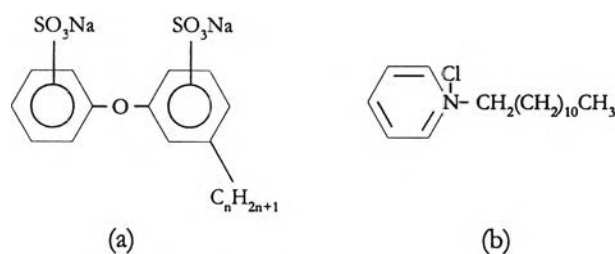


## CHAPTER 3

### METHODOLOGY

#### 3.1 Materials

##### 3.1.1 Mixed anionic and cationic surfactants



**Figure 3.1** The structures of (a) anionic surfactant - sodium hexadecyl diphenyloxide disulfonate (SHDPDS) and (b) cationic surfactant- dodecyl pyridinium chloride (DPC)

**3.1.1.1 Anionic surfactant.** Sodium hexadecyl diphenyloxide disulfonate (SHDPDS), a mixture of single-tailed and double-tailed diphenyloxide disulfonate (about 3 to 1 mixture), was obtained as Dowfax 8390 (36 % active) from Dow Chemical Company (Midland, MI). Chemically, this surfactant has two-negatively charged sulfonate groups.

**3.1.1.2 Cationic surfactant.** Dodecyl pyridinium chloride (DPC) 98% purity was purchased from Aldrich chemical Co., Inc. (Milwaukee, WI). The chemical structures of anionic and cationic surfactants are shown in Figure 3.1, and properties of these surfactants are shown in Table 3.1.

**Table 3.1** Properties of the surfactants

Surfactant	Molecular formula	M.W. <sup>a</sup>	CMC <sup>a</sup> (mM)
SHDPDS	-	642	6.3
DPC	C <sub>17</sub> H <sub>30</sub> NCl	283	4.0

<sup>a</sup> data from Doan et al., 2002

### 3.1.2 Organic solutes

Styrene and ethylcyclohexane were selected as the organic solutes for solubilization and adsolubilization studies. Styrene and ethylcyclohexane (99% purity) were purchased from Fisher Scientific. Properties of the organic solutes are shown in Table 3.2.

**Table 3.2** Properties of the organic solute

Organic solute	Molecular formula	M.W. <sup>c</sup>	Water solubility	K <sub>ow</sub>
Styrene <sup>b</sup>	C <sub>8</sub> H <sub>8</sub>	104.15	310 mg/L	2.95
Ethylcyclohexane <sup>c</sup>	C <sub>8</sub> H <sub>16</sub>	112.21	-	4.40 <sup>d</sup>

<sup>b</sup> data from <http://www.risk.lsd/ornl.gov>. <sup>c</sup> data from <http://www.chemfinder.com>. <sup>d</sup> data from (Gustafson et al., 1997)

### 3.1.3 Adsorbent

Aluminum oxide or alumina (Al<sub>2</sub>O<sub>3</sub>), mesh size 150, was purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI) and used as received. The surface area was determined to be 133 m<sup>2</sup>/g (N<sub>2</sub> BET adsorption method). The specific surface area reported by the manufacturer product was 155 m<sup>2</sup>/g. The pH of the point of zero charge (PZC) of alumina is 9.1 (Sun and Jaffe, 1996). Water suspensions of alumina were weakly acidic (pH of 6.75).

### 3.1.4 Chemicals

All chemicals used were ACS analytical reagent grade and used as received. All solutions were made with double-distilled water. Plastic and glassware were rinsed well with double-distilled water three times prior to use.

## 3.2 Experimental method

This study was divided into three experimental parts: adsorption, solubilization and adsolubilization. All experiments were conducted as batch experiments at electrolyte concentration of 0.015M NaCl, equilibrium pH of 6.5-7.5 and temperature of  $20 \pm 2$  °C.

The mixtures of anionic and cationic surfactants were varied in mole fraction to investigate the synergistic effects of mixed anionic and cationic surfactants. Mole fractions of SHDPDS and DPC were prepared by adding 3:1, 10:1 and 30:1 SHDPDS and DPC mole fractions with a constant SHDPDS concentration and varying DPC concentration. The mixed surfactant ratios were selected based on the precipitation phase diagram for the SHDPDS and DPC system (Doan et al., 2000; see Appendix A.1). The ranges of parameters studied are shown in Table 3.3.

**Table 3.3** Range of parameters evaluated in this study.

<b>Parameter</b>	<b>Range studied</b>
Anionic surfactant (SHDPDS)	$10^{-5} - 10^{-1}$ M
Cationic surfactant (DPC)	$10^{-6} - 10^{-1}$ M
AIS:CIS	3:1, 10:1 and 30:1
pH	6.5-7.5
Electrolyte concentration	0.015 M (NaCl)
Temperature	$20 \pm 2$ °C

### 3.2.1 Adsorption study

Adsorption experiments were conducted in 40 ml vials using a constant volume of 10 ml of mixed anionic and cationic surfactant solution and different amounts of alumina (based on the estimated adsorption amount of the surfactant on the alumina). The solution was equilibrated by shaking for at least 48 hours. After shaking for 12 hours, the pH of the solution was measured and adjusted. This process was repeated, but with a minimum waiting time of 3 hours, until the pH of the solution remained constant at the desired level. After equilibration, the solution was centrifuged to remove the solids. The concentration of anionic and cationic surfactants in aqueous phase were then measured by Liquid Chromatography (LC 20, Dionex). The amount of anionic and cationic surfactant adsorption was calculated by equation 2.1 (also see Appendix 2).

### 3.2.2 Solubilization study

The extent of organic solute solubilization into surfactant micelles (no alumina present) was studied for the single surfactants and the three mixtures of mole fractions for SHDPDS and DPC. The solubilization study was conducted in 40 ml glass vials with 20 ml of surfactant solution. The excess volume of organic solute was added to the vials. The vials were equilibrated for 24 hours, and then the organic solute concentration in aqueous solution was analyzed by Gas Chromatography (GC3000, Varian).

### 3.2.3 Adsolubilization study

For adsolubilization studies, the adsorption isotherms were used to determine an appropriate initial concentration of the mixed surfactant. The appropriate concentration from adsorption isotherms was one that equilibrated

just below the CMC of the surfactant (transition point) to ensure maximum surfactant coverage without the presence of micelles in the bulk solution.

Adsolubilization experiments were conducted in 40 ml glass vials by varying organic solute concentration with the appropriate surfactant concentration and the amount of alumina from the adsorption study. The solution was shaken for 48 hours and centrifuged to remove alumina. The surfactant concentration and the organic solute concentration in aqueous solution were analyzed by LC and GC, respectively.

### 3.3 Analytical method

Liquid Chromatography (LC20, Dionex) was used to quantify the individual surfactant components of anionic and cationic mixtures. Analytical methods for detecting anionic and cationic surfactants followed that use in previous research (Doan et al., 2002). The anionic surfactant (SHDPDS) was analyzed using the coupling agent tetrabutyle ammonium hydroxide (25 mN). The natural complex was separated with a reverse phase column (Dionex-NS1) with an acetonitrile-water mobile phase. The complex was then eluted from the column and de-coupled by anionic suppression (Dionex-ASRS) and detected by an electrical conductivity detector (Dionex-CD25). The cationic surfactant (DPC) was analyzed using the coupling agent methyl sulfonic acid (10 mN). The natural complex was separated with a reverse phase column (Dionex-NS1) with an acetonitrile-water mobile phase. The complex was then eluted from the column and de-coupled by cationic suppression (Dionex-CSRS) and detected by an electrical conductivity detector (Dionex-CD25).