

CHAPTER III

METHODOLOGY



3.1 Materials

3.1.1 Mixed anionic and cationic surfactants

Cationic surfactant: Pentamethyloleyl alkyl-1, 3-propane diammonium dichloride (PADD or Duoquad® T50), twin-headed and single-tailed surfactant, was donated by Akzo Nobel Surface Chemistry LLC as a 50% solution in isopropanol. Before an experiment isopropanol in the surfactant was evaporated by cyclic heating at 80°C and vacuum extraction. The purified sample was re-diluted and titrated by deionized water until the fraction of PADD was > 99%.

Anionic surfactant: sodium dodecyl sulfate (SDS, 98% active), single-headed and single-tailed surfactant, was purchased from Aldrich Chemical Company (Milwaukee, WI). Properties of these surfactants are shown in Table 3.1.

Table 3.1 Structures and properties of the surfactants used in this study.

Chemicals	Molecular structure	Molecular weight	CMC (mM)
Pentamethyloleyl alkyl-1,3-propane diammonium dichloride ^{a, b, c} (PADD or Duoquad)	$\begin{array}{ccc} \text{CH}_3 & & \text{CH}_3 \\ & & \\ \text{R} - \text{N}^+ - \text{C}_3\text{H}_6 - \text{N}^+ - \text{CH}_3 \cdot 2\text{Cl}^- \\ & & \\ \text{CH}_3 & & \text{CH}_3 \end{array}$	463.62	1.3 ^d
Sodium dodecyl sulfate (SDS)	$\text{C}_{12}\text{H}_{25}\text{SO}_3\text{Na}$	288.38	6.8 ^e

^a data from <http://www.chembuyersguide.com/partners/akzosurface.html>

^b data from http://www.lion.co.jp/laco/e/prod/p/44dqad_e.htm

^c data from <http://surface.akzonobelusa.com/cfm/2page2.cfm?PID=101>

^d data from Fuangswasdi, et al. (Personal Communication)

^e data from Doan, et al., 2003.

3.1.2 Organic Solutes

Styrene and ethylcyclohexane were chosen as model NAPLs to be represent polar and non-polar organic compounds, respectively. 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 organic solutes

Chemicals	Chemical formular	Molecular Weight	Water solubility (mg/L)	Log K_{ow}	Density	Vapor Pressure (mm Hg)
Styrene ^{f, g}	C_8H_8	104.15	310	2.95	0.9059	5 (highly volatile)
Ethylcyclohexane ^{h, i}	C_8H_{16}	112.24	81	3.13	0.788	N/A

^f data from <http://www.epa.gov/OGWDW/dwh/t-voc/styrene.html>

^g data from <http://chemfinder.cambridgesoft.com/result.asp>

^h data from <http://chemfinder.cambridgesoft.com/result.asp>

ⁱ data from <http://risk.lsd.oml.gov/tox/profiles/ethylbenzene.doc>

3.1.3 Adsorbent

Silica material (SiO₂, Hi-Sil 233) used for column studies. was donated by PPG Industries Inc. Hi-Sil 233 is a porous, amorphous and precipitated silica which has surface area of 142.6 m²/g, a mean particle size of 18.95 μm, and 100% surface-silanol group coverage.

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 Procedure

The experimental procedure was divided into four steps; column preparation, transport of organic solutes, adsorption and adsolubilization in silica-packed column. The solution for all experiments contained 0.01 M NaCl to maintain a constant ionic strength for all systems.

The mixture of anionic and cationic surfactants was used in mole fraction in order to investigate the synergistic effects of mixed anionic and cationic surfactants. Mole fractions of SDS and PADD were prepared by 1:3 SDS to PADD molar ratio. The mixed surfactants ratio was selected based on adsorption isotherm from batch studies (Fuangwasdi et al., Personal Communication) as shown in Appendix A.

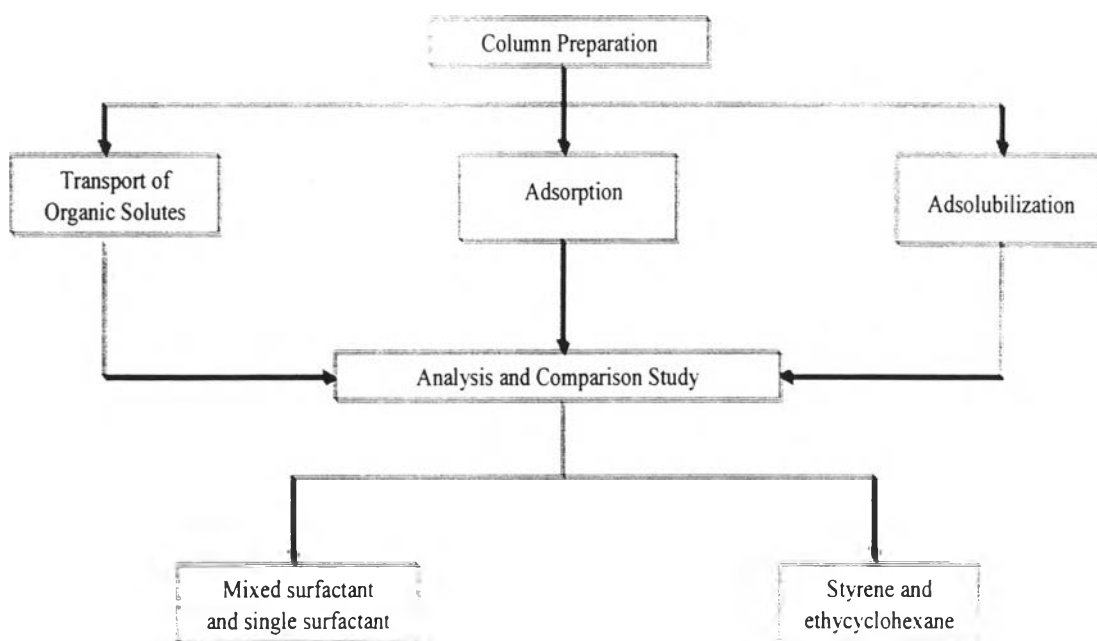


Figure 3.1 Schematic of this experiment.

3.2.1 Column preparation

The column studies used glass columns. Approximately 2 g of Silica Hi-Sil 233 and 30 g of glass bead were incrementally packed into the column until the height is 5 cm. The column media was saturated by introducing flow from bottom using deionized water bubbled with helium. Peristaltic high precision pump (Masterflex[®] L/S digital standard drive, Cole-Parmes Instrument) was used to maintain a constant flow rate (0.36 mL/min). Nitrate (0.01 M NaNO₃) was used as a tracer during column studies with silica (Flury, 2004). Sodium Nitrate breakthrough was monitored using a UV/VIS spectrophotometer (DVW-10, D-Star Instruments) at the wave length of 240 nm. The release of various concentrations versus volume from column test, were plotted into a breakthrough curve. From the breakthrough curve of the tracer, information of pore volume in the column was obtained.

3.2.2 Transport of organic solutes

The organic solutes were used at concentrations less than their solubilization capacity, which are 300 mg/L and 80 mg/L for styrene and ethylcyclohexane, respectively. Following the tracer flow, the organic solutes, styrene or ethylcyclohexane were pumped in an upflow mode with constant flow at 0.36 mL/min. Distilled water was then pumped through the bottom of column to ensure that media was completely clean. The concentrations of organic solutes were analyzed by UV/VIS spectrophotometer. Their breakthrough curves were plotted by the relative pore volume (volume eluted/pore volume) against the relative styrene or ethylcyclohexane concentration (C/C_0). Column characteristics of organic solutes breakthrough curves were examined. Then the retardation factors of the column were determined.

3.2.3 Adsorption study

Adsorption experiments were conducted in a column, using the optimum ratios of mixed SDS/PADD obtained from batch experiments, which is 1:3 (cationic-rich), comparison with a single surfactant (PADD). The concentrations of surfactants were used above the critical micelle concentration (CMC), which were 20 mM and 4 mM for PADD alone and mixed SDS/PADD, respectively.

PADD was pumped into the bottom of the column with constant flow rate (0.36mL/min). A time controlled fraction collector was used to gather discrete samples. The concentration of individual PADD was determined by

using a UV-visible spectrophotometer at the wave length of 240 nm. A similar procedure was used for the system SDS/PADD at ratio of 1:3. The concentrations of anionic and cationic surfactants were measured by Liquid Chromatography (LC 20, Dionex). Their breakthrough curves were plotted by the relative pore volume (volume eluted/pore volume) against the relative surfactant concentrations (C/C_0). Then, the adsorptions of both single PADD and mixed SDS and PADD were calculated by the mass balance (Knox et al., 1993) and equation 2.2 (Scamehorn, et al. 1981) as shown in Appendix C.

3.2.4 Adsolubilization study

For adsolubilization studies, the adsorption isotherms were used to determine an appropriated concentration of the surfactants. The appropriated concentration from adsorption isotherm was the one that equilibrated just below the CMC of the surfactant (transition point) to ensure the maximum surfactant coverage without the present of micelles in the bulk solution. The concentration of PADD alone and mixed SDS/PADD were 1 mM and 0.4 mM, respectively.

Adsolubilization experiment was conducted in the column, which had admicelle formation, from the adsorption experiment. The mixing solution of styrene or ethylcyclohexane and 1 mM PADD was pumped through the column in an upward mode with constant flow rate. The concentrations of organic solutes were analyzed by UV/VIS spectrophotometer. A similar procedure was used for the mixed SDS/PADD system. The adsolubilization of styrene and ethylcyclohexane in both single PADD system and mixed SDS

and PADD system were calculated by the mass balance (Knox et al., 1993) and equation 2.2 (Scamehorn, et al. 1981) as shown in Appendix C.

Their breakthrough curves were plotted by the relative pore volume (Volume eluted/pore volume) against the relative styrene or ethylcyclohexane concentration (C/C_0). Then the retardation factor can be determined and compared to untreated system.

3.3 Analytical methods

Liquid Chromatography (LC 20, Dionex) was used to quantify the individual surfactant components of anionic and cationic mixtures. Analytical methods of anionic and cationic surfactants followed previous research (Doan et al., 2002). The anionic surfactant, sodium dodecyl sulfate (SDS), was analyzed using the coupling agent tetrabutyl ammonium hydroxide (25 mN). The cationic surfactant, pentamethyloleyl alkyl-1, 3-propane diammonium dichloride (PADD) was analyzed using the coupling agent methane sufluric acid. The natural complex was separated with reverse phase column (Dionex NS-1) with an acetronitrile-water mobile phase, the complex was eluted from the column and de-coupled by ionic suppression and finally detected by an electrical conductivity detector (Dionex-CD25). All calibration runs resulted in linear fits with good correlations ($R^2 > 0.99$).

For the determination of tracer, single cationic surfactant and organic solutes concentrations, a UV/VIS spectrometer was used. A DVW-10 spectrophotometer was used to analyze nitrate, PADD, styrene and ethylcyclohexane. A wavelength of 240 nm was used to analyze nitrate and PADD; a wavelength of 275 nm was used to analyze styrene and a wavelength of 260 nm was used to analyze ethylcyclohexane.