

Chapter III

Experimental

3.1 Apparatus

The Infrared spectra were recorded on a Perkin Elmer 1760X. The heat stability analysis¹⁹ was analyzed in a stoppered test tube with diameter 20 mm. and length 150 mm. The reactions were carried out at 26°C. Temperature was changed by temperature controlling water bath.

3.2 Reagents and raw materials

Chemicals used in this work were obtained from various suppliers as shown in Table 3.1

Table 3.1 Source of materials

Materials	Company
Benzene , Reagent grade	Baker
Toluene , Reagent grade	Baker
Xylene , Reagent grade	Merck
Methanol , Reagent grade	Baker
Calcium Oxide	Merck
Calcium Hypochlorite 25% available chlorine	THASCO
Hydrochloric acid , Reagent grade	Baker
Sodium Hydroxide , Reagent grade	Baker

Source of materials (continued)

Materials	Company
Polyacrylate, sodium salt (homopolymer); Acusol 445N 45% Solid in water solvent, molecular weight = 4,500, pH7	Rohm and HAAS
Acrylic acid / Maleic acid (copolymer); Acusol 479N 40% Solid in water solvent, molecular weight = 70,000, pH7	Rohm and HAAS
Acrylic acid / Sulfonate / nonionic function (terpolymer); Acumer 3100 43.5% Solid in water solvent, molecular weight = 4,500 pH2.5	Rohm and HAAS
Sodium carbonate	Merck
Sodium thiosulfate	Merck
Potassium iodide	Merck
Glacial acetic acid	Merck

3.3 Prevention of calcium salt precipitation by polyacrylate

3.3.1 Determination of insoluble matter in calcium hypochlorite solution.

25% Calcium hypochlorite (2.86 g) was dissolved in 50 mL distilled water. The solution was transferred into a 1000 ml volumetric flask and then the distilled water was added to the mark. The resulting solution was shaken through and then suction filtered through a fluted whatman No.42 filter paper. The residue was dried in an oven at 100-105 °C until weight constant to obtain white powder (0.0030 g) of calcium salt precipitation.

3.3.2 Determination of insoluble matter in solution of mixed calcium hypochlorite and sodium carbonate.

25% Calcium hypochlorite (2.86 g) was dissolved in 50 mL distilled water and the solution was transferred to a 1000 mL volumetric flask. Sodium carbonate (2.12 g.) was added to the solution of calcium hypochlorite in the volumetric flask. The resulting solution was shaken through and the distilled water was added to the mark and then suction filtered through a fluted whatman No.42 filter paper. The residue was dried in an oven at 100-105 °C until weight constant to obtain white powder of calcium carbonate(1.9542 g).

3.3.3 Determination of ability the prevention of calcium salt precipitation by polyacrylate.

25% Calcium hypochlorite (2.86 g) was dissolved in 50 mL distilled water and the solution was transferred to 1000 ml. volumetric flask. The same procedure was repeated five times to obtain five solutions of calcium hypochlorite. To each solution was added polyacrylic acid, sodium salt, Acusol 445N at different amounts; 2.86g, 5.72g, 8.58g, 11.44g, 14.30g, respectively. Each resulting mixture was shaken through and then sodium carbonate (2.12 g) was added to each volumetric flask. The distilled water was added to the mark and each solution was suction filtered through a fluted whatman No.42 filter paper . The residues were dried in a oven at 100-105 °C until weight constant. The results were shown in Table 3.2

Table 3.2 Determination of the prevention of calcium salt precipitation by polyacrylate.

No.	Weight of 25% calcium hypochlorite (g)	Weight of polyacrylate (g)	Weight of sodium carbonate (g)	Weight of calcium carbonate (g)
1	2.86	2.86	2.12	1.9392
2	2.86	5.72	2.12	1.5424
3	2.86	8.58	2.12	1.1236
4	2.86	11.44	2.12	0.0036
5	2.86	14.30	2.12	0.0027

3.4 Determination of weight ratios of mixed solution.

Calcium Oxide and polyacrylate or acrylate copolymers were mixed at various weight ratios as shown in Table 3.3, 3.4, 3.5. The amounts of the two components were weighed accurately using electrical balance and mixed well in a 50 mL glass beaker. The mixture was magnetic stirred at the agitation rate of 400 rpm. The agitation was stopped after 30 min. and the sample was dissolved in 50 mL distilled water. The solution was transferred to a 500 mL volumetric flask and then the distilled water was added to the mark. The resulting solution was kept stirring for 4 hours at 400 rpm. Then the solution was filtered (by whatman No.42 filter paper). The percent of insoluble matter was then determined and shown in Table 3.3, 3.4, 3.5.

The above procedure was repeated by using calcium hypochlorite instead of calcium oxide. The amount of each reagent was shown in Table 3.3, 3.4, 3.5 and quantity of calcium hypochlorite was equal to 1000 ppm. of available chlorine after distilled water was added to the mark of volumetric flask.

Table 3.3 Acusol 445N ; Polyacrylate , Sodium salt(homopolymer)

Polymer	30%	40%	50%	60%	70%	80%	90%
Amount of polymer (g.)	0.86	1.33	2.00	3.00	4.66	8.00	18.00
Amount of calcium oxide (g)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Amount of calcium hypochlorite (g)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
% insoluble matter of mixed polymer with calcium oxide	0.82	0.61	0.47	0.25	0.15	<0.01	<0.01
% insoluble matter of mixed polymer with calcium hypochlorite	0.73	0.52	0.36	0.12	0.06	<0.01	<0.01

Table 3.4 Acusol 479N ; Acrylic acid/Maleic acid, Sodium salt(copolymer)

Polymer	30%	40%	50%	60%	70%	80%	90%
Amount of polymer (g.)	0.86	1.33	2.00	3.00	4.66	8.00	18.00
Amount of calcium oxide (g)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Amount of calcium hypochlorite (g)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
% insoluble matter of mixed polymer with calcium oxide	0.99	0.99	0.99	0.63	0.33	<0.01	<0.01
% insoluble matter of mixed polymer with calcium hypochlorite	0.82	0.69	0.43	0.19	0.06	<0.01	<0.01

Table 3.5 Acumer 3100 ; Acrylic acid/Sulfonate/nonionic function (terpolymer)

Polymer	30%	40%	50%	60%	70%	80%	90%
Amount of polymer (g.)	0.86	1.33	2.00	3.00	4.66	8.00	18.00
Amount of calcium oxide (g)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Amount of calcium hypochlorite (g)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
% insoluble matter of mixed polymer with calcium oxide	0.53	0.36	0.25	<0.01	<0.01	<0.01	<0.01
% insoluble matter of mixed polymer with calcium hypochlorite	0.32	0.19	0.08	<0.01	<0.01	<0.01	<0.01

3.5 Characterization of the chelation by Fourier-Transform Infrared Spectrophotometer (FTIR)

Each calcium Oxide (2g) was mixed with Acusol 445N (8g), Acusol 479N (8g), or Acumer3100 (3g) in three 50 mL beakers. The compositions of each mixture were determined as describe in section 3.4 that did not give any precipitation. Each resulting mixture was magnetic stirred at 400 rpm for 30 min. The pH of each solution was determined to be 11, 11, or 4 for Acusol 445N, Acusol 479N, or Acumer 3100 mixture , respectively. Each sample was transferred to barium fluoride cell with diameter 32 mm. and thickness 3 mm. The infrared spectrum of each reaction mixture was recorded using water as a background correction.

The above procedure was repeated by using calcium hypochlorite instead of calcium oxide.

3.6 The effect of solvent on reactivity of the reaction.

Polyacrylate(8g), Acusol 445N, acrylate copolymers(8g), Acusol 479N, or terpolymer(3g), Acumer 3100, was mixed with calcium oxide(2g) in a 50 ml glass beaker. Each solution was magnetic stirred at 400 rpm for 30 min. Each sample was dissolved with a variety of solvents (50 mL), water , methanol , benzene , toluene or xylene and then all solution was transferred to a 500 ml volumetric flask and diluted to mark with the according solvent. The resulting solution was kept stirring for 4 hours at 400 rpm. and was then suction filtered through a No 42 Whatman filter paper. The residue was dried at 100-105 °C and the percent of insoluble matter were determined.

The above procedure was repeated by using calcium hypochlorite instead of calcium oxide.

3.7 The effect of pH on reactivity of the reaction.

Polyacrylate(8g), Acusol 445N, acrylate copolymers(8g), Acusol 479N, or terpolymer(3g), Acumer 3100, was mixed with calcium oxide(2g) in a 50 ml glass beaker. Each solution was magnetic stirred at 400 rpm for 30 min. Each sample was dissolved with 50 ml distilled water and transferred to a 500 ml volumetric flask and dissolved with the distilled water until near the mark and adjust pH to 3, 7, 11, 14 by HCl or NaOH and then distilled water was added to the mark. The remaining solution was kept stirring for 4 hours at 400 rpm. and was then suction filtered through a No 42 Whatman filter paper. The residue was dried at 100-105 °C and the percent of insoluble matter were determined.

The above procedure was repeated by using calcium hypochlorite instead of calcium oxide.

3.8 The effect of temperature on reactivity of the reaction.

Polyacrylate(8g), Acusol 445N, acrylate copolymers(8g), Acusol 479N, or terpolymer(3g), Acumer 3100, was mixed with calcium oxide(2g) in a 50 ml glass beaker. Each solution was magnetic stirred at 400 rpm for 30 min. Each sample was kept at the required temperature (such as 25 , 50 , 90 °C) for 30 min. After that all sample was dissolved with 50 ml distilled water and transferred to a 500 ml volumetric flask and then distilled water was added to the mark. The resulting solution was kept stirring for 4 hours at 400 rpm. and was then suction filtered through a No 42 Whatman filter paper. The residue was dried at 100-105 °C and the percent of insoluble matter were determined.

The above procedure was repeated by using calcium hypochlorite instead of calcium oxide.

3.9 Determination of Heat stability.

Polyacrylate(8g), Acusol 445N, acrylate copolymers(8g), Acusol 479N, or terpolymer(3g), Acumer 3100, was mixed with calcium hypochlorite(2g) in a 50 ml glass beaker. Each solution was magnetic stirred at 400 rpm for 30 min. After that all sample was dissolved with 50 ml distilled water and transferred to a 500 ml volumetric flask and then distilled water was added to the mark. The resulting solution was kept stirring for 4 hours at 400 rpm. This solution was divided into 2 portions. The first portion (20 g.) was used to determine the percent of available chlorine by TIS 225-2533 method¹⁹. The second portion (25 g) was transferred to a test tube (20 mm. diameter and 150 mm. length). The test tube was opened and heated at 70 ± 2 °C for 4 hours. It was then left stand at room temperature for 10 min. The resulting mixture was analyzed the percent of available chlorine by TIS 225-2533 method¹⁹.