Chapter Four

Experimental
4.1 Materials

N,N-Diethyl monoethanolamine (purity 98%) used in all experiments was purchased from Spectrochem Pvt. Ltd., Mumbai. N-Ethyl monoethanolamine, N-(2-aminoethyl)ethanolamine, diethanolamine, diisopropanolamine, sodium hydroxide and piperazine, with a minimum assay of 98%, were purchased from S. D. Fine Chemicals Pvt. Ltd., Mumbai. Monoethanolamine and sulfolane, with a given purity of 99%, were purchased from S. D. Fine Chemicals Pvt. Ltd., Mumbai, too, whereas 1,6-hexamethyl diamine (purity 98%) was purchased from Aldrich, USA. Carbon dioxide standard and buffer solutions were purchased from Thermo-Fisher Scientific, USA. CO2, nitrogen (N2) and nitrous oxide (N2O) cylinders, with a given purity of 99.95%, were purchased from Inox Air Products Ltd., Mumbai.

4.2 Kinetics Measurement

A glass stirred-cell reactor (design pressure 202.6 kPa) with a plane, horizontal gas-liquid interface was used for the absorption studies (Vaidya and Mahajani, 2005). Fig. 4.1 shows a schematic diagram while Fig. 4.2 gives a pictorial representation of the stirred-cell apparatus. The main advantage of the stirred cell is that the rates of absorption can be measured using a liquid with a single, known composition. This easy-to-use experimental device (inner diameter 0.097 m, height 0.187 m) was operated batch-wise. The total volume of the reactor was $1.45 \times 10^{-3}$ m$^3$ and the interfacial surface area was $7.5 \times 10^{-3}$ m$^2$. The reactor was equipped with a flange made of stainless steel (SS-316) fabricated by Sharad Autoclave Engineers, Mumbai. A pressure transducer (Trans Instruments, UK) mounted on this flange and coupled with a data acquisition system (Jekins Electro Control, Mumbai), enabled measurement of gauge pressure inside the reactor, the uncertainty in this measurement being ±0.01 kPa. The lower and higher pressure limits in the transducer were 0 and 100 kPa, respectively. The reactor was also equipped with inlet and outlet ports for gas and liquid. The entire assembly was proven to have no leak. The setup was provided with a variable speed magnetic drive (Premex Instruments, Switzerland). The gas and liquid phases were stirred by two disk blade turbine impellers (six blades, diameter 0.04 m), which were mounted on the same shaft. A disadvantage of the stirred-cell technique is that the stirrer must be driven by a constant speed motor (Vaidya and
Kenig, 2007c). In addition, the value of liquid-side mass transfer co-efficient \( (k_L) \) might be sensitive to the depth of immersion of the stirrer blades in the liquid. The stirrer was driven by a 1/20 HP geared motor (Eltek/Remi Motors, Mumbai). The speed of stirring could be adjusted to the desired value with an accuracy of \( \pm 1 \) rpm. The impeller speed during kinetic measurements was limited to 60 rpm to ensure that the gas-liquid interface was undisturbed. By this way, the gas-liquid interfacial area is exactly known. The reactor was immersed in a water bath to guarantee isothermal conditions. The bath temperature was maintained at the desired value using a temperature indicator and controller (Alot/T-star Instruments, Mumbai) with an accuracy of \( \pm 0.1 \) K. The solute gas was passed through a coil, which was also kept in the water bath, before being charged inside the reactor.

A series of experiments was conducted at 298, 303 and 308 K. A schematic depicting the experimental procedure is shown in Fig. 4.3. In each experiment, the reactor was charged with \( 4 \times 10^{-4} \) m\(^3\) of the fresh amine solution. Then, the gas inside the reactor was purged with nitrogen to ensure an inert atmosphere. After the desired temperature was attained, CO\(_2\) from the gas cylinder was rapidly charged into the reactor, this being considered as the starting point for the reaction. The reactor content was stirred at the desired speed of agitation. The decrease in system pressure due to reaction was monitored by the pressure transducer and the \( "P_{CO_2} versus t" \) data were recorded during 30 seconds using the data acquisition system. These data were plotted for the time interval between \( t=5 \) s and \( t=25 \) s and fitted to a third degree polynomial using the least-squares regression. It was found that a linear fit resulted in a poor R-squared value and hence the relationship was non-linear. In contrast, a fit of the data to a third degree polynomial provided the best R-squared value \( (R^2=0.99) \). Since the initial concentration of the amine is known, reaction rate constant can be determined using only the initial rates of absorption. Also, the rate of absorption of CO\(_2\) into the fresh amine solution is the maximum at the start. Hence, the value of the derivative \(-dP_{CO_2}/dt\) at time \( t=0 \) is used to calculate the initial rate of absorption using the following rate expression:

\[
R_{CO_2a} = \frac{V_G}{V_L \cdot RT} \left( -\frac{dP_{CO_2}}{dt} \right)
\]  

(4.1)
This measurement method based on the fall-in-pressure technique enabled a simple and straightforward estimation of the absorption rates. Furthermore, no analysis of the liquid phase was required and the pressure decrease was the only factor necessary for the evaluation of the kinetic parameters. To verify the measurement technique, CO₂-MEA reaction kinetics were investigated in the stirred-cell reactor. The second-order reaction rate constant which was found to be 7311 m³/(kmol s) at T=303 K and (MEA)_0 = 2.5 kmol/m³ was in line with that reported by Hikita et al. (1977).

The reproducibility of experiments was checked and the relative error in the absorption rate measurements was found to be less than 3%. It was found that, in the range of agitation speeds studied, the rate of absorption varied insignificantly with the increase in impeller speed. Thus, it was concluded that the mass transfer rate is independent of the gas-side mass transfer coefficient (k_G). The absence of any gas side resistance was determined experimentally by plotting (P_{CO₂}/R_{CO₂}) vs. (1/√(amine)_0 ). It yielded a straight line passing through origin (see Fig. 4.4). Thus, the intercept representing the gas side resistance is negligible (1/k_G ≈ 0). Therefore, it was concluded that the CO₂ absorption process is liquid-phase controlled. The reaction kinetics was determined from the absorption rate measurements under fast pseudo-first order conditions.

4.3 Estimation of Physical Properties

Knowledge of physical properties is essential for the estimation of kinetic parameters. Solution densities and viscosities were measured over wide ranges of temperature and amine concentration. Density (ρ) of aqueous amine solutions was measured using a standard pycnometer (SCAM Lab Glass, Mumbai) having a volume of 1×10⁻⁵ m³ and an electronic weighing balance (Shimadzu Corporation, Japan) with a capacity of 2.2 kg and accuracy ±0.00001 kg. The kinematic viscosity (ν) of the solutions was measured using an Ostwald viscometer (No.4, PYREX Glass, USA). The dynamic viscosities (μ) were calculated by multiplying the kinematic viscosities with the corresponding densities of the solutions, which were further used to calculate the diffusivity of N₂O in aqueous amine solutions using the following modified Stokes-Einstein (Versteeg and van Swaaij, 1988b):

\[(D_{N₂O} \mu^{0.8})_{\text{Amine}} = \text{constant} = (D_{N₂O} \mu^{0.8})_{\text{water}}\]  

(4.2)
The diffusivity of N$_2$O and CO$_2$ in water was calculated using the following correlations earlier reported by Versteeg and van Swaaij (1988b):

\[
(D_{\text{N}_2\text{O}})_{\text{water}} = 5.07 \times 10^{-6} \exp\left(\frac{-2371}{T}\right) \text{ m}^2/\text{s} \tag{4.3}
\]

\[
(D_{\text{CO}_2})_{\text{water}} = 2.35 \times 10^{-6} \exp\left(\frac{-2119}{T}\right) \text{ m}^2/\text{s} \tag{4.4}
\]

Using the stirred-cell reactor, the solubility of N$_2$O in aqueous alkanolamine solutions was measured, too. During solubility measurements, the reactor was initially filled with $4 \times 10^{-4}$ m$^3$ of the fresh amine solution. Then, the gas inside the reactor was purged with nitrogen to ensure an inert atmosphere. After the desired temperature was attained, N$_2$O was rapidly charged into the reactor and the contents were stirred till equilibrium was attained. The stirrer was driven by a high speed motor (Universal/Remi Motors, Mumbai) with a maximum speed of stirring of 1500 rpm. After about 6 hours, a constant value of pressure reading indicated that equilibrium was reached. Using the initial and equilibrium values of pressure, the solubility of N$_2$O in the solution was determined according to the following relation:

\[
(H_{\text{N}_2\text{O}})_{\text{Amine}} = \left[\frac{P_{\text{N}_2\text{O}} - \hat{P}_{\text{N}_2\text{O}}}{\hat{P}_{\text{N}_2\text{O}}}\right] \frac{V_G}{V_LRT} \tag{4.5}
\]

The solubility of N$_2$O and CO$_2$ in water was calculated using the following correlations earlier mentioned by Versteeg and van Swaaij (1988b):

\[
(H_{\text{N}_2\text{O}})_{\text{water}} = 1.17 \times 10^{-7} \exp\left(\frac{2284}{T}\right) \text{ kmol/(kPa m}^3\text{)} \tag{4.6}
\]

\[
(H_{\text{CO}_2})_{\text{water}} = 3.54 \times 10^{-7} \exp\left(\frac{2044}{T}\right) \text{ kmol/(kPa m}^3\text{)} \tag{4.7}
\]

The diffusivity and solubility of CO$_2$ in aqueous alkanolamine solutions was found using the N$_2$O analogy method (Versteeg and van Swaaij, 1988b):

\[
(D_{\text{CO}_2})_{\text{Amine}} = \frac{(D_{\text{CO}_2})_{\text{water}}}{(D_{\text{N}_2\text{O}})_{\text{water}}} \times (D_{\text{N}_2\text{O}})_{\text{Amine}} \tag{4.8}
\]
(HCO₂)_{Amine} = \frac{(HCO₂)_{water}}{(HNO₂)_{water}} \times (HN₂O)_{Amine} \quad (4.9)

The liquid-side mass transfer co-efficient (kₖ) was determined by measuring the physical absorption of CO₂ in water and using the relation reported by Littel et al. (1991):

\ln \left[ \frac{P(t) - \hat{P}_{CO₂}}{P_{CO₂} - \hat{P}_{CO₂}} \right] = -\left[ \frac{(m'V_L + V_G)}{V_LV_G} \right]k_L A't \quad (4.10)

The LHS of above equation was plotted vs. time. From the value of the slope of this graph and knowing the values of other relevant parameters (m' = 0.75 mol/mol, V_G = 1.05×10^{-3} m³, V_L = 4×10^{-4} m³, A' = 7.5×10^{-3} m²), the value of k_L was found to be 3.3×10^{-5} m/s.

4.4 Vapour-Liquid-Equilibrium (VLE) Measurement

To measure the equilibrium solubility of CO₂, an apparatus comprising an equilibrium cell, gas reservoir, saturators and gas re-circulator/blower was used (see Fig. 4.5). It was described in detail in Jagushte and Mahajani (1999, 2000). The equilibrium cell (volume 2.5×10^{-4} m³) was provided with a conductivity probe (EQ-610, combined electrode with functions pH and mV, Equiptronics, Mumbai) and a magnetic stirrer (Remi Motors, Mumbai). Its inlet and outlet ports were connected to the saturator and gas reservoir, respectively. The exit of the gas reservoir was connected to the blower, which ensured proper circulation of gas inside the apparatus. The outlet of the blower was connected to the saturator, which was filled with water. Thus, the gas entering the equilibrium cell was humidified to prevent any change in amine concentration due to evaporation of water. The entire assembly was proven to have no leak. The system pressure was 101.3 kPa. The setup (excluding the blower) was immersed in a water bath to guarantee isothermal conditions. The bath temperature was adjusted to the desired value using a temperature indicator and controller (Alot/T-star Instruments, Mumbai) with an accuracy of ±0.1 K. A CO₂ ion-selective electrode (ORION, Thermo-Fischer Scientific, USA) was used for carbonate analysis.
Vapour-liquid equilibrium (VLE) data for aqueous amine solutions was determined at \( T=303 \) K. A known volume of amine solution at 273 K was loaded with CO\(_2\) by bubbling the gas into the liquid over a certain period of time. For each experiment, the duration for which CO\(_2\) was bubbled and the flow rate of CO\(_2\) was altered so as to vary the loading. Thereafter, the CO\(_2\)-loaded amine solution was charged inside the equilibrium cell. Then, the gas was circulated through the apparatus using the blower, while stirring the equilibrium cell content; and the approach to equilibrium was monitored using the conductivity probe. Since the reaction of CO\(_2\) with amine is ionic in nature, the concentration of ionic species remains constant after reaching equilibrium. A constant value of conductivity over 6 hours implied that equilibrium was achieved. At this stage, the gas compositions in the equilibrium cell and in the gas reservoir were identical. The reservoir was then isolated from the setup with the help of valves and aqueous sodium hydroxide solution (1 N) was injected into it using a syringe. Then the reservoir content was mixed by shaking and left at rest for about 48 hours to ensure that all CO\(_2\) was absorbed in the caustic solution. To determine the CO\(_2\) content of the gas phase, this solution was analysed using the CO\(_2\) ion-selective electrode. A liquid sample was collected from the equilibrium cell using a syringe and mixed with caustic solution (0.1 N) to convert it to Na\(_2\)CO\(_3\). It was examined in order to determine CO\(_2\) content in the liquid phase. Prior to the analysis, the CO\(_2\) ion-selective electrode was calibrated using standard solutions (see Fig. 4.6).
Figure 4.1: Experimental setup for kinetics measurement
Figure 4.2: Photograph of stirred-cell reactor
Figure 4.3: Experimental procedure for kinetics measurement
Figure 4.4: A plot of \( \frac{P_{CO_2}}{R_{CO_2}} \) vs. \( \frac{1}{\sqrt{(amine)_o}} \)
Figure 4.5: Experimental setup for VLE measurement
Figure 4.6: Calibration curve for CO₂ ion selective electrode