

CHAPTER III EXPERIMENTAL

3.1 Materials

Poly(diallyldimethyl ammonium chloride) -- QUAT or MERQUAT[®] having an average molecular weight of approximately 240,000 daltons, was supplied by Calgon Corporation (Pittsburgh, USA). Poly(diallyldimethyl ammonium chloride) monomer has the empirical formula $(H_2C=CHCH_2)_2N(CH_3)_2Cl$. Sodium chromate was analytical grade supplied by Reidel-deHaen with a purity of 99%. Sodium sulphate (AR grade) with a purity of 99.5% was obtained from Carlo Erba (Milan, Italy). p-Hydroxybenzoic acid (99%) and sym-diphenylcarbazide were manufactured by Fluka (Buch, Switzerland). Ethyl alcohol (absolute, 99.8%), absolute methanol (99.8%), and barium chloride dihydrate (AR grade) were obtained from Merck Company (Darmstadt, Germany). Univar Company (Auburn, Australia) supplied potassium hydroxide (AR grade). Glacial acetic acid (99.9%) was obtained from J.T. Baker (Phillipsburg, USA). Deionized and distilled water was used to rinse glassware and prepare all solutions in all experiments.

Membrane for purification of QUAT was Prep/Scale-TFF Cartridges supplied by Millipore Corporation. Spectrum[™] cellulose acetate (type C) ultrafiltration membranes from Spectrum Medical Company (Houston, USA) were used in these experiments with molecular weight cut-off equal to 10,000 daltons.

3.2 Purification

The QUAT solution was purified in a Prep/Scale-TFF spiral wound ultrafiltration (UF) column. It was operated at the pressure of 25 psig and the flow rate of 300 mL/min. Permeate and retentate exited vertically at the top of the column. Retentate was sent back to the feed reservoir and permeate was released. Initial QUAT solution was filtrated to approximately 85% volume as permeate. Distilled water was added to the feed reservoir to restore the original solution volume and the solution then was refiltered. The purification process was repeated for 6 cycles.

3.3 Analysis Methods

3.3.1 Determination of Chromate Ion

The concentration of chromate in permeate and retentate solutions were colorimetrically determined by UV/VIS spectrophotometry. Sym-diphenylcarbazine was added to the solutions to develop color of the violet complex with chromate ion. Then the absorption of complex solution was determined with a UV/VIS spectrophotometer (Perkin Elmer, Lambda 10) at 541.2 nm.

Sym-diphenylcarbazine reagent was prepared by dissolving 0.1 g sym-diphenylcarbazine in 50 mL ethyl alcohol and adjusting the volume to 250 mL by adding a solution of 10% acetic acid in distilled water.

3.3.2 Determination of Total Organic Carbon

The concentrations of QUAT in the permeate and retentate solutions were determined by a total organic carbon (TOC) analyzer (TOC-5000A, Shimadzu) as described by the following procedures:

3.3.2.1 *Measurement of Total Carbon (TC)*

A total carbon combustion tube is filled with oxidation catalyst and heated to 680°C. Carrier gas (high purity air) is supplied into this tube after it is controlled at flow rate of 150 mL/min by a pressure controller and a mass controller and moistened by a humidifier. When sample 100 µL has been introduced by a sample injector into the TC combustion tube, the TC component in the sample combusted or decomposed to become CO₂. The carrier gas which contains combustion product from the TC combustion tube flows through an inorganic carbon reaction vessel cooled and dried by a dehumidifier. It is then sent through a halogen scrubber into a sample cell set in a non-dispersive infrared gas analyzer (NDIR) where CO₂ is detected. The NDIR outputs a detection signal (analog signal) which generates a peak whose area is calculated by a data processor.

3.3.2.2 *Measurement of Inorganic Carbon (IC)*

A sample of 2000 μL is introduced with an injector into an IC reactor vessel where carrier gas is flowing in form of tiny bubbles in the solution acidified by IC reagent. Only IC component in the sample is decomposed to become CO_2 , which is detected by the NDIR. The IC concentration can be determined in the same procedure as the TC concentration. Carbon in the form of carbonate and hydrogen carbonate can be measured as IC.

3.3.2.3 *Measurement of Total Organic Carbon (TOC)*

TOC concentration can be obtained by subtracting the IC concentration calculated in section 3.3.2.2 from the TC concentration calculated in section 3.3.2.1.

3.4 Experimental Procedures

3.4.1 Ultrafiltration Experiments

Ultrafiltration experiments were carried out in a 400 mL stirred cell which was submerged into an acrylic plexi-glass plastic box having circulating water to control the solution temperature. Ultrafiltration membrane which has molecular weight cut-off equal to 10,000 daltons was used. A 300 ml solution of polyelectrolyte, chromate ion, and sulfate ion was placed in the stirred cell and controlled at 30°C . The initial pH of the solution was measured about 8.5. The solution was stirred at a speed of 250 rpm with a pressure drop of 60 psi across the membrane using nitrogen gas. Approximately 200 mL of the solution was filtered through the membrane as permeate to produce eight samples of 25 mL each. Fluxes were determined by timing and weighing samples of the permeate. The permeate samples were measured for concentrations of polyelectrolyte, chromate, and sulfate. The rejection of chromate or sulfate was determined at the midpoint where 100 mL of permeate had passed through the membrane. By knowing permeate concentrations during the run, the retentate concentrations at any point in the run were calculated from a material balance. In this work, the rejection and flux of chromate and sulfate anions were simultaneously investigated as the mixture at various specific concentration ratios of [QUAT]:[chromate]:[sulfate] by fixing the QUAT

concentration in the retentate to approximately 100, 200 and 300 mM to determine rejection of anions.

3.4.2 Equilibrium Precipitation Experiments

The equilibrium precipitation experiments were performed by mixing purified QUAT, sodium chromate and sodium sulfate solutions in 50 mL volumetric flasks. QUAT solutions which containing chromate and sulfate ion and barium chloride in separate solutions were equilibrated at 30°C for 30 minutes in the temperature controlled bath. Then the barium chloride solution was transferred into the QUAT solution containing chromate and sulfate ions. The volume of mixed solution was made to 50 mL with distilled water and allowed to equilibrate in the temperature controlled bath for 1 day. The solution which reach equilibrium precipitation was centrifuged at 2000 rpm for 30 minutes and allowed to reach equilibrium again in the temperature controlled bath for 1 day. Then precipitated solution was filtered by Whatman's filter paper (no. 40) and analyzed for the concentration of QUAT and chromate.