

CHAPTER 3

EXPERIMENTAL METHODS AND TECHNIQUES

This chapter describes the materials used. Techniques and procedures adopted in this work to generate the experimental data on the density of aqueous piperazine, activated DEA and CO₂ solubility in this system.

3.1 Materials.

The alkanolamines used in this work were anhydrous piperazine crystal with stated purity of 99 % from Acros Chemical Company, Belgium and DEA with 98 % purity from Merck Company. Barium chloride is a Merck reagent grade with 99 % purity. Standard solutions of sodium hydroxide and hydrochloric acid were purchased from J.T. Baker, Company. All chemical were used as purchased without any further treatment. The gases, CO₂, with minimum purity of 99.8 % and oxygen-free nitrogen were purchased from a local company, Sitt Tatt. Glass microfibre filter paper GF/C, Whatman, was used throughout this research to ensure all the solid carbonate was collected in the analysis section.

3.2 Solutions preparation.

The aqueous alkanolamine solutions were prepared by adding distilled water to pure alkanolamine to the desired strength. Prior to solution preparation, the distilled water was degassed by boiling to remove any dissolved CO₂. The aqueous alkanolamine solution concentration was determined by titration with 1.0 M of HCl standard solution. All the aqueous alkanolamine used were found to be within 1 % of the desired concentration. Necessary precautions were taken to avoid exposure of the sample to the air during the preparation period.

3.3 Method and procedures

3.3.1 Density measurements of aqueous piperazine, DEA-H₂O , DEA-PZ and activated DEA

The density measurements were performed using an Anton Paar DMA 4500 Density Meter with an accuracy of 5×10^{-5} g/cm³. Two integrated Pt100 platinum thermometers were used to provide high accuracy of temperature control and are traceable to international standards. The density meter was calibrated using degassed distilled water before each series of measurements were made to ensure accurate density readings. To check the reliability of the apparatus, the density measurement of 20 % mass DEA was measured at 40, 50 ,60 °C and compared with the density data that have been reported in the literature. The results are in good agreement with the densities reported by Rinker et al. (1994) and Hsu et al (1997) as indicated in Table 4.1.

Densities of aqueous piperazine solutions, DEA-H₂O, DEA-PZ and activated DEA with amine total concentration of 2 M and 4 M were measured at temperature range of 30 to 80 °C with piperazine concentration varying from 0.1 M to 1 M.

3.3.2 Solubility of carbon dioxide into aqueous piperazine and activated DEA

3.3.2.1 Experimental apparatus

The experiments were conducted in a laboratory double-jacketed stirred cell reactor with an inside diameter 60 mm and height of 85 mm. The cell body is made up from a glass with a cover which has 4 ports to provide connection to the reaction gas inlet, temperature sensor, pressure sensor in the liquid phase and also an outlet for unreacted gas. To control the temperature, the reactor was connected to a water bath with accuracy of ± 0.5 °C. A magnetic stirrer was used to disperse the reaction gas in the aqueous amine solution. A thermocouple, pressure transducer and pH meter were used to monitor the operating conditions. The gases, pure CO₂ and oxygen-free nitrogen gas were supplied from separate gas cylinders and their flowrate was regulated by a Brooks mass flow controller before entering the reactor. Figure 3.1 shows the schematic diagram of the experimental set-up.

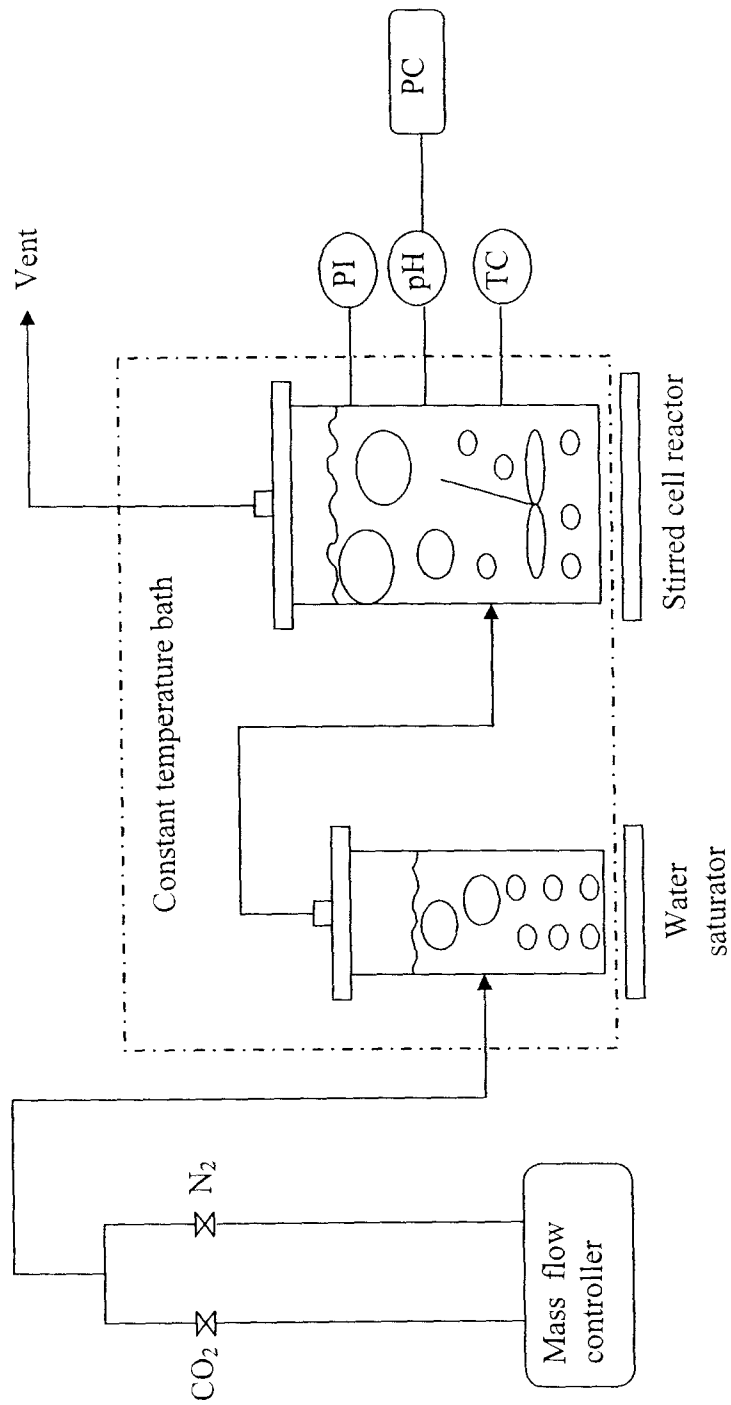


Figure 3.1: The schematic diagram of the equipment.

3.3.2.2 Experimental procedure

The aqueous piperazine solutions were prepared by mixing distilled water with anhydrous piperazine crystal of 99 % purity to the desired strength. About 150 cm³ of the solution was charged to the reactor for each run. Heat was supplied to the reactor from a water bath. Brooks mass flow controllers were used to regulate the flow of carbon dioxide and oxygen-free nitrogen gas from a cylinder. The reaction gas fed into the reactor depends on the desired CO₂ partial pressure, which can be pure CO₂ or a mixture with nitrogen gas. Once the temperature had stabilized the reaction gas was passed through a water saturator before introducing it into the solution by bubbling the desired proportion of gas mixture. Exhaust from the reactor was vented to the atmosphere. The reactor was connected to a PC controlled data acquisition system to monitor the variation of pH during the reaction where the changes of pH were recorded continuously. It is necessary to calibrate the pH meter prior to any experiment to ensure the sensitivity of the pH electrode is consistent at all times. The pH decreases gradually as more CO₂ gas is absorbed by the aqueous piperazine solution. The experiment ended when equilibrium was reached, indicated by the constant pH for at least 30 minutes. The time required to reach equilibrium depends on the reacting gas composition as well as its flow rate and solution concentration. Rapid flow rates have the advantage of allowing equilibrium to be reached sooner; however, too rapid flow rate results in excessive removal of water and hence appreciable change in the final amine concentration. Once equilibrium was reached, some liquid samples were withdrawn from the reactor to be analyzed by the titration method to determine the amine concentration, CO₂ loading and total

carbamate concentration. Figure 3.2 shows a typical pH obtained during the experiment. The experiment procedure was repeated for other solution concentrations. The same procedure was used for the piperazine-DEA mixtures.

3.3.2.3 Determination of amine concentration.

At the end of every experiment, 5 ml of liquid sample was withdrawn from the reactor and immediately titrated with 1 M standard solution of HCl to determine the final concentration of the total amine. Figure 3.3 shows a typical titration curve. This is to conform a constant amine concentration throughout the experiment. In all cases the difference between the initial and final concentration is less than 5% . Thus, we can assume that the total amine concentration is constant throughout the experiment. The same procedure is also applied to the freshly prepared amine solutions to ensure the concentration of the amine prepared corresponds to the desired value.

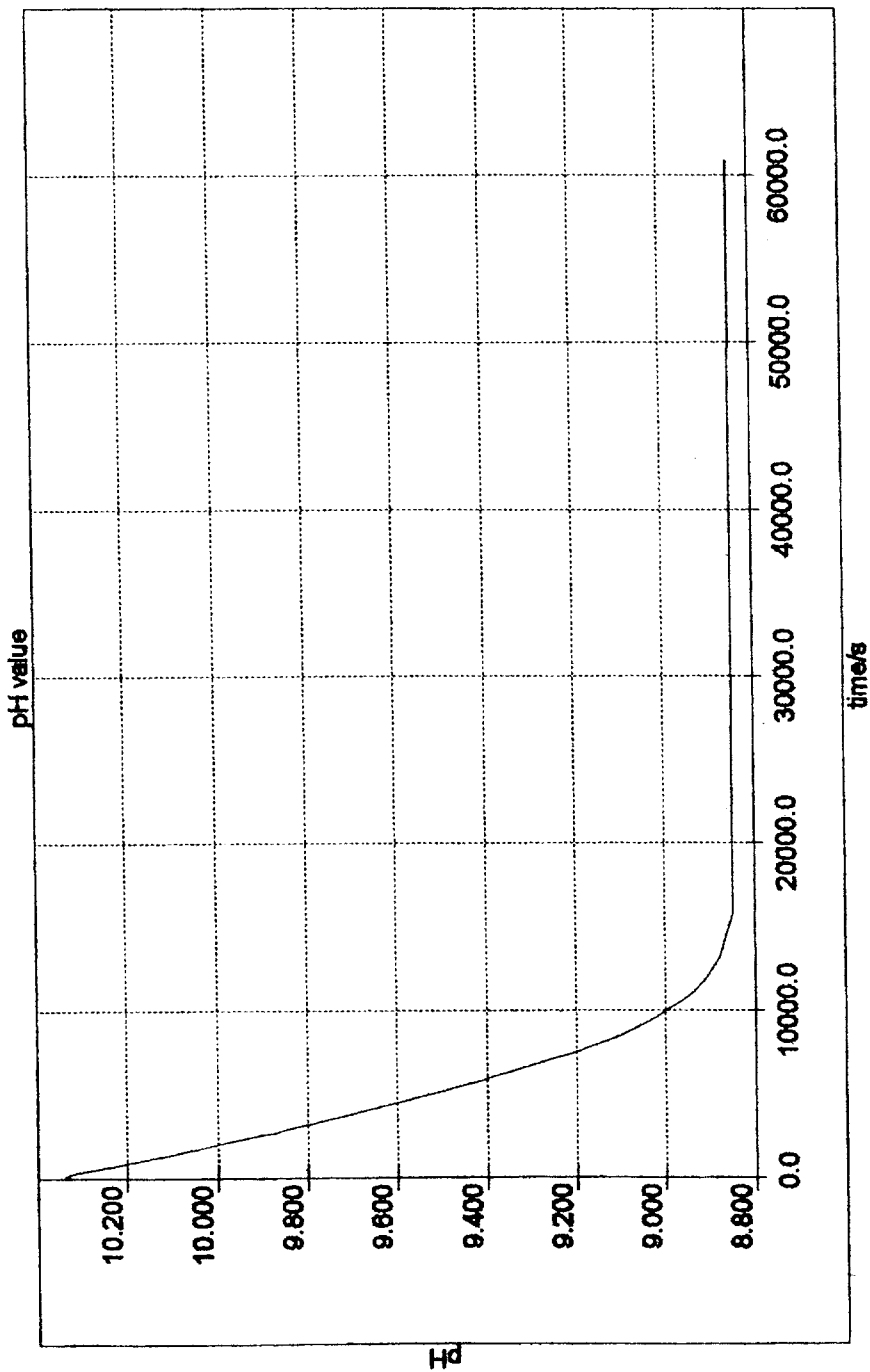


Figure 3.2 : The variation of pH as the function of time during the CO₂ absorption process.

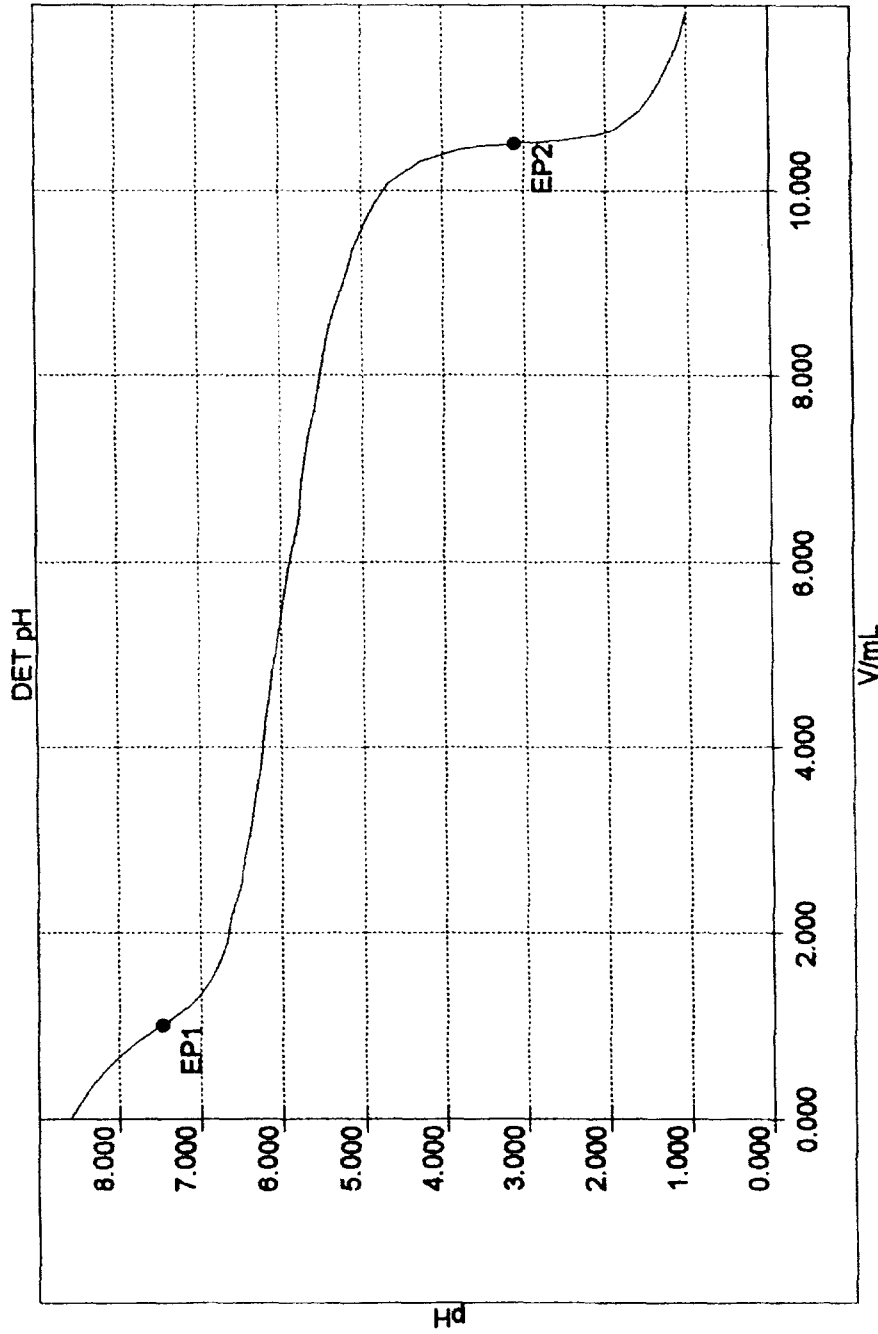


Figure 3.3 : Typical titration curve of carbonated amine with 1M HCl solution to determine final amine concentration.

3.3.2.4 CO₂ loading analysis

Measurement of CO₂ loading was performed by withdrawing 5 ml or 10 ml of carbonated sample depending on the amine concentration and CO₂ partial pressure from the reactor into 75 ml of a mixture of 0.5 M barium chloride and 0.5 M of sodium hydroxide solution. The solution was mixed and heated for about 3 hours at 70 °C under atmospheric pressure. This is to ensure that all the carbamates are transformed to carbonates to form barium carbonate which is in the form of white precipitate. Excess NaOH is needed to convert the free dissolved CO₂ into non-volatile ionic species. The precipitate was separated from the solution by using a Buchner filter with glass microfibre filter paper. The filtrate was kept aside for 24 hours before titrating it with HCl to identify in case there is any bicarbonate being formed. This will also confirm that all the barium carbonate formed was entirely captured in the filtration process. Excess sodium hydroxide was removed from the precipitate by washing it with distilled water. The precipitate was titrated with 1 M of HCl standard solution. The titration curve was recorded by autotitrator, Metrohm 716 DMS titrino connected to a PC data acquisition system to determine the end point. It was based on the dynamic equivalence point titration technique where the volume increments are adopted to the slope of the titration curve. The volume of HCl solution used in the titration was taken from the first reading of the end point recorded from the titration curve. A typical titration curve is shown in figure 3.4. The CO₂ loading can be calculated from the equation 3.3.1

$$\alpha = \frac{V_{\text{HCl}}}{V_s 2[\text{AM}]} \quad (3.3.1)$$

where :

α = CO₂ loading, mol CO₂/mol Amine.

V_{HCl} = volume of HCL used, ml.

V = volume of sample used, ml.

$[\text{AM}]$ = total amine concentration, molarity.

A detailed description on the derivation of this equation can be referred to Benamor work (1998).

3.3.2.5 Carbamate concentration

The values of the carbamate concentration were determined by a titration method. The loaded carbonated sample was withdrawn from the reactor and immediately titrated with 1 M of NaOH standard solution. Figure 3.5 shows the typical titration curve. The amount of NaOH solution utilized to neutralize the carbonated sample was used to calculate the total carbamates as describe by equation 3.3.2.

$$\text{Total carbamates} = 2[\text{AM}]_t - B \quad (3.3.2)$$

where :

$[\text{AM}]_t$ = total amine concentration.

B = concentration of NaOH used.

In the case of aqueous piperazine solution the total carbamates consist of PZCOO⁻, H⁺PZCOO and ⁻OOC PZCOO⁻, where as in the activated DEA solution DEACOO⁻

was also present beside the piperazine carbamate. The detailed derivation of equation 3.3.2 can be found in the Benamor work (1998).

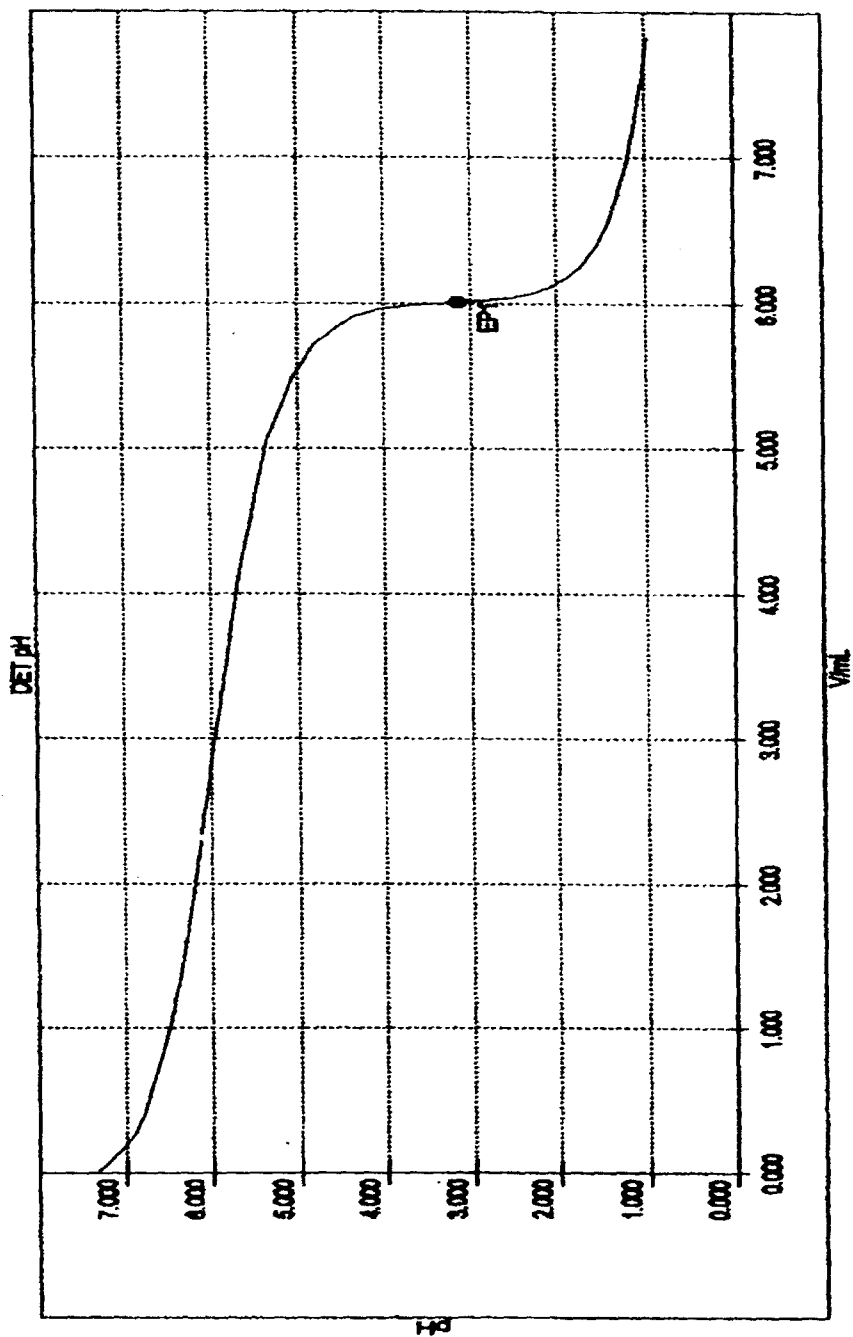


Figure 3.4 : Typical titration curve of the sample with 1 M HCl solution added to determine the CO₂ loading.

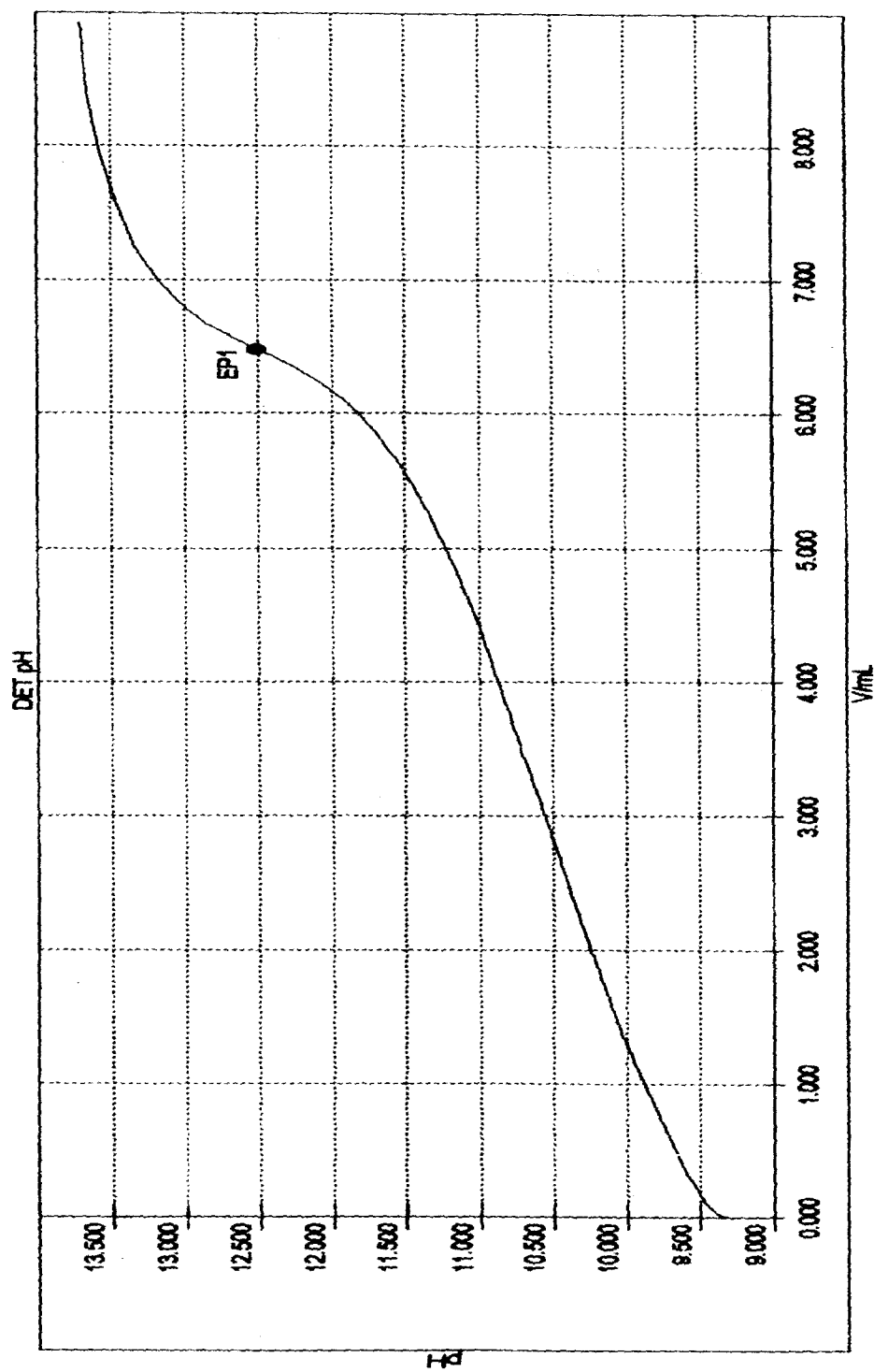


Figure 3.5 : Typical titration curve of carbonated amine solution with 1 M NaOH added to determine the total carbamate.