Abstract—In this work new experimental data on the rate of absorption of CO\(_2\) into PZ activated concentrated aqueous AMP in the temperature range of \((323–333)\) K are presented. Rate activator PZ is used with a concentration of \((2–8)\) wt\%, keeping the total amine concentration in the solution at 50 wt\%. The vapour-liquid equilibrium (VLE) of CO\(_2\) into aqueous solutions of (AMP+PZ) have also been measured and modeled in order to determine the liquid phase speciation of (AMP+PZ+CO\(_2\)+H\(_2\)O) system and equilibrium CO\(_2\) loading. The theoretical absorption-rate model used to interpret the experimental kinetic data is based on all possible chemical reactions in the liquid phase. The average absolute deviation between the experimental and model results is about 6.8 %.

Index Terms—CO\(_2\) capture, 2-Amino-2-methyl-1-propanol, piperazine, diffusion-reaction model.

I. INTRODUCTION

Growing environmental concerns today for global warming have motivated extensive research activities towards developing more efficient and cost effective processes for CO\(_2\) capture from large point sources of CO\(_2\), such as power plants, steel plants, etc, since fossil fuel will continue to hold the major role in meeting the global energy demand, which is projected to rise up to 55% by 2030. Amine based regenerative chemical absorption processes have been widely practiced for several years for CO\(_2\) removal from natural gas and synthesis gas streams. But, the major challenges for CO\(_2\) capture from the flue gas of coal based power plants are the large volumetric flow rates of flue gas at essentially atmospheric pressure with large amount of CO\(_2\) at low partial pressures. A common industrial choice is to use 15–30 wt\% aqueous mono ethanol amine (MEA) for regenerative absorption of CO\(_2\). However, this process is very energy intensive due to the high regeneration energy requirement. Besides, high degradation rate and high corrosiveness of MEA contribute further to the increase in the cost of electricity by about 70–80% if MEA based absorption process is implemented for CO\(_2\) capture in a power plant. Thus, improved cost effective processes with lower energy penalty for CO\(_2\) capture from flue gas streams of coal based power plants is essential today in order to implement CO\(_2\) capture in power plants. There is a recent interest in using activated alkanolamine solvents by employing a reaction rate accelerator e.g., piperazine (PZ), a cyclic secondary diamine, in the aqueous alkanolamine solutions. Piperazine activated aqueous sterically hindered amine 2-amino-2-methyl-1-propanol (AMP) for CO\(_2\) capture takes advantage of the high rate of reaction of CO\(_2\) with the rate activator PZ and the high CO\(_2\) loading capacity and lower regeneration energy requirement of AMP. The ability of a solvent for CO\(_2\) capture is governed primarily by the equilibrium solubility of CO\(_2\) in the solvent as well as mass transfer and chemical kinetics characteristics. Increasing the concentration of solvent allows for increased solvent capacity, higher rate of removal of CO\(_2\) and lower circulation rate.

Experimental and theoretical investigation of absorption of CO\(_2\) into PZ activated concentrated aqueous AMP is presented here. The rates of absorption of CO\(_2\) into aqueous solutions of (AMP + PZ) have been measured in a wetted wall contactor over the temperature range of \((303–333)\) K. PZ, as an activator, has been used with a concentration of \((2–8)\) wt\%, while the concentration of AMP has been kept 42–48 wt\% keeping the total amine concentration in the solution at 50 wt\%. In keeping with the flue gas condition, the CO\(_2\) partial pressure has been kept in the range \((5–15)\) kPa, while the total pressure for the absorption measurements has been 100kPa. The VLE of CO\(_2\) into aqueous solutions of (AMP+PZ) has also been measured using an equilibrium cell over the temperature range of \((303–323)\) K. The partial pressures of CO\(_2\) for VLE studies were in the range of \((0.1–140)\) kPa. The ENRTL model [1] has been used to determine the CO\(_2\) partial pressure over aqueous concentrated (AMP+PZ) and the liquid bulk concentrations of all chemical species present in the solution at equilibrium. The ENRTL model has been incorporated in the mass transfer-reaction kinetics model, which is capable of predicting gas absorption rates and enhancement factors for absorption of CO\(_2\) into activated amine solvents.

II. REACTION SCHEME AND MATHEMATICAL MODEL

A. Reaction Scheme

The diffusion-reaction model to describe the rates of mass transfer of CO\(_2\) in aqueous blends of PZ and AMP is based on several complex parallel reversible reactions in the liquid phase. When CO\(_2\) is absorbed into an aqueous mixed amine solution of AMP and PZ, the following reactions may take place in the liquid phase [2].

\[
\text{CO}_2 + \text{AMP} + \text{H}_2\text{O} \xrightleftharpoons[k_{11}^{-1}]^{k_{11}} \text{AMP}^+ + \text{HCO}_3^- \tag{1}
\]

\[
\text{CO}_2 + \text{PZ} + \text{H}_2\text{O} \xrightleftharpoons[k_{22}^{-1}]^{k_{22}} \text{PZCOO}^- + \text{H}_3\text{O}^+ \tag{2}
\]
CO₂ + AMP + PZ $\xrightleftharpoons[k_{22}]{k_{21}}$ PZCOO⁻ + AMPH⁺ (3)  
CO₂ + PZCOO⁻ + H₂O $\xrightleftharpoons[k_{23}]{k_{22}}$ PZ(COO)₂ + H₂O⁺ (4)  
CO₂ + AMP + PZCOO⁻ $\xrightleftharpoons[k_{24}]{k_{25}}$ PZ(COO⁻)₂ + AMPH⁺ (5)  
CO₂ + 2H₂O $\xrightleftharpoons[K_{62x}]{K_{61}}$ HCO₃⁻ + H₃O⁺ (6)  
HCO₃⁻ + H₂O $\xrightleftharpoons[K_{72x}]{K_{71}}$ CO₂⁻ + H₃O⁺ (7)  
PZ + H₂O⁺ $\xrightleftharpoons[K_{82x}]{K_{81}}$ PZH⁺ + H₂O (8)  
PZCOO⁻ + H₂O⁺ $\xrightleftharpoons[K_{92x}]{K_{91}}$ H⁺PZCOO⁻ + H₂O (9)  
AMPH⁺ + H₂O $\xrightarrow[K_{10x}]{K_{10}}$ AMP + H₂O⁺ (10)  
2H₂O $\xrightarrow[K_{11x}]{K_{11}}$ H₂O⁺ + OH⁻ (11)

Reactions (1)–(6) have finite reaction rates and are reversible. Reactions (7)–(11) are reversible and instantaneous with respect to mass transfer and at equilibrium, since they involve only proton transfer.

**B. Reaction Mechanism**

The two step zwitterion mechanism [3] considered for the reaction between CO₂ and PZ, (and PZCOO⁻) in presence of AMP involves the formation of a zwitterion followed by the deprotonation of the zwitterion by a base (PZ, AMP, PZCOO⁻) to produce PZ-carbamate, PZ-dicarbamate and protonated base. In this work, reaction (2) represents the reaction between CO₂ and PZ to produce carbamate. The rate constant, k₂₂, is considered the global rate coefficient for the formation of zwitterion and for zwitterion deprotonation. Likewise, the rate constant, k₃₈, is viewed as the global rate coefficient for the formation of PZ-dicarbamate, PZ(COO⁻)₂, by reaction (4). For CO₂-AMP reaction, AMP catalyzed hydration of CO₂ is considered and thus the CO₂-aqueous AMP reaction is represented by reaction (1) neglecting the formation of carbamate by AMP due to the very low stability constant of AMP carbamate.

**C. Diffusion-Reaction Model**

The mathematical model is developed according to Higbie’s penetration theory following Samanta and Bandyopadhyay [2] to interpret the experimental results of absorption of CO₂ into PZ-activated aqueous solutions of AMP.

For convenience the liquid phase species are renamed as, u₁ = [CO₂], u₂ = [AMP], u₃ = [AMPH⁺], u₄ = [HCO₃⁻], u₅ = [OH⁻], u₆ = [CO₂⁻], u₇ = [H₂O⁺], u₈ = [PZ], u₉ = [PZH⁺], u₊₀ = [PZCOO⁻], u₁₁ = [PZH⁺COO⁻] and u₁₂ = [PZ(COO⁻)₂]. Reactions (1)–(6) have finite reaction rates which are given by the following reaction rate expressions:

$$R_i = -k_{2u1}u_1u_2 + \frac{k_{2u1}}{K_1}u_1u_3u_4$$ (12)

$$R_2 = -k_{2u1}u_1u_8 + \frac{k_{2u1}}{K_2}u_1u_{10}$$ (13)  
$$R_3 = -k_{2u1}u_1u_8 + \frac{k_{2u1}}{K_3}u_1u_{10}$$ (14)  
$$R_4 = -k_{2u1}u_1u_{10} + \frac{k_{2u1}}{K_4}u_1u_7$$ (15)  
$$R_5 = -k_{2u1}u_1u_{10} + \frac{k_{2u1}}{K_5}u_1u_{12}$$ (16)  
$$R_6 = -k_{2u1}u_1 + \frac{k_{2u1}}{K_6}u_4$$ (17)

The mass transfer model describing the diffusion-reaction process consists of the following equations:

**CO₂ balance:**

$$\frac{\partial u_1}{\partial t} = D_1 \frac{\partial^2 u_1}{\partial x^2} + \sum_{i=0}^{6} R_i$$ (18)

**Total carbon (from CO₂) balance:**

$$\frac{\partial u_1}{\partial t} + \frac{\partial u_4}{\partial t} + \frac{\partial u_5}{\partial t} + \frac{\partial u_{10}}{\partial t} + 2 \frac{\partial u_{11}}{\partial t} + 2 \frac{\partial u_{12}}{\partial t} = D_1 \frac{\partial^2 u_1}{\partial x^2} + D_1 \frac{\partial^2 u_4}{\partial x^2} + D_1 \frac{\partial^2 u_5}{\partial x^2} + D_1 \frac{\partial^2 u_{10}}{\partial x^2} + 2D_1 \frac{\partial^2 u_{11}}{\partial x^2} + 2D_1 \frac{\partial^2 u_{12}}{\partial x^2}$$ (19)

**Total AMP balance:**

$$\frac{\partial u_1}{\partial t} + \frac{\partial u_4}{\partial t} + \frac{\partial u_5}{\partial t} + \frac{\partial u_8}{\partial t} + \frac{\partial u_{10}}{\partial t} + \frac{\partial u_{11}}{\partial t} + \frac{\partial u_{12}}{\partial t} = D_1 \frac{\partial^2 u_1}{\partial x^2} + D_1 \frac{\partial^2 u_4}{\partial x^2}$$ (20)

**Total PZ balance:**

$$\frac{\partial u_1}{\partial t} + \frac{\partial u_4}{\partial t} + \frac{\partial u_5}{\partial t} + \frac{\partial u_8}{\partial t} + \frac{\partial u_{10}}{\partial t} + \frac{\partial u_{11}}{\partial t} + \frac{\partial u_{12}}{\partial t} = D_1 \frac{\partial^2 u_1}{\partial x^2} + D_1 \frac{\partial^2 u_4}{\partial x^2} - R_2 - R_3 - R_4 + R_5$$ (21)

**Carbamate balance:**

$$\frac{\partial u_1}{\partial t} + \frac{\partial u_4}{\partial t} + \frac{\partial u_5}{\partial t} + \frac{\partial u_8}{\partial t} + \frac{\partial u_{10}}{\partial t} + \frac{\partial u_{11}}{\partial t} + \frac{\partial u_{12}}{\partial t} = D_1 \frac{\partial^2 u_1}{\partial x^2} + D_1 \frac{\partial^2 u_4}{\partial x^2} - R_2 - R_3 - R_4 + R_5$$ (22)

**Dicarbamate balance:**

$$\frac{\partial u_1}{\partial t} + \frac{\partial u_4}{\partial t} + \frac{\partial u_5}{\partial t} + \frac{\partial u_8}{\partial t} + \frac{\partial u_{10}}{\partial t} + \frac{\partial u_{11}}{\partial t} + \frac{\partial u_{12}}{\partial t} = D_1 \frac{\partial^2 u_1}{\partial x^2} - R_2 - R_3 - R_4$$ (23)

**Electroneutrality Balance:**

$$\frac{\partial u_1}{\partial t} + \frac{\partial u_4}{\partial t} + \frac{\partial u_5}{\partial t} + \frac{\partial u_8}{\partial t} + \frac{\partial u_{10}}{\partial t} + \frac{\partial u_{11}}{\partial t} + \frac{\partial u_{12}}{\partial t} = D_1 \frac{\partial^2 u_1}{\partial x^2}$$ (24)

Instantaneous reactions (7)–(11) assumed to be at equilibrium are represented by the equilibrium constants using respective species concentrations. There are twelve partial differential-algebraic equations which are solved for the concentration profiles of the twelve chemical species.
\((u_1, \ldots, u_{12})\) present in the liquid phase of \(\text{CO}_2-(\text{AMP} + \text{PZ})\). The partial differential equations are transformed into ordinary differential equations in \(n\) by discretizing the special variable \(x\) using the method of lines. The resulting system of ordinary differential equations coupled with nonlinear algebraic equations is solved using the subroutine DDASSL [4].

D. Initial and Boundary Conditions

At \(t = 0\) (for all \(x \geq 0\)) and at \(x = \infty\) (for all \(t \geq 0\)), the concentration of all chemical species in the liquid are set equal to their equilibrium bulk concentrations, i.e.,

\[ u_i = u_i^0, \quad i = 1, \ldots, 12 \]  

(25)

The fluxes of the non-volatile components (i.e., for \(i = 2, 3, \ldots, 12\)) at gas-liquid interface (i.e., at \(x = 0\)) are equal to zero, which implies following boundary conditions:

\[ \frac{\partial u_i}{\partial x} = 0 \quad \text{at} \quad x = 0 \quad \text{and} \quad t > 0 \]  

(26)

For volatile component, \(\text{CO}_2\), the mass transfer rate in the gas phase near the gas-liquid interface is equal to the mass transfer rate in the liquid near the interface:

\[ -D_{i-1} \frac{\partial u_i}{\partial x} = k_f (\rho_l - H_l u_i(0,t)) \quad \text{at} \quad x = 0 \quad \text{and} \quad t > 0 \]  

(27)

For negligible mass transfer resistance in the gas phase, the boundary condition for \(\text{CO}_2\) at the gas-liquid interface (\(x = 0, \ t > 0\)) reduces to:

\[ u_i(0, t) = u_i^* = \rho_l / H_l \]  

(28)

The differential equations are integrated from \(t = 0\) to \(t = \theta\), the contact time, using the above initial and boundary conditions. The time-averaged absorption rate per unit interfacial area is obtained as given in Eq. (29).

\[ R = -\frac{D_{i-1}}{\theta} \int_0^\theta \frac{\partial u_i}{\partial x}(0, t) \, dt \]  

(29)

According to Higbie’s penetration model, the liquid-phase mass transfer coefficient \(k_{L,1}\), for physical absorption of \(\text{CO}_2\) can be estimated by using Eq. (30).

\[ k_{L,1} = 2 \sqrt{\frac{D_{i-1}}{\pi \theta}} \]  

(30)

and the enhancement factor, \(E\), for absorption of \(\text{CO}_2\) is given by

\[ E = \frac{R}{k_{L,1}(u_1 - u_1^0)} \]  

(31)

III. PHYSICOCHEMICAL PROPERTIES AND MODEL PARAMETERS

A. Physicochemical Properties

Knowledge of the physicochemical and transport properties of the alkanolamines and \(\text{CO}_2\) e.g., density and viscosity of the aqueous amine solutions and diffusivity and physical solubility of \(\text{CO}_2\) in the aqueous amine solutions are necessary for analyzing the results of absorption studies using the numerical model developed in this work. The densities and viscosities of the PZ activated concentrated aqueous AMP have been measured by standard methods. \(\text{N}_2\text{O}\) analogy has been adopted to estimate physical solubility (H) and diffusivity of \(\text{CO}_2\) in PZ activated AMP as described by Samantha and Bandyopadhyay [2].

B. Kinetic Parameters for the Model

The reaction rate constant \(k_{21}\) for the reaction of \(\text{CO}_2\) with aqueous AMP has been calculated from the following correlation presented by Samanta and Bandyopadhyay [2].

\[ \ln k_{21} = 23.69 - \frac{5176.49}{T} \]  

(32)

The forward rate constants, \(k_{22}\) and \(k_{24}\) of both reactions (2) and (4) have been calculated from the following Arrhenius equations as proposed by Samanta and Bandyopadhyay [2]:

\[ k_{22} = 5.8 \times 10^4 \exp \left[ -\frac{3.5 \times 10^4}{R} \left( \frac{1}{T} - 1 \right) \right] \]  

(33)

\[ k_{24} = 5.95 \times 10^4 \exp \left[ -\frac{3.55 \times 10^4}{R} \left( \frac{1}{T} - 1 \right) \right] \]  

(34)

Values of the forward rate coefficient \(k_{26}\) of reaction (6) was calculated using Eq. (35)

\[ \log_{10} k_{26} = 16.35 - \frac{2895}{T} \]  

(35)

Similarly, the forward rate constants \(k_{23}\) and \(k_{25}\) for reactions (3) and (5) are calculated using following Arrhenius equations.

\[ k_{PZ(\text{CO}_2)\text{OG}} = 3.516 \times 10^4 \exp \left[ -\frac{65225}{R} \left( \frac{1}{T} - 1 \right) \right] \]  

(36)

\[ k_{PZ(\text{CO}_2)\text{OG}} = 1.836 \times 10^4 \exp \left[ -\frac{70550}{R} \left( \frac{1}{T} - 1 \right) \right] \]  

(37)

IV. EXPERIMENTAL

A. Materials

Reagent grade PZ (> 99% pure) is obtained from E. Merck, Germany. Reagent grade AMP (> 97% pure) is obtained from Sigma-Aldrich, USA. The \(\text{CO}_2\) gas (> 99.9% pure) and nitrogen gas (> 99.999% pure) were obtained from Chemtron Science Lab Pvt. Ltd., India.

B. Absorption Measurement

Absorption rates of \(\text{CO}_2\) in PZ activated concentrated aqueous AMP were measured using a 2.81 \times 10^{-7} \text{ m o.d.} stainless-steel wetted wall contactor. A jacketed corning glass shroud with gas inlet at the top and three equally spaced gas outlets at the bottom made the enclosure for the gas space for absorption. The gas and liquid film temperatures were maintained at the desired level with circulator temperature controllers (JULABO, FRG). The gas flow rates of \(\text{CO}_2\) and
N\textsubscript{2} were controlled using two recalibrated mass flow controllers (Sierra Instruments, USA). The gas and liquid flows are co-current for the absorption measurements in this contactor. In this work the absorption length was 6.5×10\textsuperscript{-3} m. Since turbulence appears when liquid film Reynolds number is greater than 250, liquid flow rate for all runs was kept at about 2×10\textsuperscript{4} m\textsuperscript{3}.s\textsuperscript{-1} so that liquid flow was well within the laminar region. With this flow rate the Reynolds number is about 30.

The measured and model absorption results of rates of absorption of CO\textsubscript{2} in the model. The AAD between the experimental and model experimental results after incorporating Eqs. (36) and (37) in predicted rates are in excellent agreement with the

Reynolds number is about 30. 6.5×10\textsuperscript{-2} m

flows are co-current for the absorption measurements in this

controller. In this work the absorption length used was

range of (303–323) K and CO\textsubscript{2} partial pressure of

33 K. It has been observed that the solvent capacity increases markedly with the increase in the total amine concentration of activated solvent (AMP+PZ). For instance, for a rich and lean CO\textsubscript{2} partial pressure of 10 kPa and 1 kPa, respectively, the solvent capacity of 50 wt% total amine (45 wt% AMP+5 wt% PZ) is higher by about 12% than that of 40 wt% total amine (35 wt% AMP+5 wt% PZ) at 323 K.

VI. CONCLUSION

In this work, the absorption of CO\textsubscript{2} into aqueous solutions of PZ activated AMP has been studied experimentally and theoretically. Absorption measurement over the temperature range of (303–323) K and CO\textsubscript{2} partial pressure range of (5–15) kPa were performed using a wetted wall contactor. It has been found that the addition of small amounts of PZ to an aqueous solution of AMP significantly enhances the rate of absorption of CO\textsubscript{2} and enhancement factor. The solvent capacity has been found to increase with total amine strength.
in the CO₂ partial pressure range of 5-15 kPa, which is typical condition for CO₂ partial pressure in the power plant flue gas streams, indicating improved CO₂ capacity of PZ-activated concentrated aqueous AMP solvents. Relative to MEA, higher oxidative and thermal degradation resistance, and lower regeneration energy requirement add to the advantages of this solvent for CO₂ capture.

REFERENCES

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