

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

3.1.1 Silica

The precipitated silica (Hi-Sil 255) used in this synthesizing process was manufactured by PPG-Siam Silica Co., Ltd. (Rayong, Thailand) and it has the surface area of 170 m²/g.

3.1.2 Surfactants

The quaternary ammonium surfactants (C_nH_{2n+1}(CH₃)₃NBr): Octyltrimethylammonium bromide, Decyltrimethylammonium bromide, Dodecyltrimethylammonium bromide and Cetyltrimethylammonium bromide. All of these surfactants have a purity of 98 %. The lower tetraalkylammonium compounds (C_nH_{2n+1})₄NOH, n=1, 2 (here abbreviated as TMA, TEA respectively). All of these chemical reagents were obtained from Fluka. Tetramethylammonium silicate (10% wt silica, molar ratio of TMA⁺ to silica is 0.5) was purchased from Sachem.

Table3-1 Chemical structures of cationic surfactants

Chemical Name	Formula
Octyltrimethylammonium bromide	CH ₃ (CH ₂) ₇ N(CH ₃) ₃ Br
Decyltrimethylammonium bromide	CH ₃ (CH ₂) ₉ N(CH ₃) ₃ Br
Dodecyltrimethylammonium bromide	CH ₃ (CH ₂) ₁₁ N(CH ₃) ₃ Br
Cetyltrimethylammonium bromide	CH ₃ (CH ₂) ₁₅ N(CH ₃) ₃ Br
Tetraethylammonium hydroxide	(C ₂ H ₅) ₄ NOH
Tetramethylammonium hydroxide	(CH ₃) ₄ NOH
Tetramethylammonium silicate	C ₄ H ₁₃ NO ₅ Si ₂

3.2 Experimental Procedures

3.2.1 Synthesis of MCM-41.

MCM-41 materials were prepared by following the procedure given by Ioneva (1996). Three different pore sizes (21, 26 and 36 Å) were synthesized in this study.

Table 3-2 The Mixed solution for synthesized MCM- 41

Pore size (Å)	Solution 1	Solution 2
21	180g. of 25 wt% C ₁₀ TAB + 25 g Hisil-255	10g.Hisil255+123 g. 20 wt% +TEAH+30g H ₂ O
26	197g. of 25 wt% C ₁₂ TAB + 25 g Hisil-255	10g.Hisil255+123 g. 20 wt% +TEAH+30g H ₂ O
36	190 g. of 25 wt% C ₁₆ TAB +58 g of 25 wt% TMAH	25 g. of Hisil-255 +100 g. TMAS 10 wt% silica; ratio of TMA to Si is 0.5

The prepared solution following Table 3-2 was mixed well for about 30 minutes. The prepared solution was placed in a PARR reactor and heated at 150°C for 24 hours with stirring at autogeneous pressure. The solution was then taken out and quenched to room temperature (25°C). The solution was filtered to obtain the solid product. The filtered solid was continually washed with running water until the absence of foam. Then it was dried at ambient air. Finally, this solid product was calcined at 560°C for 7 hours in static air.

3.2.2 Surfactant Adsorption

15 ml of each surfactant solution was added to MCM-41(0.122 g) in a screw top test tube separately and then shaken in a shaking water bath at 30°C. The test tubes were shaken once a day for approximately 5 hours. After that, the suspension was poured into a centrifuge tube. The suspension was centrifuged by ALC CENTRIFUGE at 3,000 rpm, for 1.0 hours, to remove particles solid. Part of the supernatant was separated from the solid by disposal pipette and transferred to find the concentration by HPLC. Allow the rest suspension to be adsorbed and repeated all above procedures everyday until the supernatant concentration reached equilibrium (constant concentration). The number of days required for each surfactants adsorption to be adsorbed on MCM-41 could be read out by plotting a graph between surfactant concentration (μm) versus day adsorbed.

The stock solutions of 1 M of each surfactant were prepared and then diluted to various desired concentrations. MCM-41(0.122 g) as an adsorbent was put into a series of screw top test tubes with a PTFE lined cap. Each test tube then contained 15 ml with the various surfactant concentrations. The test tubes were capped, sealed with paraffin and placed in a shaking water bath at 30°C. The test tubes were shaken at a low speed once a day for the required adsorption days which depended on type of the surfactant. The suspension was then poured into a centrifuge tube. The pH of the suspension was measured by a pH meter (Benchtop H/ISE Meter, Model 420A with Triode pH electrode Model 91-57BN) before centrifuging and the pH was found about 5. The suspension was centrifuged by using a ALC 4236 CENTRIFUGE at 3,000 rpm each time for 1.0 hours, to remove all MCM-41. The supernatants of the samples were separated from the precipitated solid by using disposable pipettes. The supernatants were finally filtered through a membrane filter(Gelman science Membrane Filter, Model FP-450 13 mm dia. 0.45 μm).

The equilibrium concentrations of each surfactant were determined by High Performance Liquid Chromatography (HPLC) (Hewlett Packard series 1050) and conductivity detector (All tech, Model: Lambda 16), and HPLC Software (HPLC 2D Chemstation Rev. A.03.02 Hewlett Packard 1990-1995). The HPLC column was a 3.9*150 mm. Nova-Pak C18 reverse-phase column (Water Division of Millipore, Millipore Corporation, Milford, MA). The mobile phase solvent for all cationic surfactants was 90% HPLC grade methanol and 10% deionized water for approximately 3 minutes to elute analyte and remove impurities. The flow rate of the mobile phase solvent was 0.5 ml/min. The sensitivities of the detector at high surfactant concentration, it was adjusted to about 100 μ S and for low surfactant concentration was about 5 μ S to get the sharpest desired peak. In each experiment, blank solutions were also used to correct for background interferences. And BET surface analyzer were employed to measure the surface area of solid.