CHAPTER III
EXPERIMENTAL

3.1 Materials

Precipitated silica, Hi-Sil® 233, with a specific surface area of 150 m^2/g was supplied by PPG Industries Inc. (Pittsburgh, PA) and used as the solid substrate. The cationic surfactant cetylpyridinium chloride (CPC) was obtained from Sigma (St. Louis, MO). The studied solutes include diphenylmethane (99+ wt%) from Aldrich (St. Louis, MO), diphenylether (99+ wt%) from Aldrich (St. Louis, MO), 4-bromotoluene (99+ wt%) from Fluka (St. Lois, MO) and p-tolunitrile (98+ wt%) from Fluka (St. Louis, MO) diphenylamine 98+wt% (Fluka, St. Louis, MO) and 4,4'-bipyridine 99% (Riedel-deHaën, Seelze) as shown in Table 3.1 with their useful physicochemical properties [20]. The solvent was de-ionized water with a resistivity of 18.2 MΩ-cm purified by a Barnstead E-pure water system. All chemicals were used as received.

3.2 Experimental Procedures

3..2.1 Surfactant Adsorption / Admicelle Formation

Surfactant stock solutions were made and adjusted to pH 8 with a dilute sodium hydroxide solution. These solutions were diluted with pH 8 de-ionized water to form a series of 20 mL solutions with varying surfactant concentrations. These were added to vials containing 0.4 g of silica and then sealed. The mixtures were shaken daily and allowed to equilibrate for two days at temperatures of 20, 35, 50 or 65 °C. They were then allowed to settle at those constant temperatures for one day. After that the supernatants were removed and centrifuged by a Fisher Scientific model MARATHON 300 at 3000 rpm for 15 minutes. The supernatants were removed and analyzed for the bulk surfactant concentrations through UV spectroscopy at λ = 258 nm by using a SHIMADZU UV spectrophotometer model UV-1201S. Through a simple mass-balance, the amount of surfactant adsorbed per

gram of silica was calculated and plotted as a function of the surfactant equilibrium bulk concentration.

3.2.2 Adsolubilization

In case of studying temperature effect on adsolubilization, the adsolubilization isotherms have been examined at 20, 35, 50 and 65 °C. The appropriate initial surfactant concentrations for the adsolubilization studies were determined from the adsorption isotherms. An "appropriate concentration" is one that equilibrates just below (~90% of) the critical micelle concentration (CMC), 0.91 mM, ensuring that (1) no micelles is present in the bulk solution and (2) near maximum surface coverage is achieved. In case the differences between ability of admicelles in surfactant adsorption region III and high region II were investigated. The studied surfactant concentrations in adsorption region II and III for the adsolubilization studies will be determined from the adsorption isotherms. There are only two studied surfactant concentrations; one in high region II and another in region III. Both concentration are in the high zone of the adsorption isotherm aiming to maintain the admicelles covering on the whole solid surface (minimize the presence of adsorbed surfactant monolayer area) because our work focused only on studying the effect of different packing density of surfactant molecules in the admicelles on adsolubilization). The initial surfactant concentration was chosen for each temperature. Solute was then added into a pH 8 surfactant solution to make a stock solution with a concentration equal to the aqueous solubility of the solute. The solute stock solutions were then diluted to varying solute concentrations by adding pH 8 surfactant solution of the same surfactant concentration. Twenty millilitres was added to a vial with 0.4 g of silica and then sealed. The vials were shaken daily and allowed to equilibrate for 3 days at constant temperature. The samples were allowed to settle for 1 day before the supernatant was removed from the vials and then quickly centrifuged at room temperature. The supernatant was removed for analysis of the equilibrium solute bulk concentration using a dual-wavelength UV spectroscopic technique. The wavelengths used for analyzing diphenylmethane, diphenylether, 4-bromotoluene and p-tolunitrile were 262, 269, 248 and 272 nm, respectively. Calibration curves were developed, and the measured absorbance used to calculate the solute concentrations in the supernatant. Through a simple mass-

balance, the amount of adsolubilized solute in the admicelles per gram of silica was calculated. This data was converted to the intra-admicellar mole fractions of solutes X_{ia} and plotted against their partition coefficients K_p and amount of adsolubilized solute in the admicelles per gram of silica.

3.2.3 Determination of Aqueous Solubility of Solutes

Excess amount of solute was added to 20 mL de-ionized water in a glass vial and then sealed and vigorously stirred at room temperature for 3 days. This aqueous solution was then brought into water bath with temperature controlling accuracy of $\pm 0.1^{\circ}C$. The solution has been kept in the water bath at desired temperature for 10 days prior to determining the amount of dissolved solute in the aqueous phase by UV spectrophotometry at wavelengths of 262, 269, 248 and 272 nm for diphenylmethane, diphenylether, 4-bromotoluene and p-tolunitrile, respectively.

3.2.4 Atomic Force Microscopy

An aqueous CPC solution of 0.72 mM (80% of its CMC) was prepared with no pH adjustment. The surfactant solution was then mixed with solute. Most of the studied solute concentrations in the surfactant solution are at their aqueous solubility. These aqueous solutions have been then analyzed by using atomic force microscope.

Atomic force microscopy was performed using a multimode scanning probe microscope with E-scanner controlled by Nanoscope IIIa (Veeco Instruments, NY). The experiment was conducted in contact mode directly imaging in the aqueous solution. The imaging method was to use the double layer (or steric) repulsion between the AFM tip and adsorbed surface layer by "flying" the tip over the adsorbed layer on the mica surface. Silicon nitride model NP cantilever (Veeco Instruments, NY) with a nominal spring constant of 0.06 N/m was used. It was cleaned with methanol and de-ionized water and then dried prior to use.

For observation of initial admicelle structure, the mica disc was freshly cleaved and mounted on a metal disc. The metal disc was then mounted on top of the scanner and the fluid cell placed on top. A prepared aqueous solution was then placed on the mica disc by injection through the fluid cell port. The system was allowed to equilibrate thermally for 10 minutes before imaging.

To investigate the equilibrium admicelle structure, the admicelle formation on mica surface was equilibrated in the surfactant-solute aqueous solution for 10 days in separate glass vials. The wet mica disc was then removed from the solution and mounted in the fluid cell along with the equilibrium aqueous solution in the vial.

Imaging processing used scan rates, integral gains, proportional gains and *z*-deflection ranges of 12-15 Hz, 0.15-0.3, 3 and 1-1.5 nm, respectively. All experiments were performed at room temperature (23°C). All images are raw deflection images that have been flattened along the scan lines to remove any tilt from the sample. No other image processing was used. Only key images were presented in this paper.

3.2.5 Differential Scanning Calorimetry

We examined both the solubilization and adsolubilization of organic solutes by DSC. To prepare samples for DSC study of solubilization, we primarily assumed the critical micelle concentration of CPC to be 900 μmol/L. A stock micellar solution of 5880 μmol/L (~6×CMC) was prepared and adjusted to pH 8. The CMC at pH 8 is also approximately 900 μmol/L, thus the concentration of micellar surfactant is around 4980 μmol/L. Twenty milliliters of this solution was mixed with a measured amount of the solute in a glass vial and then sealed. The solutions were equilibrated for two days prior to analyzing by DSC.

For adsolubilization study, a stock micellar solution was prepared for the same concentration of the micellar solution and the solution pH was adjusted to 8 using NaOH solution. The desired amount of solute was dissolved in 20 ml of the micellar solution in a glass vial, vigorously stirred and then sealed. After that, 0.4 g of silica powder was added to the solution. A bulk aqueous surfactant concentration at equilibrium after silica addition was just below the critical micelle concentration (~0.9×CMC). The surfactant molecules consequently self-assemble as admicelles at silica/aqueous interface without a presence of micelles in the bulk aqueous phase. This system was equilibrated for two days prior to sampling to be analyzed by DSC.

DSC experiments were performed on Calorimetry Sciences Corporation (CSC) 6100 Nano II Differential Scanning Calorimeter, which is suitable for analysis of even small amount of solute in aqueous solution. The liquid

sample and reference were each loaded into DSC cells (with nominal volume of 0.33 mL) in the cell chamber. The cell chamber was then tightly closed and pressurized to 4.5 atm. Before running the DSC, the stable heat transfer rate through those liquids must be lower than 30 μW as the pressure was increased from 0 to 3 atm to ensure that no small bubbles, which will significantly disturb solution properties leading to wrong DSC curve, are present in the cells. The sample and reference were equilibrated at the initial temperature (5°C) for 10 minutes. The DSC measures the heat transfer rate (μW) through the sample background-corrected by a corresponding reference. Heat transfer rate data were normally collected between 5 and 60 °C at a constant scan rate of 1 °C/min. However, only the temperature range between 5-30 °C in the DSC curve was presented in this paper because results above this range did not show any peaks. Our analysis on DSC curve is qualitatively based on the observed phase transition temperature. Only DSC heating curve was used to interpret the locus of solubilization and adsolubilization.