CHAPTER III

EXPERIMENTAL

3.1 Materials and Equipments

Extractant A (Sigma-Aldrich) in chloride form was used for preparing extractant B (extractant A in hydroxide form). Sodium hydroxide (p.a. grade, Merck) was used to react with extractant A to obtain extractant B. Silver nitrate (analytical grade, Merck), sodium chromate (anhydrous, extra pure, Riedel-de Haen) and ethanol (99.99 %, RCI Labscan, Thailand) were used in a titration of chloride ions remaining in extractant B after the conversion.

Formic acid (85 %, Carlo Erba), acetic acid (99.7 %, RCI Labscan), sodium glycolate (analytical grade, Tokyo Chemical Industry), and sodium oxalate (puro grade, Carlo Erba) were used as heat stable salts (HSS). Monoethanolamine (MEA) (99.5 %, Merck) was mixed with HSS to simulate the industrial condition of degraded MEA solution. Alcohols as a polar diluents suggested by Tamada *et al.* (1990), Yang *et al.* (1991), and Grzenia *et al.* (2008) that alcohols can improve the extraction efficiency by stabilizing the carboxylic acid – amine complex formation. Thus, diluents used in this study were 1-octanol (≥99.5 %, Fluka), 2-ethyl-1-hexanol (≥99 %, Fluka), 1-heptanol (≥99 %, Fluka), 1-hexanol (≥99 %, Merck), and 1-pentanol (≥98 %, Fluka).

All HSS solutions were analyzed by using a high performance liquid chromatography (HPLC), which consisted of pump (LC-20AD, Shimadzu Scientific Instrument); column oven (CTO-10AS VP, Shimadzu Scientific Instrument); and UV detector (SPD-20A, Shimadzu Scientific Instrument) at 210 nm. A HPLC column was C18 5u, 150mm x 4.6mm (Apollo, Alltech). A mobile phase for HPLC analysis was prepared according to Supap *et al.* (2006). The mobile phase was 0.05 M dipotassium phosphate (A.C.S. grade, Carlo Erba) which the solution pH was adjusted to 2.6 by adding phosphoric acid (A.C.S. grade, J.T. Baker).

3.2 Experimental Procedures

The experiment procedures including extractant preparation, HSS extraction, and back extraction followed previous work of Akkarachalanont *et al.* (2010).

3.2.1 Extractant Preparation

An equal volume of extractant A in chloride form was converted to hydroxide form by reacting with 2 M sodium hydroxide (NaOH). The solution mixture was stirred on the magnetic stirrer at a speed of 1250 rpm for 30 minutes and left overnight to complete the reaction. After reaching the phase equilibrium, the organic phase of extractant B (chloride and hydroxide form) was separated from NaOH solution for further conversion. The conversion of extractant A (the organic fraction from previous conversion) to extractant B was repeated 10 times. The chloride concentration in the extractant B was determined by titration known as Mohr's method. Extractant B was dissolved in ethanol and titrated with 0.05 M of silver nitrate ($AgNO_3$), and 0.25 M sodium chromate (Na_2CrO_4) was used as an indicator. Water in extractant B was removed by using a rotary evaporator at a temperature of 60 ^{o}C for 6 hours. After evaporation, extractant B was filtered through filter paper no.1 to remove any remaining salts. A final concentration of extractant B was determined by Mohr titration method.

3.2.2 HSS Aqueous Solution Preparation

A HSS stock solution of each 10,000 ppm of formate, acetate, glycolate and oxalate in aqueous solution was prepared. A HSS 1,000 ppm solution without MEA was prepared by diluting the HSS stock solution 10 times with deionized water. A 1,000 ppm formate in 30 wt% MEA solution was prepared by diluting 98.2 μL of 85.7 wt% formic acid into 100 mL of 30 wt% MEA solution. Glycolate and oxalate (1,000 ppm each) were prepared by diluting each 0.101 g of sodium glycolate and sodium oxalate into 100 mL of 30 wt% MEA solution.

3.2.3 HSS Extraction

The HSSs extraction in the absence and presence of extractant B in various diluents was studied by using the HSS solution without MEA in the aqueous phase and the alcohol diluents as organic phase extractant. One molar of extractant B was calculated based on the average of conversion of A to B. The extraction was done at the room temperature by mixing equal volume of 10 mL 1,000 ppm HSS solution (formate, acetate, glycolate, and oxalate) with 30 wt%/without 30 wt% MEA and 10 mL of each diluent (1-octanol, 2-ethyl-1-hexanol, 1-heptanol, 1-hexanol, and 1-pentanol). The mixture of 2 phases was stirred at a speed of 1250 rpm for 10 minutes and left overnight for complete phase separation and to reach the equilibrium in the separator funnel.

The mixture of each 1,000 ppm HSS in 30 wt% of MEA was also extracted at room temperature (30 ^{o}C), 45 ^{o}C and 60 ^{o}C to study the effect of extraction temperature. The mixture of aqueous and organic phase was kept under the constant temperature at 45 ^{o}C and 60 ^{o}C in a paraffin bath, left overnight to complete phase separation and to reach the equilibrium.

All of the aqueous phase in each experiment was separated from organic phase by a separating funnel and then analyzed by HPLC to determine a HSS concentration left in the aqueous phase. The organic phase was kept for further back extraction.

3.2.4 Back Extraction

The extraction of organic phase of 10 mL which contained the extracted HSS and 1 M extractant B in diluents was reacted with 10 mL of 4 M sodium hydroxide. The mixture was stirred for 10 minutes at a speed of 1250 rpm and left overnight to reach phase equilibrium. Extractant B is restored to the active extractant in a diluents phase again for reuse and the extracted HSS gets back into the aqueous phase which was kept for the HPLC analysis for measuring the extracted HSS concentration.

3.2.5 Heat Stable Salts Concentration Analysis

The concentration of HSS remaining in the aqueous phase was analyzed by high performance liquid chromatography (HPLC) using UV detector at 210 nm wavelength. The mobile phase was fed at flow rate of 0.2 mL/min into the column at a column temperature of 40 °C.

Quantitative analysis of HSS was done using a calibration curve. For HSS in 30 wt% MEA solution and 4 M NaOH, the aqueous solution was diluted 10 times with deionized water before analysis to prevent the MEA and NaOH overloading effect. In the absence of MEA, the calibration curves of HSS standard solutions were prepared at the concentration of 5, 10, 50, 100, 500, 1,000, 1,500, and 2,000 ppm and in the 3 wt% MEA the calibration curves for formate, and glycolate with oxalate were done at the concentration of 5, 10, 25, 50, and 100 ppm.