



CHAPTER III EXPERIMENTAL

3.1 Materials

The three scale inhibitors namely Aminotri(methylene phosphonic acid) (ATMP), Diethylenetriaminepenta(methylene phosphonic acid) (DTPMP), and Phosphinopolycarboxylic acid polymer (PPCA) were commercial scale inhibitors used in this study. ATMP and DTPMP, which are in the phosphonate category of scale inhibitors, have three and five active phosphate groups, respectively, which correspond to six and ten ionizable protons. ATMP and DTPMP were supplied by Monsanto Chemical Company. PPCA used is in the polymeric category of scale inhibitors, contains twenty five ionizable protons, and has commercial name of Bellasol S30. PPCA was obtained from Bio-Lab, Inc. The physical and chemical properties and chemical structures of these scale inhibitors are shown in Table 3.1 and Figure 3.1, respectively. These scale inhibitors, which are all commercial grade, were chosen as the model inhibitors because they contain multiple active sites and are widely used in the petroleum fields. All scale inhibitor solutions were directly prepared by dilution of those commercial scale inhibitors with ultrapure deionized water.

Barium chloride and sodium sulfate (analytical grade) both obtained from Fisher Scientific, Inc. were used as precipitating constituents to form BaSO_4 precipitates. Barium chloride and sodium sulfate solutions were prepared by dissolving a desired amount of barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and sodium sulfate in ultrapure deionized water, respectively.

Ethylenediamine tetraacetic acid (EDTA) is used as a strong chelating agent to dissolve the BaSO_4 precipitates deposited in actual oil fields (Morris and Paul, 1990). Therefore, it was used to establish the correlation between the turbidities and the amount of the forming BaSO_4 precipitates. Analytical grade EDTA in the form of disodium salt was obtained from Fisher Scientific, Inc. In the same manner, EDTA solution was prepared by dissolving a desired amount of EDTA in ultrapure

Table 3.1 Physical and chemical properties of ATMP, DTPMP, PPCA and EDTA (Monsanto, 1996).

Name	Type	MW	No. of ionizable protons	Color in solution	Specific gravity	Equilibrium acid constants
ATMP	Scale inhibitor	299	6	Colorless to pale yellow	1.3	$pK_{a1} < 2, pK_{a2} < 2,$ $pK_{a3} = 4.3, pK_{a4} = 5.46,$ $pK_{a5} = 6.66, pK_{a6} = 12.3$
DTPMP	Scale inhibitor	573	10	Amber	1.4	$pK_{a1} < 1, pK_{a2} < 1,$ $pK_{a3} = 2.8, pK_{a4} = 4.45,$ $pK_{a5} = 5.5, pK_{a6} = 6.38,$ $pK_{a7} = 7.17, pK_{a8} = 8.15,$ $pK_{a9} = 10.1, pK_{a10} = 12.04$
PPCA	Scale inhibitor	1900	25	Colorless	1.2	N/A
EDTA	Chelating agent	372	4	Colorless	1.0	$pK_{a1} = 1.996, pK_{a2} = 2.672,$ $pK_{a3} = 6.161, pK_{a4} = 10.262$

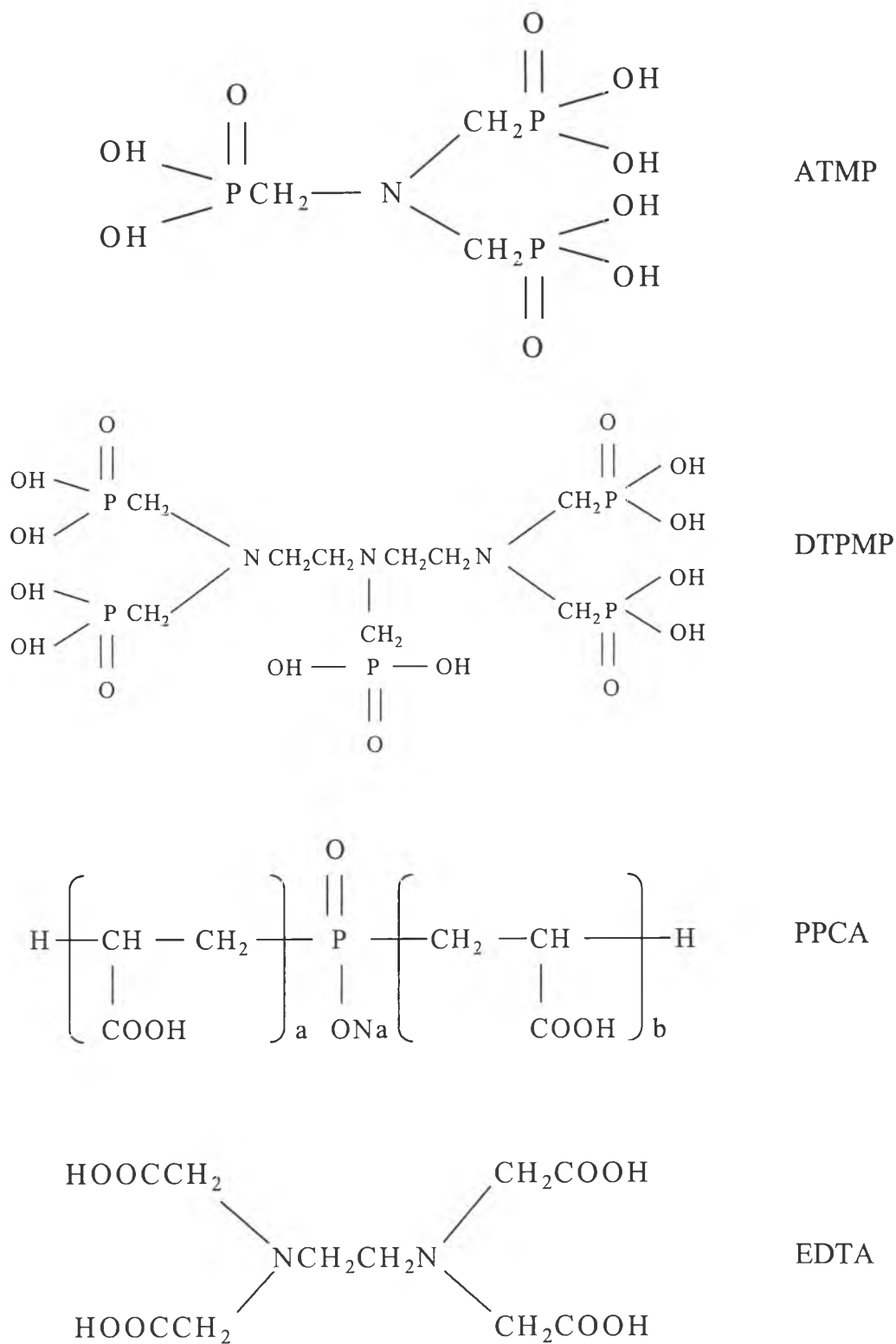


Figure 3.1 Molecular structures of ATMP, DTPMP, PPCA, and EDTA.

deionized water. The physical and chemical properties and chemical structures of EDTA are also described in Table 3.1 and Figure 3.1, respectively.

Barium sulfate (analytical grade) obtained from Aldrich Chemical Company, Inc. was used to determine the solubility in EDTA. Potassium hydroxide and concentrated hydrochloric acid (analytical grade) which were supplied by Fisher Scientific, Inc. were used to control the solution pH of all solutions at any desired values.

3.2 Batch Experiments of BaSO₄ Precipitation

The BaSO₄ precipitation experiments from two precipitating solutions of NaSO₄ and BaCl₂ were performed by using batch system. For the experiments in the presence of the scale inhibitors, the NaSO₄ solution was first mixed with the scale inhibitor solution in a series of 20 ml vials. All vials were then vigorously shaken for complete mixing. Afterwards, the BaCl₂ solution was added into the mixed solution in various proportions to NaSO₄ in order to attain various supersaturation ratios. All vials were again vigorously shaken for complete mixing. For the experiments in the absence of the scale inhibitors, the NaSO₄ solution was directly mixed with the BaCl₂ solution. It was noted that the pH of all solutions mentioned above was adjusted to a desired value before mixing. The final solution was allowed to precipitate for a desired testing time.

A small amount of such solution containing BaSO₄ precipitates after being left for a desired period of time was periodically taken to determine the turbidity by a UV-Visible Spectrophotometer (Varian, Cary 100 Bio) at 250 nm. From light scattering theory for dilute systems, the absorbance obtained from a UV-Visible Spectrophotometer measurement can be considered equivalent to the turbidity (Hiemenz, 1986). All procedures were performed at room temperature of 25°C. The turbidity data obtained from these measurements were also used to establish the correlation between the turbidity and the amount of BaSO₄ precipitates.

3.3 Determination of the Amount of BaSO₄ Precipitates

The correlation between the turbidity of the solution mixture containing BaSO₄ precipitates and the amount of the forming BaSO₄ precipitates in milligram per liter was determined. In order to achieve this correlation, it is necessary to obtain the solubility of BaSO₄ precipitates in EDTA solution first.

The solubility of the BaSO₄ precipitates in the EDTA solution was determined by using batch experiments. The excess precipitate of analytical grade BaSO₄ powder was placed into plastic centrifugal tubes. Next, a specified volume of 0.25 M EDTA solution was added into the tubes. The solution pHs used were 4.6 and 13. The solution pH of 4.6 was the original pH of the solution itself. For pH 13, potassium hydroxide was used to adjust the pH of original EDTA solution in order to completely deprotonate according to pK_a values as shown in Table 3.1. The tubes containing BaSO₄ with the EDTA solution were left on a rotator (Lab Industries, Inc.) and continuously agitated for a week in order to ensure that equilibrium was certainly achieved. After equilibrium, the supernatants were withdrawn to measure the barium concentration by using an Atomic Absorption Spectrophotometer (Perkin Elmer, 3100). The solubility of BaSO₄ in 0.25 M EDTA solution pH 4.6 and 13 was subsequently obtained. It was observed that the 0.25 M EDTA solution pH 13 had sufficient capability of completely dissolving the forming BaSO₄ precipitates in the experiments, although it was assumed that barium ions in solution entirely reacted with sulfate ions to form BaSO₄ precipitates.

The solution mixtures which were left for a desired testing time (from section 3.2) were filtered through 0.22 micron membrane filters (Millipore). The membrane filters holding the BaSO₄ precipitates were then washed with ultrapure deionized water to eliminate the remaining solution, dried in an oven at 70°C for a day, and introduced into the EDTA solution of pH 13 in centrifugal tubes. The tubes were continuously agitated on a rotator for a week to ensure that complete dissolution of the BaSO₄ precipitate was attained. Thereafter, the barium concentration contained in the solutions was subsequently determined by using an Atomic Absorption Spectrophotometer. Finally, the required correlation was achieved. This correlation was advantageously used as a calibration curve to relate

the turbidity measured by a UV-Visible Spectrophotometer to the amount of the forming BaSO₄ precipitates.

3.4 Characterization of BaSO₄ Precipitates

3.4.1 Morphology and Elemental Analysis

In order to study the morphologies of BaSO₄ precipitates, a small amount of BaSO₄ precipitate-containing solution mixtures was collected and then filtered out using 0.22 micron membrane filters. Afterwards, the membrane filters holding BaSO₄ precipitates were washed with ultrapure deionized water, dried in an oven at 70°C for a day, and then placed onto sample holders to be ready for the characterizations. The morphologies of BaSO₄ precipitates formed at different precipitating conditions were examined by using a Scanning Electron Microscope (SEM) (Philips, XL 30 FEG). The qualitative analysis of elemental compositions of the precipitates was simultaneously investigated by using an Energy Dispersive X-ray Spectroscopy (EDS, Phoenix) attached to the microscope.

3.4.2 Particle Size Distribution Analysis

A Centrifugal Particle Size Distribution Analyzer (Horiba Instruments Inc., CAPA-500) was utilized to determine the particle size distribution of the BaSO₄ precipitates formed in various conditions. A small amount of solution mixtures was also taken and introduced into sample cells. In order to disperse the BaSO₄ particles homogeneously, the ultrapure deionized water was carefully added into the cells until the appropriate level of dispersed solution was reached. The cell containing the dispersed solution was placed into the sample cell holder. Another cell filled with the ultrapure deionized water which was used as the dispersion medium was also placed into the reference cell holder. The measurements were conducted at the rotating speed of 500 rpm.

The measurement is based on the Stokes' centrifugal sedimentation theory. The relationship between the sedimentation time and the particle diameter is expressed in the Stokes' sedimentation equation for centrifugal sedimentation as:

$$D = \sqrt{\frac{18\eta_0 \ln(x_2/x_1)}{(\rho - \rho_0) \omega^2 t}} \quad (3.1)$$

where

- D = Particle diameter (cm)
- η_0 = Viscosity coefficient of fluid (cp)
- ρ = Density of sample (g/cm^3)
- ρ_0 = Density of fluid (g/cm^3)
- t = Sedimentation time (sec)
- x_1 = Distance between center of rotation and sedimentation plane (cm)
- x_2 = Distance between center of rotation and measuring plane (cm)
- ω = Rotational angular velocity (rad/sec)

In addition, this measurement can be applied for non-spherical particles. In this case, the resulting particle diameter is equivalently considered as the Stokes' diameter of spherical particles which possess the same density and have the same falling velocity in the given dispersion medium. According to the measurement, the particle size distribution and the mean diameter of BaSO_4 particles in term of Stokes' diameter were subsequently obtained.

All experimental procedures are summarized as shown in Figure 3.2.

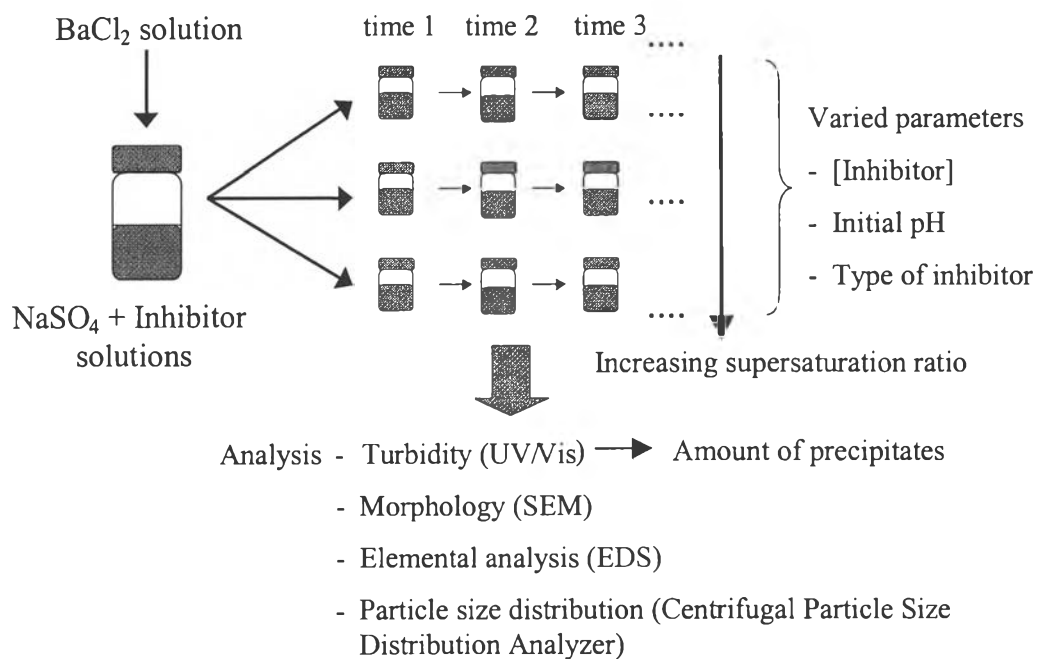


Figure 3.2 Schematic diagram of overall experiments.