CHAPTER III
EXPERIMENTAL

3.1 Chemicals and Equipment

Monoethanolamine (MEA) (99.5 %, Merck) mixed with the neutral MEA degradation products to simulate the industrial condition of degraded MEA solution. The aqueous solutions were prepared by dissolving 1,000 ppm of each neutral MEA degradation solution, i.e. imidazole (99 %, Merck), N-acthylethanolamine (88.6 %, Sigma-Aldrich), 2-oxazolidone (98 %, Sigma-Aldrich) and N-(2-hydroxyethyl)-succinimide (95 %, Sigma-Aldrich)) in deionized water or 5 kmol/m^3 of MEA solution. 2-Ethyl-1-hexanol (≥99 %, Fluka) was used as an alcohol diluent.

Aliquat-336 (74 %, Sigma-Aldrich) in chloride form was used for preparing extractant. Aliquat-336 in hydroxide form was prepared by using sodium hydroxide (p.a. grade, Merck) to react with Aliquat-336 in chloride form. Silver nitrate ($AgNO_3$, analytical grade, Merck) as a titrant and anhydrous sodium chromate (Na_2CrO_4, extra pure, Riedel-de Haen) as an indicator were used to determine the conversion of chloride to hydroxide form in the titration method (Mohr's method).

All the neutral MEA degradation products were analyzed by using a gas chromatography- with flame ionization (GC-FID). Chromatographic capillary column was DB-waxert (high-polarity) having cross-linked polyethyleneglycol as a stationary phase. The column dimension was 1-μm thickness × 320-μm i.d. × 30-m length.

3.2 Experimental Procedures

3.2.1 Extractant Organic Solution Preparation

Quaternary amine extractant can be prepared by conversion from chloride form of Aliquat-336 to hydroxide form using equal volume of 2 M sodium hydroxide (NaOH). The solution was mixed and stirred by magnetic stirrer at 1250 rpm of speed for 30 minutes and equilibrated overnight to complete a phase separation in a separatory funnel. The extractant phase was separated and the

procedure for the second conversion cycle was repeated by adding NaOH solution and following the above procedure. This conversion was repeated for 13 times.

Water in the extractant was removed under vacuum by using rotary evaporation method (model RLL, BÜCHI Labortechnik AG, Flawil, Switzerland) at 60 °C for 7 hours and sodium chloride (NaCl) presence in the conversion reaction was removed by filtering paper no.1. The chloride concentration remaining in the extractant origin was determined by the titration using Mohr's method. The extractant was dissolved in ethanol and titrated with 0.05 M $AgNO_3$ using 0.25 M Na_2CrO_4 as an indicator.

3.2.2 Preparation of Neutral MEA Degradation Products in Aqueous Solution

The neutral MEA degradation simulation was prepared as a stock solution of each 1000 ppm of imidazole, N-acthylethanolamine, 2-oxazolidone and N-(2-hydroxyethyl)-succinimide. Table 3.1 is properties of each MEA degradation product in an aqueous solution.

Table 3.1 Properties of the neutral MEA degradation in aqueous solution

Properties	Molecular Formula	Molecular Weight	Density (g/cm^3)	Concentration (ppm)
Imidazole	$C_3H_4N_2$	68.07	1.03	1000
N-acethylethanolamine	$C_4H_9NO_2$	103.12	1.12	1000
2-Oxazolidone	$C_3H_5NO_2$	87.07	1.23	1000
N-(2-hydroxyethyl)-succinimide	$C_6H_9NO_3$	143.3	1.30	1000

In case of neutral MEA degradation products with MEA, they were prepared in 30 wt% MEA in aqueous solution.

3.3 Neutral MEA Degradation Product Extraction

One molar of extractant in 2-ethyl-1-hexanol was calculated based on the average conversion of Cl to OH. The extraction was done by mixing equal volume of 5 mL 1,000 ppm the neutral MEA degradation product solution (imidazole, N-acethylethanolamine, 2-oxazolidone and N-(2-hydroxyethyl)-succinimide with/ without 30 wt% MEA to 5 mL of 1 M extractant in 2-ethyl-1-hexanol. The mixture of 2 phases was shaken at a speed of 250 rpm using a shaker (SI-600, JEIO Tech, Korea) for 10 minutes, left overnight (24 h.) in a water controlled bath to complete extraction (equilibrium extraction) and centrifuge (HERMLE Z 383) at 5000 rpm for 30 minutes to complete the two phases separation.

3.3.1 Effect of Diluent Alone

The diluent, 2-ethyl-1-hexanol may have influence on the extraction, so a background extraction using diluent alone was also tested by mixing equal volume ratio (5 mL) of diluent to the neutral MEA degradation product solution with and without MEA solution and left overnight to complete the separation.

3.3.2 Effect of Extractant in 2-Ethyl-1-Hexanol

One molar of extractant in 2-ethyl-1-hexanol was used in the extraction of the neutral MEA degradation product solution with/without 30 wt% MEA. It was investigated at various extraction temperature (25 °C, 40 °C and 60 °C). The two phases mixing was shaken at a speed of 250 min^{-1} for 10 minutes, and left overnight in a water bath (Model WNB 14, Memmert, Germany) for complete extraction (equilibrium extraction).

3.3.3 Effect of CO_2 Loading

The neutral MEA degradation product solution with 30 wt% MEA was loaded with CO_2 at 25 °C before contacting with the extractant solution. The effect of CO_2 loading (0.05, 0.10 and 0.30 $kmol/m^3$) was studied.

All neutral MEA degradation products in the aqueous phase were separated to organic phase and analyzed by GC-FID for determining the neutral MEA degradation product concentration remain in the aqueous phase.

3.4 Analysis of Neutral MEA Degradation Products Using GC-FID Technique

The neutral MEA degradation products concentration remaining in the MEA aqueous solution was analyzed by gas chromatography with flame ionization (GC-FID). Chromatographic capillary column was DB-wax (high-polarity) having cross-linked polyethyleneglycol as a stationary phase. The introduction of sample was done by using a manual injector. A 1-μL of sample was injected at the GC inlet set at 250 °C using a split injection mode with a split ratio of 2:1. The GC oven was initially set at 120 °C and ramped to 240 °C at a rate of 7.15 °C/min. The temperature was kept at 240 °C for 10 minutes to ensure complete elution of all degradation products. Ultra-high-purity (UHP) grade helium was used as a carrier gas and was regulated at a constant flow rate of 1 mL/min. Standard mixture was containing 1000 ppm of each imidazole, N-acetylethanolamine, 2-oxazolidone and N-(2-hydroxyethyl)-succinimide, in MEA solution were carefully prepared and analyzed 3 times using the GC-FID conditions described earlier. The standard curves were generated by plotting averaged areas and the corresponding concentrations of the neutral MEA degradation products. Similar procedures were applied to the samples obtained before and after extraction. The exact concentration of the neutral MEA degradation products were identified by calibrating the averaged peak areas with the corresponding standard curves.