

CHAPTER III

EXPERIMENTS

3.1 Materials

Anionic sodium dodecyl sulfate (SDS) surfactant was the product of Henkel Company, with washing active substance min. 90%, sodium sulphate max. 7%, and water max. 2%. Phenol was obtained from AJAX Chemicals Company, Australia, and was analytical grade. Acetic acid from J. T. Baker Inc., USA. Distilled, .45 μ M filtered water, pH value = 6.1. Porous activated acidic gamma alumina and porous neutral gamma alumina was obtained from different companies as indicated below.

3.2 Pore Size Distribution Measurements and Details of Alumina Powders

Eight different alumina powders were used in the experiment. BET surface areas and pore size distributions were measured. The mean pore size and related details are as follows:

Alumina powder #1:

From: Johnson Matthey Company, USA.

Surface Properties: acidic, activated, gamma

Mean Pore Size: 28.84 Angstrom

BET Report: See Appendices

Alumina powder #2:

From: Aldrich Chemical Co., Inc., USA

Surface Properties: acidic, activated

Mean Pore Size: 28.96 Angstrom

BET Report: See Appendices

Alumina powder #3:

From: E. Merck, Germany

Surface Properties: Neutral, active

Mean Pore Size: 39.78

BET Report: See Appendices

Alumina powder #4:

From: Johnson Matthey Company, USA.

Surface Properties: Calcined from Aluminum Oxide Powder #1

Mean Pore Size: 113.4 Angstrom

BET Report: See Appendices

Alumina powder #5:

From: Johnson Matthey Company, USA (Sieved with 75 μ M mesh from Aluminum Oxide Powder #1)

Surface Properties: Acidic, activated

Mean Pore Size: 28.58 Angstrom

BET Report: See Appendices

Alumina powder #6:

From: Johnson Matthey Company, USA.

Surface Properties: gamma

Mean Pore Size: 75.11 Angstrom

BET Report: See Appendices

Alumina powder #7:

From: Johnson Matthey Company, USA.

Surface Properties: activated

Mean Pore Size: 41.97 Angstrom

BET Report: See Appendices

Alumina powder #8:

From: Johnson Matthey Company, USA.

Surface Properties: gamma, 96+% (Assay) inc. 3% C

Mean Pore Size: 40.89

BET Report: See Appendices

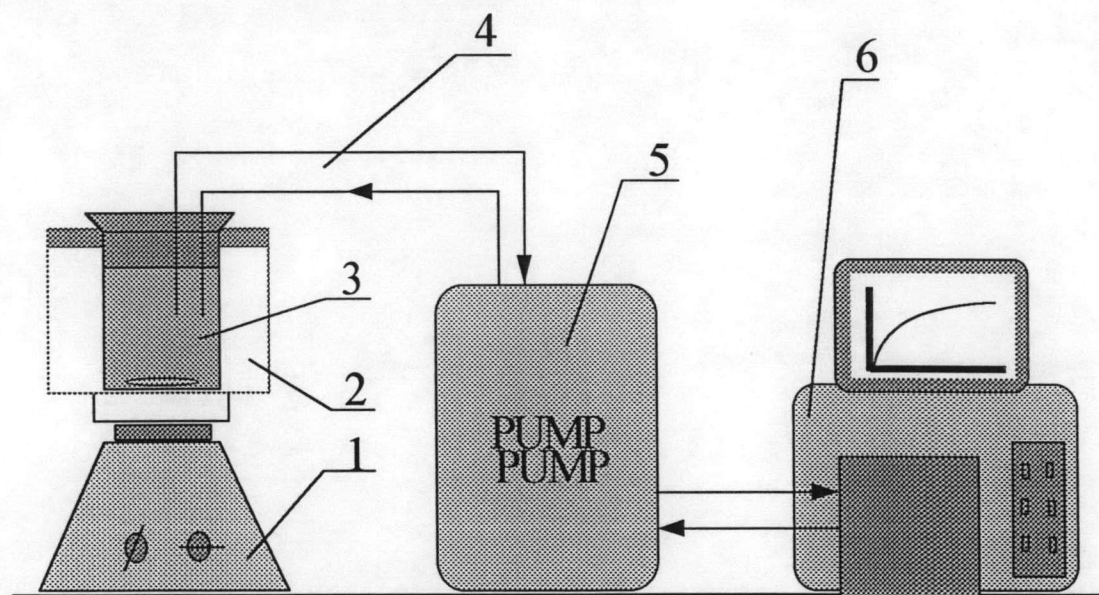
All alumina powders are washed with distilled, filtered water and dried.

3.3 Experimental Procedures

3.3.1 The Experimental System

As shown in Figure 3.1, the experimental system consists of an external circulation water bath with a PolyScience digital temperature controller, a CECIL/CE2040 UV-spectrometer with flow cell, a Masterflex model 7518-10 mini-pump and a magnetic stirrer.

Experimental System



- | | |
|---------------------|-----------------------------------|
| 1. Magnetic Stirrer | 4. Tubing |
| 2. Water Bath | 5. Pump |
| 3. Beaker | 6. UV-spectrometer with flow cell |

Figure 3-1 Experimental system.

Operating Procedure:

The water bath temperature controller was set to the desired value and water circulation was begun. The UV-spectrometer was turned on for warming-up. The beaker with experimental solution was placed in the water bath, the solution was stirred constantly. After the system was stable and the solution temperature reached the same as the water bath the experiment was started.

3.3.2 The Experimental Procedures

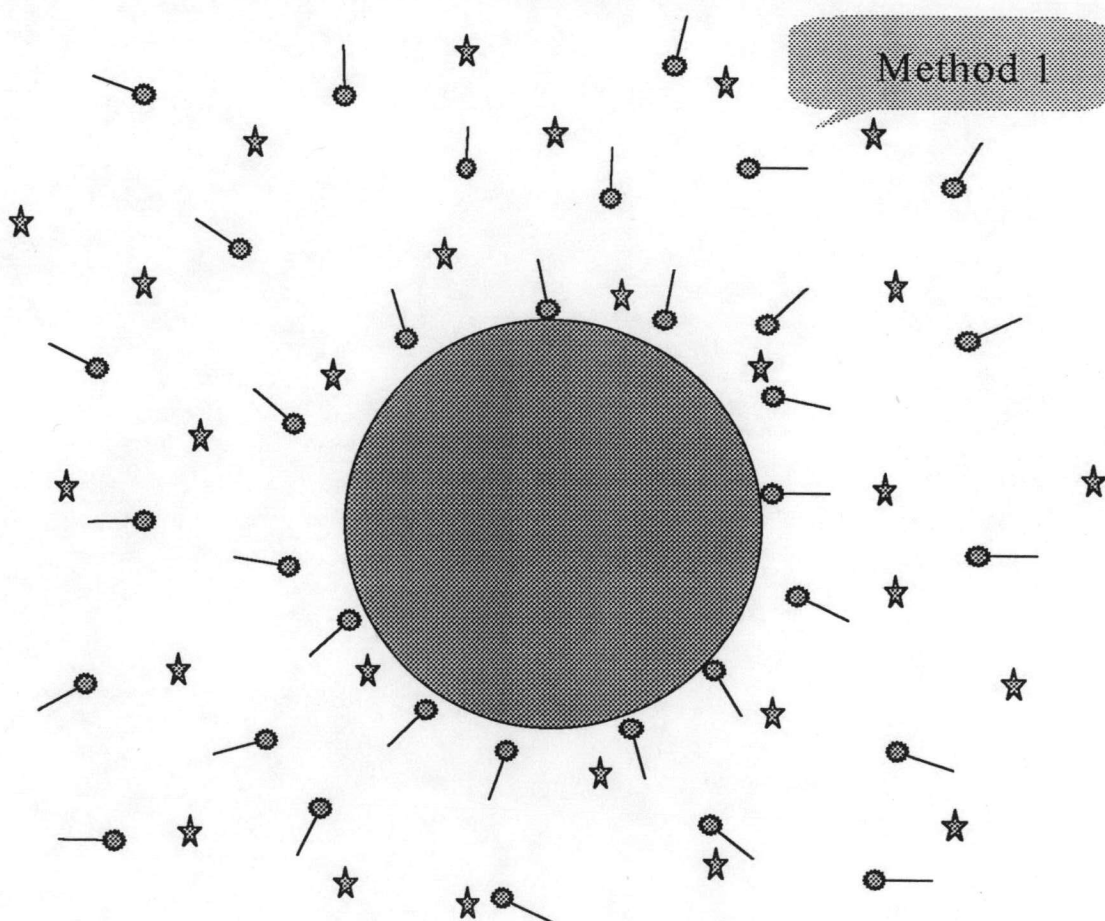


Figure 3-2 Experimental method 1.

Two experimental procedures or methods were used for the present research:

Method 1. Put 250 ml distilled, filtered water in a glass bottle, inject 500 μl acetic acid in the bottle (to keep the initial pH of the solution at 3.2), add 0.3605 g SDS in (The initial SDS concentration equals 5000 μM), then inject 400 μl 0.25 M filtered phenol solution in the bottle (The initial phenol concentration equals 400 μM), keep the bottle in the water bath at 40 degrees Celsius and stirred constantly for at least 40 minutes, then add 3 g alumina powder. Seal the bottle with Parafilm, sample the mixture solution continuously through an HPLC 0.45 micron mesh metal filter placed in the bottle by pumping a side stream to a flow cell on a CECIL/CE2040 UV-spectrometer. The filter is used to preclude alumina particles' interference with the UV measurements. Timely record the absorbance at $\lambda = 271$ nm, an absorbance maximum of the phenol, in order to follow the aqueous bulk concentration change of phenol with time. After passage through the UV flow cell, the sample was returned to the mixture solution.

Method 2. Put 250 ml distilled, filtered water in a glass bottle, inject 500 μl acetic acid in the bottle (to keep the pH of the solution at 3.2), add 0.3605 g SDS, then add 3 g alumina powder in, keep the bottle in the water bath at 40 degrees Celsius and stirred constantly for enough time (at least as long as the equilibrium time of method 1). Then inject 400 μl of 0.25 M filtered phenol solution in, seal the bottle with parafilm. Sample the mixture solution continuously through an HPLC 0.45 micron mesh metal filter placed

in the bottle by pumping a side stream to a flow cell on a CECIL/CE2040 UV-spectrometer. The filter is used to preclude alumina particles'

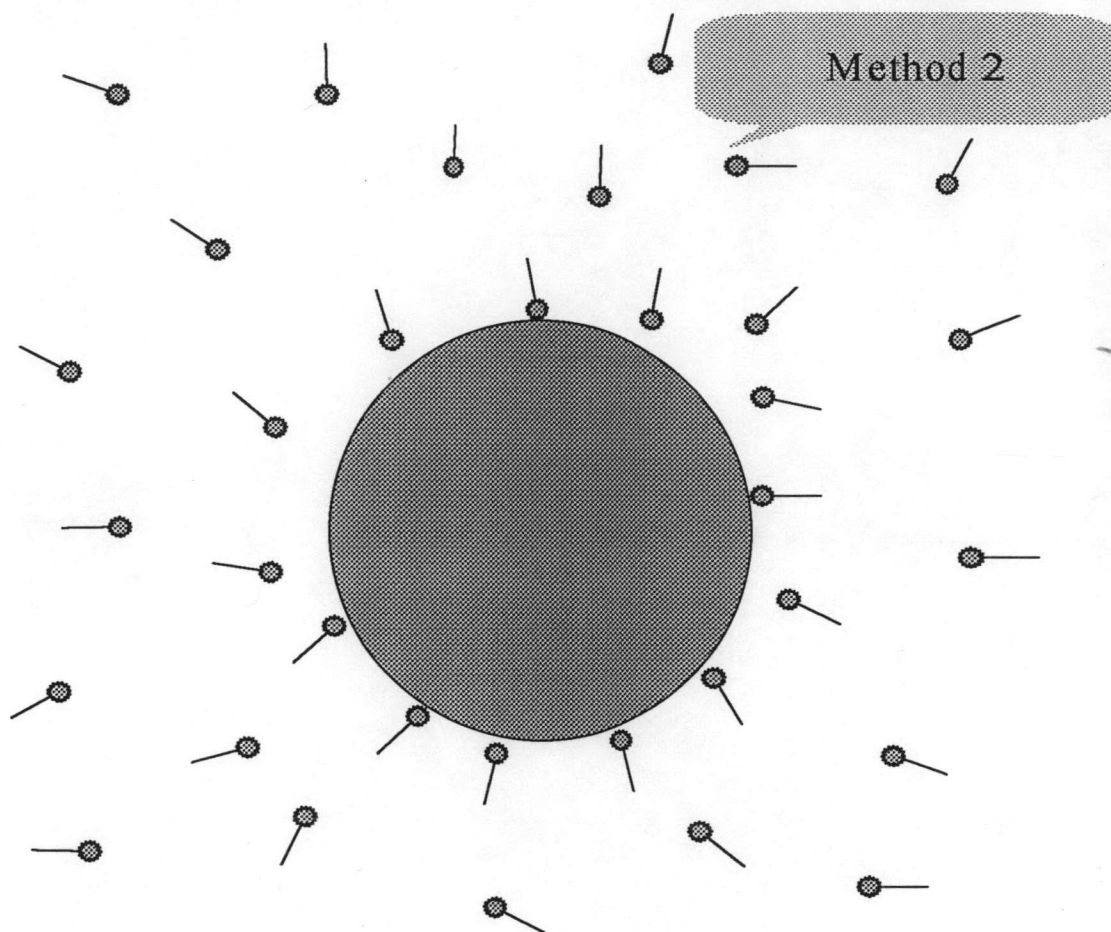


Fig. 3-3 Experimental method

interference with the UV measurements. Timely record the absorbance at $\lambda = 271 \text{ nm}$, an absorbance maximum of the phenol, in order to measure the aqueous bulk concentration change of phenol with time. After passage through the UV flow cell, the sample was returned to the mixture solution, and follow

3.3.3 The Reason to Design the Two Methods

There are two reasons to set up these two experimental methods. One is to see if there is permanent blockage for the adsolubilization of phenol if the phenol is added to the solution after the SDS adsorption. The second is to study the effect of pore size/pore size distribution on the adsolubilization.

3.4 SDS Measurements

The aqueous phase SDS concentration was measured using a Perkin-Elmer high performance liquid chromatograph (HPLC) with a Supelco 15 cm C18 reversed-phase silica column and an Alltech conductivity detector. The concentration is then calculated by interpolating the SDS calibration curve which is from the SDS peak areas. The amount of SDS adsorbed on the alumina can then be determined by a simple mass balance ($\mu\text{moles SDS/g alumina}$).

3.5 Kinetics Measurements

The experimental apparatus for kinetics measurements is shown in Figure 3.2. The basic procedure to follow the adsolubilization process of phenol is given as in 3.3.2.

3.6 Discussion

Each experiment has been repeated several times, and the results are reproducible. For method 1, when the alumina powder is added to the solution, some very fine air bubbles appeared, which passed the flow cell

and caused a high initial absorbance measurement. The effect of the air bubbles disappeared within 10 to 15 minutes. Eventual phenol levels of both method 1 and method 2 were equal, indicating that using either experimental method leads to the same equilibrium state, i.e., regardless of whether the phenol is added with the SDS or after the adsorption of SDS, pore blockage by adsorbed SDS apparently does not occur.

3.6.1 Comparison of the Results

The experimental curves show that the absorbance at 271 nm wavelength decreases more rapidly in method 1 than in method 2. Curves of method 1 are generally smooth over the whole time of the experiment. The curves of method 2, however, show a break which divides the curves into two parts: one corresponding to very fast adsolubilization and the second part in which adsolubilization is slower. We interpret the later segment to be one of hindered diffusion.

3.6.2 A Support Experiment

To make sure the absorbance reduction of phenol is caused by the adsolubilization of phenol into SDS admicelles, an experiment was conducted as following:

1. At 40 degrees Celsius, keep the solution (250 mL distilled, filtered water added by 500 μ L acetic acid) constantly stirred, wait for at least the same time as required for the equilibrium of method 1, then inject 400 μ L 0.25 M filtered phenol solution.
2. Seal the bottle with Parafilm.

3. Sample the solution continuously through a HPLC metal filter (namely 0.45 micron mesh) placed in the bottle by pumping a side stream to a flow cell on a CECIL/CE2040 UV-spectrometer. The filter is used to preclude alumina particles' interference with the UV measurements.
4. Timely record the absorbance at $\lambda = 271$ nm, an absorbance maximum of the organics phenol. After passage through the UV flow cell, the sample was returned to the mixture solution.

No absorbance reduction was recorded in this experiment, which indicates that the reduction of phenol absorbance was caused by the adsolubilization of phenol into SDS admicelles.

3.6.3 The Time for SDS Adsorption Equilibrium

Most references report a long time (several days at room temperature) for SDS adsorption onto the alumina surface. In our experiments, however, the adsorption was considered to be essentially completed at the equilibrium point of the method 1 experiments (typically about 40 minutes), at 40 degrees Celsius with fixed initial SDS concentration and solution volume and pH value. An additional experiment was designed and conducted to see if the estimated time is enough for SDS adsorption, and in particular to see if results would differ if a longer time were allowed for SDS adsorption. In this experiment 0.3605 g alumina powder of type 1 was put in 250 mL distilled, filtered water at 40 degrees Celsius, in which 500 μ L acetic acid was injected. The solution was sealed and kept at room temperature for 4 days, then a phenol adsolubilization experiment was done according to method 2. The absorbance reduction -- time curve was found to be virtually identical to those obtained using method 2. This indicates that the estimated time for SDS adsorption in the

experiment is enough for a fairly complete formation of admicellar layers inside alumina pores.

3.6.4 CMC (Critical Micelle Concentration) of the SDS

The CMC of SDS in this experiment was measured in the presence of 3 g alumina in 250 ml distilled, filtered water at pH 3.2, room temperature, by measuring the change of conductivity (the conductivity of a surfactant solution shows a sudden increase at the CMC). The value was about 6000 μM .