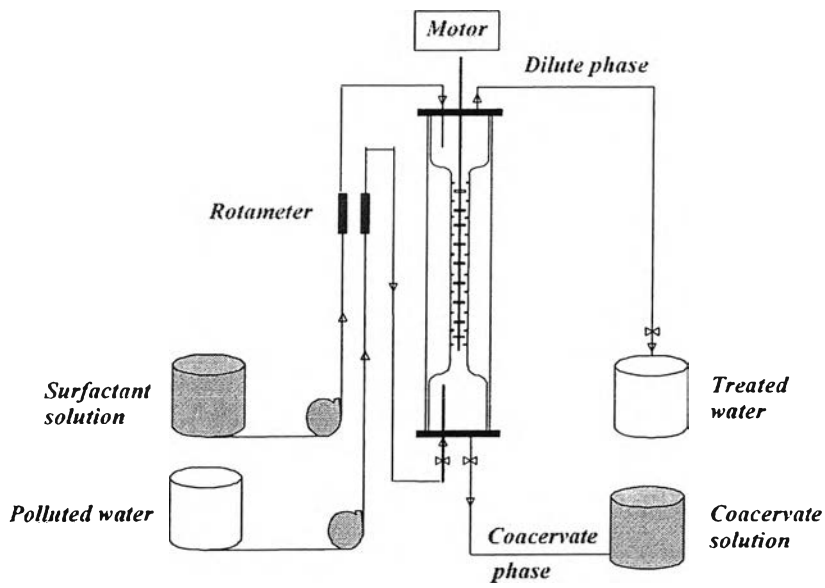

Figure 3.1 Schematic of the cloud point extraction pilot unit.

3.2.3 Equilibrium Parameters Calculation

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

3.2.3.1 Fractional Coacervate Volume

Volumes of both coacervate and dilute phase are obtained by measuring the phase height of the solution. The calculation of phase volume into a coacervate phase fractional volume is performed as follows:

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

3.2.3.2 Surfactant Partition Ratio

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

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

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

3.2.3.3 Organic Solute Partition Ratio

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

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

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

3.2.3.4 Percentage of Surfactant Extraction

The concentrations of surfactant in two phases are used to calculate the amount of surfactant extracted, which is defined as follows:

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

3.2.3.5 *Percentage of Organic Solute Extraction (%)*

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

$$\textit{Percentage of Solute Extraction} = \frac{\textit{Weight of Organic Solute in Coacervate Phase}}{\textit{Total Weight of Organic Solute}} \times 100$$

3.2.4 Determination of number of transfer unit (NTU) and height of transfer unit (HTU)

The HTU is the column height required to attain the separation which is equivalent to one equilibrium batch extraction and the NTU is the number of these single stage, batch extraction equivalents in the experimental column used. The HTU is particularly important in the design of industrial scale extraction columns. Based on the design of differential extractors in the literature, the graphical method can be used to determine the NTU by constructing the equilibrium line and the operating line on a plot between the mass fraction of toluene in the coacervate phase (X_{tou}) and the mass fraction of toluene in the dilute phase (Y_{tou}). The slope of the equilibrium line is a partition ratio obtained from batch experiments at equilibrium, whereas the slope of the operating line is the ratio of mass flow rate of the coacervate phase to mass flow rate of the dilute phase at the relevant position in the extractor. In our case, we assume that the mass flow rates of both phases are constant since the volumes of the separated phases are governed by the operating temperature, which is held constant throughout the column. Therefore, the operating line is a straight line with a constant slope. The NTU can be evaluated by either drawing a step line between those two lines as in the McCabe-Thiele method or by a numerical method (King, 1980). Since the total active height of the extraction column is a product of NTU and HTU, the HTU is calculated.