CO₂ Absorption Capacity and its Enthalpy of Absorption in Aqueous Blend of MDEA/Piperazine/Arginine

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Abstract. In this work, the solubility data of CO₂ in aqueous blends of N-Methyldiethanolamine, Piperazine and Arginine (MDEA/PZ/ARG) of a total concentration of two moles is presented. CO₂ partial pressure was varied from 9 to 99 kPa while temperature ranged from 293 to 323 K in increment of 10 degrees. The experimental results showed that the solubility of CO₂ decreased with increasing ARG ration in the mixture. These results were modelled using a semi-empirical (SE) vapor liquid equilibrium (VLE) model. The model was found able to adequately represent the experimental data with an average absolute deviation (AAD) less than 3.13%. Using a truncated form of the semi-empirical model, the heat of CO₂ absorption, ΔHₘ, at low pressure was estimated and found to be in the range of 32-66 kJ/mole CO₂ absorbed.

1. Introduction

The separation of carbon dioxide (CO₂) from natural and industrial gas mixtures in important industrial process with many applications especially in natural gas sweetening industry, ammonia production and removal of CO₂ from power plants flue gases. Several technological routes for CO₂ capture are available. This includes, chemical absorption, physical adsorption, liquefaction or cryogenic separation, membrane based separation, and biological separation [1]. Out of these above mentioned capture methods, CO₂ absorption through chemical reaction is regarded as the most promising and well proven methodology, since it has the supremacy of selective capture characteristics of CO₂ escaping from power plant exhaust gas consisting of low CO₂ partial pressure and a very large volume of gas [1]. The separation of CO₂ from natural and industrial gas mixtures using aqueous amine absorbents is a well-established technology that was developed some nine decades ago [2]. The current industrial practice is fundamentally the same, with some improvements made to gas-liquid contactors, heat integration within the process and process equipment [3]. A great deal of additional knowledge of the chemistry that occurs when CO₂ is absorbed by an aqueous amine has also been generated in the intervening period [4, 5]. This has led to changes in the formulation of absorbents to yield improved process performance in terms of lower capital and operating costs [6]. CO₂ capture through chemical absorption process has several advantages, such as; (a) combination of reaction and separation in a single process unit; (b) significantly, higher CO₂ removal efficiency; (c) solvent regeneration for further use of the absorbent with added advantage of selective capture and nearly pure CO₂ can be attained after stripping of CO₂ loaded solvent; (d) mature technology for great extent of industrial appropriateness [7].

Information on heat of absorption (ΔHₘ), of acid gases such as CO₂ and H₂S in aqueous solutions of amines is of prime importance for designing acid gas removal unit operations due to its direct relation to steam
requirements for the amine regeneration and its impact on the temperature dependency of the CO₂ equilibrium. As the operating cost of the regeneration process often accounts for over half the plant running cost, it is desirable to have a low enthalpy of absorption with possible accurate data [8].

2. Theory

2.1. Chemical equilibria of MDEA-PZ-ARG-H₂O-CO₂ system

In aqueous solution of an MDEA-PZ-ARG system, CO₂ equilibrium is governed by the following equations:

Dissociation of protonated amine:

\[
MDEA H^+ \rightleftharpoons MDEA + H^+ \quad (1)
\]

Dissociation of carbon dioxide:

\[
CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \quad (2)
\]

Dissociation of bicarbonate ion:

\[
HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \quad (3)
\]

Ionization of water:

\[
H_2O \rightleftharpoons OH^- + H^+ \quad (4)
\]

Dissociation of protonated piperazine (PZ):

\[
PZH^+ \rightleftharpoons PZ + H^+ \quad (5)
\]

Formation of piperazine carbamate:

\[
PZ + CO_2 \rightleftharpoons PZCOO^- \quad (6)
\]

Dissociation of zwitterion (protonated carbamate of PZ):

\[
H^+ PZCOO^- \rightleftharpoons PZCOO^- + H^+ \quad (7)
\]

Formation of piperazine di-carbamate:

\[
PZCOO^- + CO_2 \rightleftharpoons PZ(COO^-)_2 \quad (8)
\]

Deprotonation of amino acid (arginine):

\[
^{\text{\scriptscriptstyle a}}NH_2RCOO^- + H_2O \rightleftharpoons H^+O^+ + NH_2RCOO^- \quad (9)
\]

Carbamate formation of amino acid (arginine):

\[
HCO_3^- +^{\text{\scriptscriptstyle a}}OOCNH_2^+ \rightleftharpoons^{\text{\scriptscriptstyle a}}OOCNHCOO^- + H_2O \quad (10)
\]

2.2. Semi-empirical model for CO₂ VLE

Several models are available in the literature to correlate the solubility of CO₂ in aqueous alkanolamine solutions. Among these models, the electrolyte-NRTL model of Chen and Evans [9], the Deshmukh-Mather model [10] and the Kent-Eisenberg model [11]. In this work, CO₂ VLE curves were analyzed using a semi-empirical model developed by Xu [12] that relates \( P_{CO_2}^* \) to temperature, CO₂ loading, and their cross terms in a linear combination as in Equation (11).

\[
P_{CO_2}^* = K_1 + \frac{K_2}{T} + K_3 \times \alpha + K_4 \times \alpha^2 + K_5 \times \frac{\alpha}{T} \quad (11)
\]
2.3. Estimation of Heat of CO\textsubscript{2} Absorption

The heat of CO\textsubscript{2} absorption in any solvent can be estimated from the temperature dependence of \( t (P_{CO2}) \) against its loading data using Equation (12). This expression of heat of absorption also requires the total pressure of the system to be low, which is necessary for the use of partial pressure in place of fugacity a valid approximation \[13, 14\]:

\[
\left( \frac{\Delta n P_{CO2}^*}{\Delta (t/\gamma)} \right) = \frac{-\Delta H_{abs}}{R} = K_s + K_x \times \alpha
\] (12)

3. Experimental Work

3.1. Materials

Chemicals used in the present study were Methyldiethanolamine (MDEA) with 99% purity purchased from Riedel-de-Haen, Piperazine (PZ) with 99% purity obtained from Sigma-Aldrich, and arginine (ARG) with 99% purity purchased from Fluka. The gases used were carbon dioxide (CO\textsubscript{2}) and Nitrogen (N\textsubscript{2}) which are all research grade supplied by Buzwair Scientific and Technical Gases, Qatar. The solutions were prepared by dissolving the required amounts' of MDEA, PZ and ARG in deionized water in a volumetric flask at room temperature. An analytical balance was used to weight the chemicals.

3.2. Experimental set up and procedure

Solubility of carbon dioxide (CO\textsubscript{2}) into aqueous blended solvent of (MDEA/PZ/ARG) were carried out at different conditions of solution composition, CO\textsubscript{2} partial pressures and temperatures. The absorption experiments were conducted using a double jacketed stirred cell reactor (Figure 1) where the amine solution was exposed to a flowing reaction gas which flow rates were controlled using factory calibrated 5080E series Brooks® mass flow controllers. Temperature in the reactor is measured using a J type thermocouple and is controlled by a (HAAKE A 25/Thermo) water circulator to within ±0.5°C. Other accessories include a pressure transducer and a pH probe linked to Metrohm 867 autotitrator to monitor the variation of pH with time. The experiment was terminated once the equilibrium was achieved as indicated by a constant pH value of the loaded solution. To determine the CO\textsubscript{2} loading in the solution, about 10 μl was immediately taken from the reactor using a 10 micro liter syringe and injected to an Agilent GC Analyzer. In this study, the partial pressure of CO\textsubscript{2} in the flowing gas stream was varied from 9 kPa to 99 kPa in the temperature range of 303 to 323 K. A schematic diagram of the experimental set up is shown in Figure 1.

To calculate the partial pressure of CO\textsubscript{2} (\( P_{CO2}^* \)), Equation (13) was used:

\[ P_{CO2}^* = y_{CO2} \times (P_{Total} - P_s) \] (13)

The system was kept open to the atmosphere, so that the total pressure \( P_{Total} \) is 1 atm. \( P_s \) is the solvent vapor pressure which equals to the water vapor pressure.

4. Results and Discussions

4.1. CO\textsubscript{2} solubility

The obtained experimental results on the effect of temperature for fixed amines/ amino acid proportions are given as plots of CO\textsubscript{2} partial pressure against CO\textsubscript{2} loading for temperatures ranging from 293K to 232 K as shown in Figure 2.
Figure 1. Schematic diagram of the absorption experimental set up. [1: N₂ cylinder; 2: CO₂ cylinder; 3: Water saturator; 4 & 5: Mass flow controller; 6: Water bath; 7: reactor; 8: thermocouple; 9: condenser; 10 pH meter; 11: data recording unit; 12: To fume hood].

Figure 2. The temperature effect on the solubility of CO₂ in (1.8M MDEA+ 0.1M PZ+ 0.1M ARG) at different CO₂ partial pressures.

To assess the effect of arginine in the total blend solution, a comparison between the CO₂ solubility in single 2M MDEA and Total 2M of (MDEA+PZ+ARG) at fixed temperature and different CO₂ partial pressures as shown in Figure 3. It was found that solution of 1.8M MDEA+0.2M PZ has the highest loading over the entire range of CO₂ partial pressure followed by a solution of single 2M MDEA. Progressively replacing PZ by ARG in the solution caused a progressive decrease of CO₂ loading with increased ARG proportion.
4.2. VLE Semi-Empirical model

The experimental gas loading data, at different amine concentrations, temperatures and CO₂ partial pressures were fitted to Equations (12), to generate the different K values of the equation following the same approach taken by [15, 16]. Using the generated K parameters, the correlated CO₂ loadings were compared with the experimental loadings. In general, within the studied range of temperature, pressure and amines/amino acid concentrations, predicted and measured data showed a good agreement with an average absolute deviation (AAD) 3.13%.

**Figure 3.** Effect of arginine Piperazine concentrations on the solubility of CO₂ at 303 K and different CO₂ partial pressures

**Figure 4.** Plot of experimental CO₂ partial pressures against model predicted values for [1.8MDEA+0.1PZ+0.1ARG] moles and different temperatures
4.3. Heat of absorption

The heat of absorption for the CO$_2$-MDEA–PZ-ARG-H$_2$O system will therefore differ from that of a pure MDEA, PZ or MDEA+ PZ solution. The thermodynamic relationship in Equation (12) was applied to the semi-empirical model to obtain an analytical expression for $\Delta H_{ab}$. This analytical expression for $\Delta H_{ab}$ is from the temperature dependence of the $\left(P^*_{CO2}\right)$ data and regardless of the solvent composition.

![Graph showing heat of absorption vs CO$_2$ loading]

Figure 5. Heat of absorption of CO$_2$ in the aqueous [1.8MDEA+0.1PZ+0.1ARG] molar mixed solution

It can be seen from Figure 5 that the heat of absorption for MDEA/PZ/ARG is greatly dependent on the CO$_2$ loading. The values are in the range of 32-66 kJ/mole CO$_2$ absorbed. The experimental value of heat of CO$_2$ absorption by MDEA equals to 49 kJ/mole while the estimated value at CO$_2$ partial pressure of 15.1 kPa and 313 K [17] was found to be 54.6 kJ/mole which is in the same order of magnitude with other amines such as MEA of about (50-85 kJ/mole) [15] and amino acid salts LysK which is in the range of (25-100 kJ/mole) [18-20].

5. Conclusion

Solubility of Data of CO$_2$ loading in aqueous mixtures of MDEA/PZ/ARG/H$_2$O under CO$_2$ partial pressure varying from 9 to 100 kPa and temperature ranging from 293 to 323 K and different proportions of MDEA/PZ/ARG were experimentally determined. The obtained results showed that the CO$_2$ loading increases with increased CO$_2$ partial and decreased with increased temperature. The addition of PZ to MDEA/H$_2$O solution increased the solution loading capacity. However, replacing portions of PZ with ARG caused a decrease in the solution loading capacity. A semi-empirical model developed by Xu et al. [1] was used to correlate the CO$_2$ partial pressure as function of gas loading and solution temperature. The model was found able to give relatively good prediction on the total CO$_2$ loading in solutions of blended amines. the semi-empirical model was used to obtain an analytical expression for $\Delta H_{ab}$ that was used to estimate the CO$_2$ heat of CO$_2$ absorption in MDEA/PZ/ARG/H$_2$O which was found to be in the same order of magnitude as conventional amines such as MEA.
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Nomenclature
MDEA: N-Methyldiethanolamine
PZ: Piperazine
ARG: Arginine
MEA: Monoethanolamine
ΔH_ab: Heat of CO\(_2\) absorption
P_{CO2}: CO\(_2\) partial pressure
P_{Total}: Total pressure
P_s: Solvent vapor pressure
Α: CO\(_2\) loading (mole/mole)
y_{CO2}: CO\(_2\) mole fraction

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