CHAPTER FOUR

METHODOLOGY

4.1 INTRODUCTION

Aqueous alkanolamines have been widely used for the capture and removal of CO_2 from acid gases. This chapter presents an experimental procedure for the determination of the equilibrium solubility of CO_2 in aqueous 2-methylaminoethanol (MAE), one of the newest secondary amines that can be promoted as a potentially good absorbent for capturing CO_2 from atmospheric flue gases. The absorption is done using a single cell stirred reactor in which nitrogen and carbon dioxide are mixed with the amine solution at different temperatures. The pH is monitored with time until the equilibrium is reached. The amount of CO_2 absorbed is precipitated as carbonate and determined by chemical analysis.

4.2 REAGENTS

4.2.1 Methylaminoethanol

The alkanolamine used in this work is 2-methylamino ethanol (MAE) liquid from ACROS Organics with purity 99%. The formula of MAE is $CH_3NHCH_2CH_2OH$. Its properties are given in Table 4.1. The amine was used as received without further purification. The solution is prepared by adding distilled water to the pure amine to the desired concentration. The solution concentration is then determined by titration with 1.0 $mol.dm^{-3}$ HCl standard solution for concentration validation. Necessary precautions are taken to avoid any exposure of the sample to the air during the preparation period.

The concentration is verified every two weeks to cater for any evaporation that might occur which could affect the pH of the solution.

Table 4.1**:** Chemical and physical properties of MAE (chemicalland21.com)

Property	**MAE**
Synonyms	2-(methylamino)ethanol (MAE)
Structure	$CH_3NHCH_2CH_2OH$
Molecular Weight (g/mol)	75.11
Density ($g.cm^{-3}$)	0.935
Melting Point (^oC)	-3
Boiling Point (^oC)	155-156
Flash Point (^oC)	90
Vapour Pressure, mmHg at 20^oC	0.7
pH , 1M	11.6
Physical State	Liquid
Colour	Colourless
Stability	Stable under ordinary conditions
Solubility	Soluble and Miscible

4.2.2 Barium Chloride

Solid Barium Chloride, ($BaCl_2$) is from Merck Chemicals. The solution is prepared by adding distilled water to the solid to the desired strength (1.0 $mol.dm^{-3}$) then adding equal volume of 1.0 $mol.dm^{-3}$ sodium hydroxide solution. The solution is filtered before use to remove un-dissolved solid particles.

4.2.3 Hydrochloric Acid and Sodium Hydroxide

Standard hydrochloric acid, (HCl) and sodium hydroxide, (NaOH) solutions are obtained from Merck Chemicals, and prepared according to instructions.

4.2.4 Nitrogen and Carbon Dioxide Gases

Pure, oxygen free N_2 and CO_2 gases are purchased from a local company with minimum purity of 99.8%. For the 1% CO_2 – N_2 gas mixture, a ready mixed gas cylinder from MOX-LINDE Gases Sdn. Bhd. is used.

4.2.5 Filter Paper

ALBET 502 filter papers are used throughout this experiment to ensure all solid carbonates are collected during the analysis section.

4.2.6 Water

Distilled water was used throughout the experiment

4.3 EXPERIMENTAL SETUP

The experiment setup for CO_2 solubility measurements is shown in Figure 4.1. It is made of a double-jacketed stirred cell reactor, 100 ml in volume, made of resistant glass. The reactor is equipped with a Metrohm 728 magnetic stirrer and a condenser, which is equipped with a water circulator. Temperature is measured by a J-type thermocouple and controlled by Lab Companion RW-0525G type water circulator. A pressure transducer is used to measure the total pressure in the reactor and a pH probe linked to Metrohm^R 719S auto-titrator is used to monitor and record the pH of the solution as a function of time. Another Metrohm^R 716MS auto-titrator is used to determine the final amine concentration. Both autotitrators are controlled by Tinet^R software. The feed gas is a mixture of CO_2 and N_2 with controlled flow rate using a set of Brooks[R] gas mass flow meters model 5850E for N_2 and 5850C for CO_2 and controlled by a 4 channel Brooks mass flow controller model 0154E. The same experimental setup has been used by previous investigators in this laboratory, Baki (1998), Benamor (2006), Si Ali (2007) and Hosseini (2009).

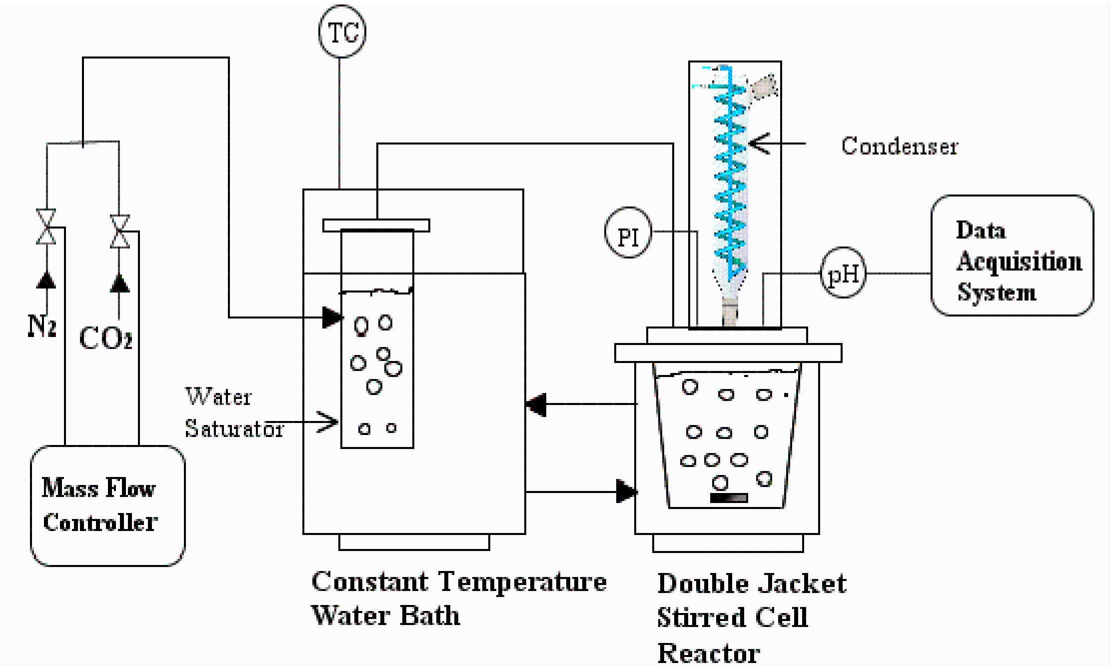

Figure 4.1: Screening apparatus for CO_2 absorption

4.4 EXPERIMENTAL PROCEDURE

In a typical run, 50 ml of the amine solution is charged into the reactor and maintained at the set temperature for about 10 min. The system is then purged with nitrogen gas for a few minutes to remove any possible contamination that might have been present from previous experiments. The gas blend, which is in the desired proportions and at the desired flow rate, is fed into the water saturator then to the bottom of the reactor through a sparger. The reaction of CO_2 with amine solvents causes a decrease in alkalinity. Thus, the variation of pH of the solution is measured continuously with time until an equilibrium is reached and maintained for at least 30 minutes. The final pH of the solution is then recorded to be used in further calculations. Figure 4.2 shows a typical plot of the variation of pH with time during the reaction of CO_2 with the amine.

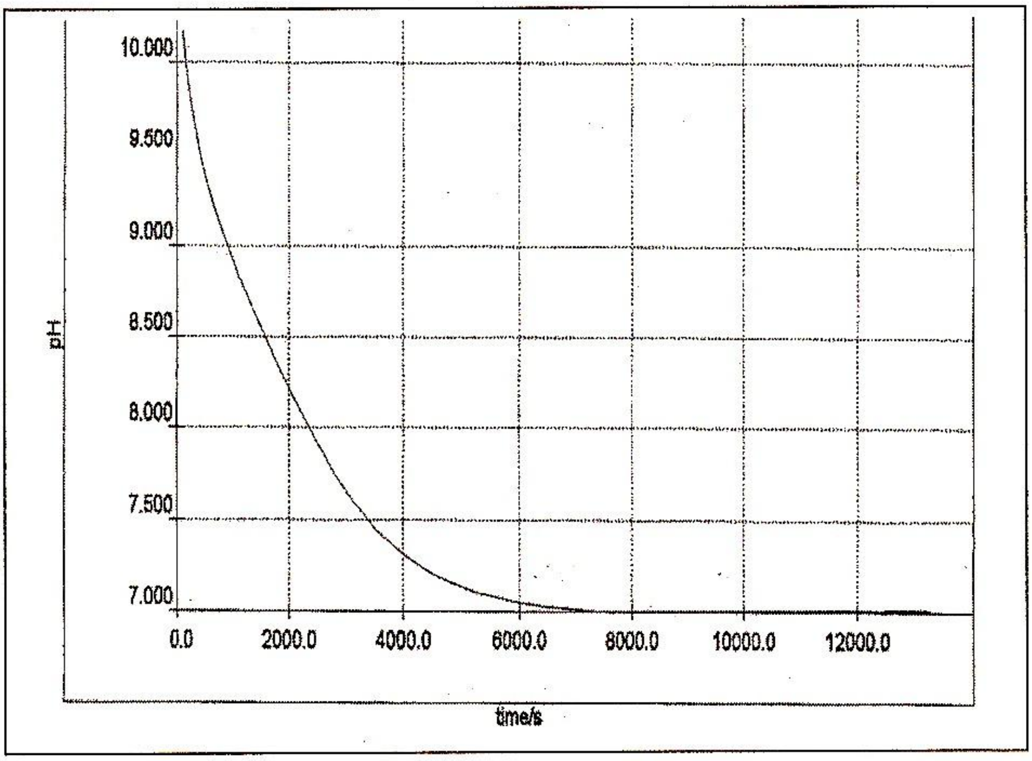

Figure 4.2: Typical curve for variation of pH with time during CO_2 absorption

Samples of carbonated amine are taken for analysis as follows;

- 10 ml is titrated with standard HCl solution to determine the concentration of the carbonated amine. Figure 4.3 shows the variation of pH with HCl volume and the end-point of the solution.
- 5 ml is titrated with standard NaOH solution to find the total moles of OH^- in solution. This can then be used to estimate CO_2 loading. Figure 4.4 shows the variation of pH with the volume of NaOH added and the end point of the solution.
- Three 10 ml samples of the carbonated amine each is reacted with 50 ml

solution containing of 0.5 mol.dm^{-3} barium chloride and 0.5 mol.dm^{-3} sodium hydroxide solutions. The three samples are kept on a heated magnetic stirrer at 70 ^{o}C and atmospheric pressure for three hours. The sodium hydroxide is used to convert all free dissolved gas into non-volatile ionic species and the barium chloride is used to precipitate all absorbed carbon dioxide in the carbonated amine solution as white barium carbonate crystals. Each sample is then settled, filtered and the residue is washed with distilled water to remove any traces of sodium hydroxide, and titrated with standard HCl. The volume of HCl used to neutralize the carbonate residue is determined using the first derivative of the titration curve, corresponding to the last end point. Figure 4.5 shows the variation of pH of the barium carbonate mixture with the volume of HCl added and the end point of the solution.

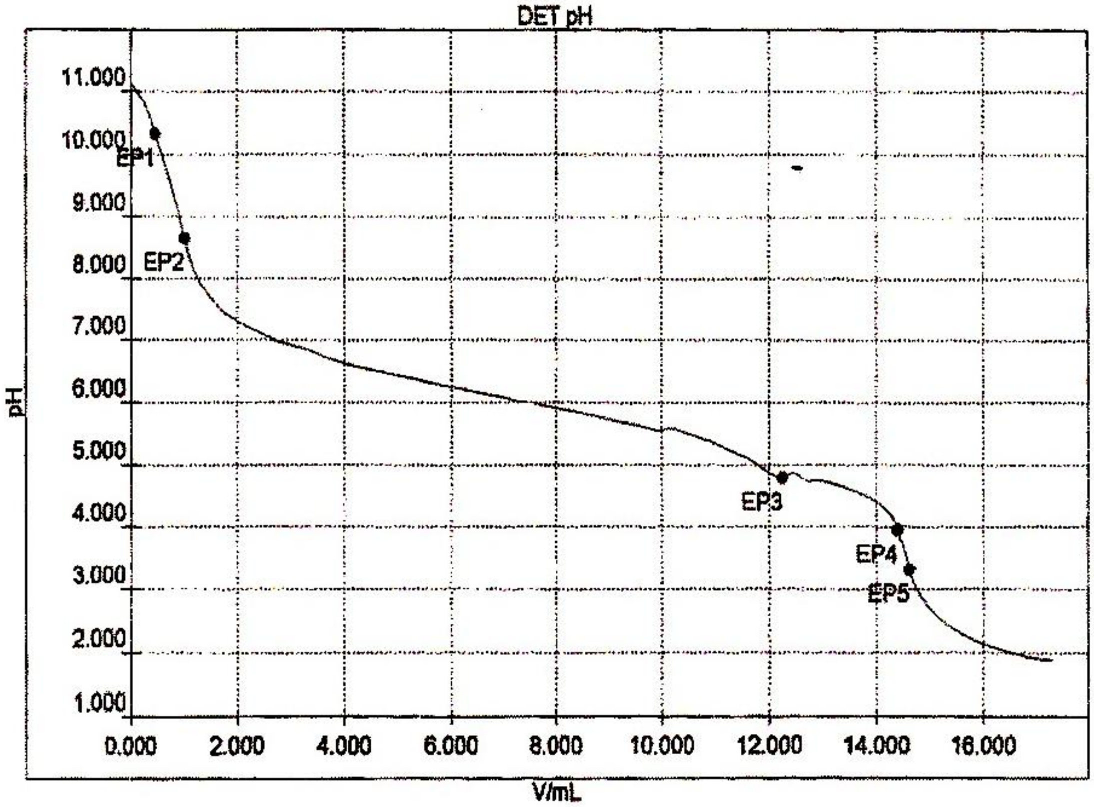

Figure 4.3: Typical curve for titration of carbonated amine with standard HCl solution

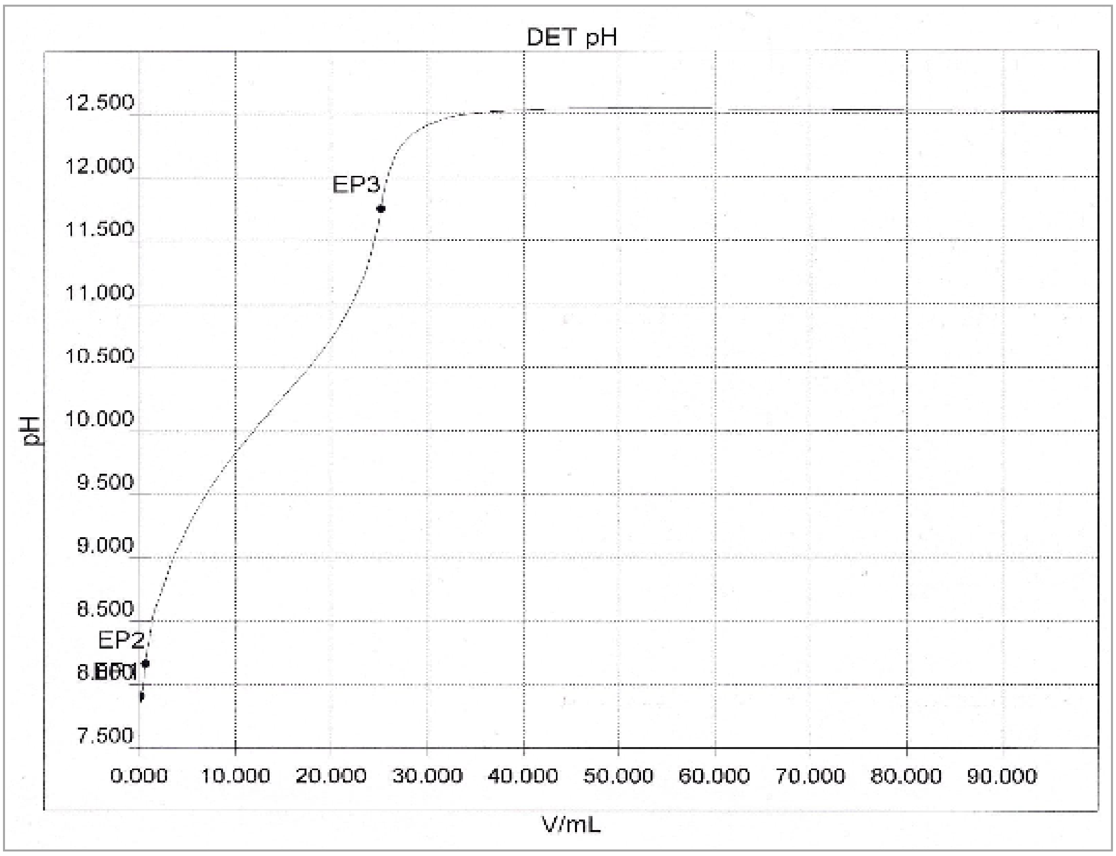

Figure 4.4: Typical curve for titration of carbonated amine, with standard NaOH solution

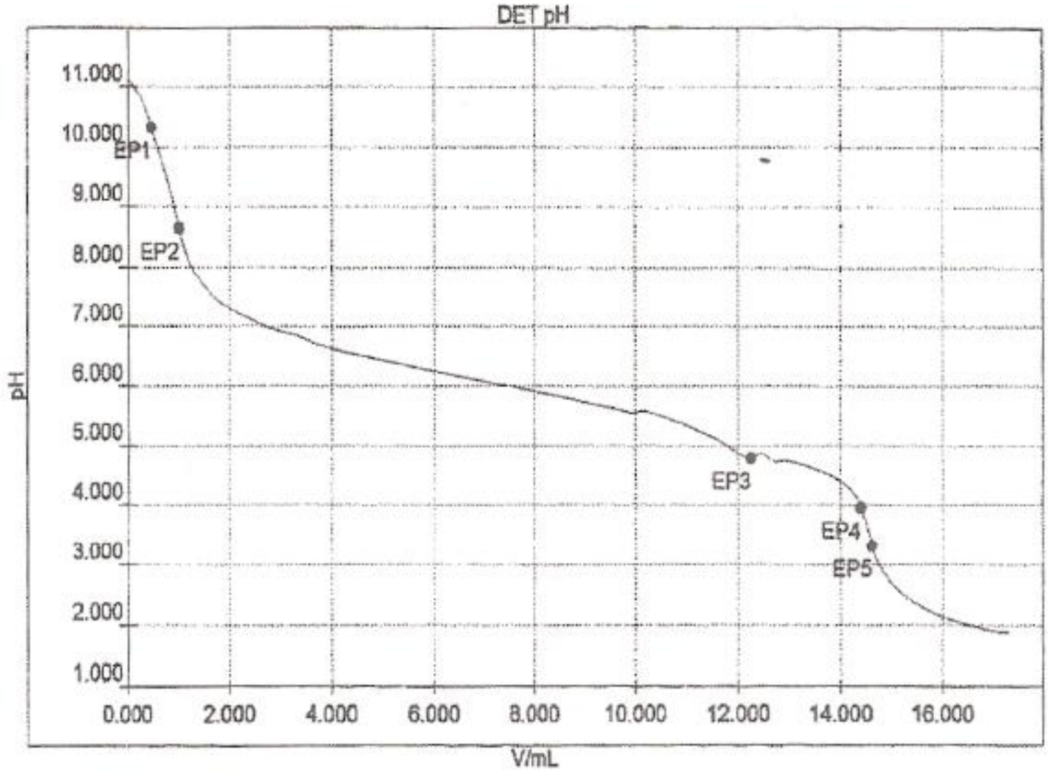

Figure 4.5: Typical curve for titration of carbonated amine, barium chloride mixture with standard HCl solution

4.5 EQUATIONS

The amine solution react with CO_2 to form protonated amine ($RR\square NH_2^+$), bicarbonate ion (HCO_3^-) and carbamate ion ($RR\square NCOO^-$) as follows;

$$CO_2 + 2RR\square NH \rightleftharpoons RR\square NH_2^+ + RR\square NCOO^- \qquad (4.1)$$

Other reactions that may occur in solution are;

$$RR\square NCOO^- + H_2O \rightleftharpoons HCO_3^- + RR\square NH \qquad (4.2)$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \qquad (4.3)$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \qquad (4.4)$$

$$H^+ + OH^- \rightleftharpoons H_2O \qquad (4.5)$$

The carbonate ions will then be precipitated as barium carbonate by reaction with excess barium chloride according to the following equation;

$$CO_3^{2-} + Ba^{2+} \rightarrow BaCO_3 \qquad (4.6)$$

The precipitate is then titrated with standard HCl solution as follows;

$$BaCO_3 + 2HCl \rightarrow BaCl_2 + H_2O + CO_2 \qquad (4.7)$$

4.6 CALCULATIONS

4.6.1 Determination of Amine Concentration

The carbonated amine concentration determined from titration with standard HCl is compared with the initial amine concentration. The difference should be less than 5% to justify the assumption of constant total amine concentration throughout the experiment.

4.6.2 Determination of CO_2 Partial Pressure

Since the gas stream is bubbled through a water saturator, it is assumed to be saturated with water vapour. The CO_2 partial pressure at equilibrium was calculated by subtracting the water vapour pressure from the total pressure of the system, as follows;

$$P_{CO2} = N_{CO2}(P_{Total} - P_{H2O}) \tag{4.8}$$

where P_{CO2} is CO_2 partial pressure in kPa, N_{CO2} is the mole fraction of CO_2 in the inlet gas stream, P_{Total} is the total pressure of the gas stream in kPa, and P_{H2O} is the water saturation pressure in kPa

4.6.3 Determination of CO_2 Loading

The average loading is calculated from the results of the titration of barium carbonate residue obtained from the three samples according to the following equation;

$$\alpha = \frac{V_{HCl}M_{HCl}}{2V_{sample}M_{Amine}} \tag{4.9}$$

where α represents CO_2 loading in mole CO_2 per mole amine, V_{HCl} is the volume of HCl needed to neutralize the basic species in ml, M_{HCl} is the molarity of HCl used for neutralization. V_{sample} is the volume of each of the three samples, and M_{Amine} is the molarity of the amine solution in mole.dm^{-3}.

4.6.4 Determination of Carbamate Ion Concentration

When equilibrium is reached, an aliquot sample of 5.0 ml. of the loaded amine solution was taken from the reactor and titrated with a standard 1.0 M NaOH using the computer-controlled autotitrator. The volume of NaOH required to neutralize the carbonated amine sample is used to determine the carbamate ion concentration using the method used by Haji-Sulaiman *et al*. (1996), and Benamor & Aroua (2005) as follows;

$$[MAECOO^{-}] = 2(\alpha . M) - B \tag{4.10}$$

where B is the concentration of NaOH at the end point which can be found from the titration as follows;

$$B = \frac{M_{NaOH} . V_{NaOH}}{V_{sample}} \tag{4.11}$$