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ABSORPTION OF CARBON DIOXIDE INTO PIPERAZINE ACTIVATED AQUEOUS N-METHYLDIETHANOLAMINE

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Abstract

This work presents a theoretical and experimental investigation on the absorption of CO_2 into piperazine (PZ) activated aqueous N-methyldiethanolamine (MDEA) solvent. A comprehensive numerical model which is based on Higbie's penetration theory has been developed to analyze the experimental data. The model involving coupled mass transfer–reaction kinetics–chemical equilibrium incorporates the important reversible reactions in the liquid phase. The model is validated with the experimental results of steady state absorption measurements of CO_2 in a 2.81×10^{-2} m o.d. stainless steel wetted wall contractor. The rates of absorption of CO_2 into this solvent have been measured over the CO_2 partial pressure range of 2-14 kPa and temperature range of 298 – 313 K under atmospheric pressure. The absorption experiments are performed over the MDEA concentration range of 1.89 - 2.41 kmol.m^{-3} along with PZ concentrations of 0.24, 0.60 and 0.95 kmol.m^{-3}. Steady state absorption measurements of this work have shown that the CO_2 absorption rates into aqueous MDEA increase significantly with the addition of small amounts of PZ in the solvent. This establishes the potential of the PZ activated aqueous MDEA solvent for industrial gas treating. Good agreement between the model results and experimental results indicates that the combined mass transfer-reaction kinetics-equilibrium model can effectively represent CO_2 mass transfer rates in PZ activated aqueous MDEA for wide range of operating conditions.

Keywords: Absorption, Kinetics, Carbon dioxide, MDEA, Piperazine

1. Introduction

The removal of acid gas impurities, such CO_2 and H_2S, from industrial gas streams is an important step in processing sour natural gas, refinery off-gases, and synthesis gas. CO_2 present in natural gas will reduce the heating value and may cause corrosion in pipelines and equipment in presence of moisture. The CO_2 specification in the treated natural gas may be about < 1% by volume for pipeline gas, but for natural gas liquefaction plants CO_2 in the treated natural gas must be below 100 ppm to avoid freezing in the cryogenic equipment. Besides removal of CO_2 from natural gas, CO_2 capture from the flue gas streams of thermal power plants is very important today to mitigate the problem of global warming. The United Nations Intergovernmental Panel on Climate Change (IPCC) identified CO_2 capture and sequestration as one of several approaches to address the problem of global warming and climate change[1]. Hence, efficient and less energy intensive capture of CO_2 from flue gases with subsequent geological storage is increasingly being viewed as a medium-term option for reducing CO_2 emissions. In view of this, extensive research activities are also in progress globally to develop efficient and economic processes for CO_2 capture from the flue gas streams of thermal power plants.

Most frequently, the removal of CO_2 from various industrial gas streams is done by the regenerative chemical absorption into aqueous solutions of alkanolamines. Commercially available alkanolamine solvents for these processes are monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), N-methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP). There is a growing interest in recent times to use mixed amine solvents instead of a single amine solution for gas treating. It has been observed that the use of blended amines in gas treating can bring about significant improvement in the absorption capacity and absorption rate, and also great saving in solvent regeneration energy requirements.

More recently, there is an interest in the use of piperazine (PZ) activated aqueous MDEA for gas treating processes. PZ is used as an activator in the activated MDEA process of BASF[2]. Being a cyclic diamine, each mole of PZ can theoretically absorb two moles of CO_2, and it may favor rapid formation of the carbamates. While there is extensive published literature on the use of primary, secondary or tertiary alkanolamines and their blends for the removal of CO_2, literature on piperazine activated MDEA solvent system is very limited.

Xu et al.[3] measured the absorption rate of pure CO_2 gas at atmospheric pressure into aqueous blends of MDEA/PZ using a disk column in the temperature range of 303 – 343 K. Zhang et al.[4] proposed the mechanism of CO_2 absorption into an aqueous solution of MDEA blended with PZ. Bishnoi and Rochelle[5] reported CO_2 absorption data in 4 M aqueous MDEA solutions with 0.6M PZ at 313 and 343 K using a wetted wall contactor. Rate model based on eddy diffusivity theory was used for prediction of the rate of absorption and enhancement factor. However, except the work reported by Samanta[6], there is no other reported literature on analyzing CO_2 absorption into blends of PZ/MDEA with a coupled mass transfer-reaction kinetics-equilibrium model. Zhang et al.[7] extended their investigation to study the effects of CO_2 partial pressure on the absorption of CO_2 into aqueous MDEA/PZ in a laboratory packed column. It is evident from the foregoing discussion that in spite of great commercial significance of the PZ activated aqueous MDEA solvent, published literature on the theoretical and experimental investigation on absorption of CO_2 into PZ activated aqueous MDEA solvent is extremely limited.

This work presents an experimental and theoretical investigation on the absorption of CO_2 into PZ activated aqueous MDEA solvent. The rates of absorption of CO_2 into aqueous solutions of PZ-MDEA have been measured in a wetted wall contactor over the temperature range of 298 -313 K. In view of industrial gas treating conditions the absorption experiments are performed over the MDEA concentration range of 1.89 - 2.41 $kmol.m^{-3}$ along with PZ concentrations of 0.24, 0.6 and 0.95 $kmol.m^{-3}$. A coupled mass transfer - reaction kinetics - equilibrium model, which is capable of predicting gas absorption rates and enhancement factors for absorption of CO_2 into activated amine solvents has been developed.

2. Reaction Scheme and Mathematical Model

2.1 Reaction Scheme and Mechanism

Based on the studies conducted by Bishnoi and Rochelle[8] and Kamps et al.[9] on absorption of CO_2 into aqueous solutions of MDEA and PZ, the following reactions are considered for the model development.

$$CO_2 + R_1R_2R_3N + H_2O \xleftrightarrow{K_1, k_{21}} R_1R_2R_3NH^+ + HCO_3^- \quad (1)$$

$$CO_2 + PZ + H_2O \xleftrightarrow{K_2, k_{22}} PZCOO^- + H_3O^+ \quad (2)$$

$$CO_2 + R_1R_2R_3N + PZ \xleftrightarrow{K_3, k_{23}} PZCOO^- + R_1R_2R_3NH^+ \quad (3)$$

$$CO_2 + PZCOO^- + H_2O \xleftrightarrow{K_4, k_{24}} PZ(COO^-)_2 + H_3O^+ \quad (4)$$

$$CO_2 + R_1R_2R_3N + PZCOO^- \xleftrightarrow{K_5, k_{25}} PZ(COO^-)_2 + R_1R_2R_3NH^+ \quad (5)$$

$$CO_2 + OH^- \xleftrightarrow{K_6, k_{26}} HCO_3^- \quad (6)$$

$$HCO_3^- + H_2O \xleftrightarrow{K_7} CO_3^{2-} + H_3O^+ \quad (7)$$

$$PZ + H_3O^+ \xleftrightarrow{K_8} PZH^+ + H_2O \quad (8)$$

$$PZCOO^- + H_3O^+ \xleftrightarrow{K_9} PZH^+COO^- + H_2O \quad (9)$$

$$R_1R_2R_3N + H_3O^+ \xleftrightarrow{K_{10}} R_1R_2R_3NH^+ + H_2O \quad (10)$$

$$2H_2O \overset{K_{11}}{\longleftrightarrow} H_3O^+ + OH^- \tag{11}$$

For MDEA, $R_1 = CH_3$, $R_2 = R_3 = C_2H_4OH$. K_i is the equilibrium constant for reaction (i) and k_{2i} is the forward rate coefficient for reaction (i). Reactions (1) – (6) are considered to be reversible with finite reaction rates, whereas reactions (7) - (11) are considered to be reversible and instantaneous with respect to mass transfer and at equilibrium, since they involve proton transfer only. As proposed by Donaldson and Nguyen[10], the reaction mechanism for CO_2 with tertiary amines (e.g., MDEA) is a base-catalyzed hydration reaction as shown in the reaction (1). The mechanism implies that MDEA does not react directly with CO_2. The proposed mechanism for the reaction between CO_2 and PZ involves the formation of a zwitterion followed by the deprotonation of zwitterion by a base to produce PZ-carbamate and protonated base.

2.2 Diffusion-Reaction Model

The mass-transfer model describing the diffusion reaction process consists of partial differential equations formulated according to eq. (12) for the reactants (e.g., CO_2, PZ and MDEA) and products (e.g., PZ-carbamate and PZ-dicarbamate) present in the liquid phase.

$$\frac{\partial u_i}{\partial t} = D_i \frac{\partial^2 u_i}{\partial x^2} + \sum_i \nu_i R_i \tag{12}$$

where, u_i and D_i are the concentration and diffusivity, respectively of the species i. The notations for chemical species are: $u_1 = [CO_2]$, $u_2 = [R_1R_2R_3N]$, u3 = $[R_1R_2R_3NH^{+]}$, $u_4 = [HCO_3^-]$, $u_5 = [OH^-]$, $u_6 = [CO_3^{2-}]$, $u_7 = [H_3O^+]$, $u_8 = [PZ]$, $u_9 = [PZH^+]$, $u_{10} = [PZCOO^-]$, $u_{11} = [PZH^+COO^-]$ and $u_{12} = [PZ\,(COO^-)_2]$. R_i is the finite reaction rate for reactions (1)-(6). R_1 for reaction (1), for instance, is expressed as

$$R_1 = -k_{21}u_1u_2 + \frac{k_{21}}{K_1}u_3u_4 \tag{13}$$

CO_2 balance:

$$\frac{\partial u_1}{\partial t} = D_1 \frac{\partial^2 u_1}{\partial x^2} + \sum_{i=1}^{6} R_i \tag{14}$$

Electroneutrality balance:

$$\begin{aligned}\frac{\partial u_3}{\partial t} + \frac{\partial u_7}{\partial t} + \frac{\partial u_9}{\partial t} - \frac{\partial u_4}{\partial t} - \frac{\partial u_5}{\partial t} - 2\frac{\partial u_6}{\partial t} - \frac{\partial u_{10}}{\partial t} - 2\frac{\partial u_{12}}{\partial t} &= D_3\frac{\partial^2 u_3}{\partial x^2} + D_7\frac{\partial^2 u_7}{\partial x^2} + D_9\frac{\partial^2 u_9}{\partial x^2} - D_4\frac{\partial^2 u_4}{\partial x^2} \\ &\quad - D_5\frac{\partial^2 u_5}{\partial x^2} - 2D_6\frac{\partial^2 u_6}{\partial x^2} - D_{10}\frac{\partial^2 u_{10}}{\partial x^2} - 2D_{12}\frac{\partial^2 u_{12}}{\partial x^2}\end{aligned} \tag{15}$$

Similarly PDEs for MDEA, PZ, PZ-carbamate and PZ-dicarbamate balances are formed following the work of Samanta[6] for PZ activated aqueous MDEA and Samanta and Bandyopadhyay[11] for PZ activated aqueous AMP. Instantaneous reactions (7)-(11) assumed to be at equilibrium are represented by the equilibrium constants using respective species concentrations. For example, K_7:

$$K_7 = \frac{u_6u_7}{u_4} \tag{16}$$

Thus, there are twelve partial differential-algebraic equations which can be solved for the concentration profiles of the twelve chemical species (u_1,……….,u_{12}) present in the aqueous solutions of (MDEA + PZ).

The differential equations are integrated from t = 0 to t = θ, the contact time, using appropriate initial and boundary conditions (Samanta[6], Samanta and Bandyopadhyay[11]). The time-averaged absorption rate per unit interfacial area is obtained as given in Eq. (17).

$$\overline{R} = -\frac{D_1}{\theta}\int_0^{\theta}\frac{\partial u_1(0,t)}{\partial x}dt \tag{17}$$

and the enhancement factor, E, for absorption of CO_2 is given by Eq. (18):

$$E = \frac{\overline{R}}{k_{L,1}(u_1^{*} - u_1^{0})} \tag{18}$$

where, k_{L1} is the liquid-phase mass transfer coefficient defined by Higbie's penetration model.

The method-of-lines (MOL) is used to transform each partial differential equation into a set of ordinary differential equations in t by discretizing the spatial variable x. The resulting system of ordinary differential equations coupled with the nonlinear algebraic equations is solved by using the subroutine DDASSL[12] in FORTRAN. The typical number of nodes used in this work is 450 and corresponding nodal spacings are of the order of 10^{-8} m.

3. Experimental

3.1 Materials

Piperazine (> 99 % pure) and MDEA (> 98 % pure) were supplied by E. Merck (Germany) and were used without further purification. Distilled water degassed by boiling and cooled to ambient temperature under vacuum, was used for preparing the amine solutions. Carbon dioxide (> 99.9 % pure) and nitrogen gas (> 99.999 % pure) used for the absorption measurements were obtained from Chemtron Science Pvt. Ltd. (India).

3.2 Apparatus and Procedure

The stainless steel wetted wall contactor (2.81×10^{-2} m o.d.) used for absorption measurements in this study was similar to the one used by Saha et al.[13]. Flow rates of CO_2, and N_2 were controlled by mass flow controllers (Sierra Instruments, USA). Two circulator temperature controllers (JULABO F 32 and FP 55, FRG) were used to control the liquid film and gas phase temperature within ± 0.2 K of the desired level.

CO_2 diluted with N_2 to make the required gas phase composition at the inlet was passed at a volumetric flow rate of about 180×10^{-6} $m^3.s^{-1}$ through the mixing tube and the coil immersed in the controlled temperature bath and finally through the saturators immersed in the same bath. When the desired gas phase temperature was reached, the concentration of CO_2 at the inlet was determined using the HORIBA NDIR on-line CO_2 analyzer. The gas, saturated with water vapor at the temperature of absorption, was fed to the top of absorption space of the wetted wall contactor. The amine solution thermostated at the temperature of absorption was then fed from the overhead storage to the contactor at the desired flow rate of about 2×10^{-6} $m^3.s^{-1}$. When the system reached the steady state with respect to the gas and liquid flow rates, the gas phase and liquid film temperature, and the gas phase concentration of CO_2 at the exit of the contactor measured by HORIBA NDIR on-line CO_2 analyzer, three liquid samples were collected from liquid outlet located at the end of the absorption length at an interval of about one minute. The amount of total CO_2 in each loaded liquid sample was determined immediately by acidulating a known volume of the sample and measuring the volume of evolved CO_2.

4. Results and Discussion

Absorption measurements for CO_2 into aqueous (MDEA + PZ) at 298, 303, 308 and 313 K have been interpreted according to the model developed and described in Section 2 to obtain estimates for the rate constants, k_{23} and k_{25}. This is achieved by adjusting the values of rate constants in our mathematical model until the predicted rates of absorption agreed with the experimentally measured rates of absorption within 5%. By comparing the model calculated results with the experimental results, it has been observed that if reaction (3) is not considered the model under-predicts the rate of absorption by about 28 % compared with the experimental rates for CO_2 partial pressure above 5 kPa. From this observation it appears that the role of MDEA in proton transfer is important. It is also observed that if reactions (4) and (5) are not considered, the model under predicts the rate of absorption by about 12% for CO_2 partial pressure above 5 kPa. Thus formation of PZ-dicarbamate (reactions (4) and (5)) are also important in the overall kinetics of CO_2-MDEA-PZ. The average absolute deviation (AAD) for the whole partial pressure range of CO_2 when reactions (3), (4) and (5) are considered is about 6.68%.

Table 1 presents a few measured and model predicted rates and enhancement factors for absorption of CO_2 into (MDEA + PZ + H_2O). As shown in Table 1, the addition of small amounts of PZ to an aqueous solution of MDEA results in significant increase in the rate of absorption and enhancement factor. For instance, at T = 313 K and CO_2 partial pressure of about 5kPa, the enhancement factors for absorption in aqueous solutions of (2.56 M MDEA, i.e., 30 mass% MDEA), (0.24 M PZ + 2.41 M MDEA), (0.6 M PZ + 2.15 M MDEA), and (0.95 M PZ + 1.89 M MDEA) are about 15.8, 118.8, 164.5 and 202.4, respectively. So, by replacing 2 mass% MDEA with 2 mass % PZ, the enhancement factor increased by about 651%. Replacing an additional 3 mass% MDEA with PZ increased the enhancement factor by an additional 38%. A further replacement of 3 mass% MDEA with an equal amount of PZ resulted in increasing the enhancement factor by an additional 23.0%.

Table 1. Experimental and model predicted results for the absorption of CO_2 into aqueous PZ/MDEA

[MDEA], kmol.m^{-3}	[PZ], kmol.m^{-3}	T, K	p_1, kPa	θ s	$k_L \times 10^5$ m.s^{-1}	Experimental results		Predicted results	
						$R \times 10^6$, kmol.m^{-2}s^{-1}	E	$R \times 10^6$, kmol.m^{-2}s^{-1}	E
2.56	0.0	313	14.24	0.40	6.57	2.40	10.9	2.17	9.9
2.41	0.24	298	4.8	0.53	4.5	6.05	96.5	5.65	90.1
2.41	0.24	308	4.95	0.43	5.85	7.16	105.5	6.83	100.6
2.41	0.24	313	1.69	0.43	6.18	4.69	209.4	4.51	201.4
2.15	0.60	303	4.83	0.41	5.22	8.87	128.8	8.71	126.4
2.15	0.60	313	4.66	0.39	5.98	10.90	164.5	10.77	162.5
2.15	0.60	313	13.27	0.40	5.90	23.20	124.5	24.57	131.8
1.89	0.95	298	4.93	0.45	4.19	9.93	164.4	8.80	145.7
1.89	0.95	313	4.70	0.39	5.57	11.90	202.4	12.72	216.4
1.89	0.95	313	6.69	0.43	5.19	15.30	196.4	16.65	213.8
1.89	0.95	313	13.51	0.45	5.13	28.80	185.1	30.09	193.4

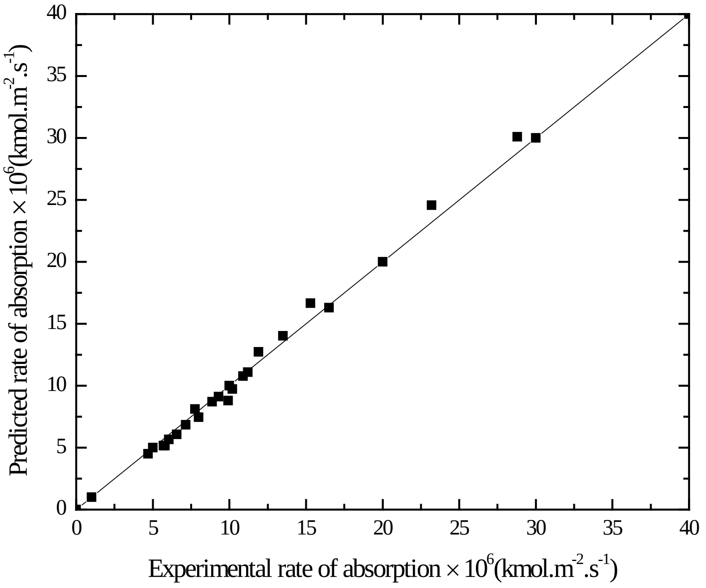

Figure 1. Parity plot of model predicted rates and experimental rates of absorption of CO_2 into aqueous (MDEA + PZ).

The measured and model predicted rates are compared in the parity plot shown in Figure 1. As shown in Figure 1, the model predicted rates of absorption of CO_2 into (MDEA + PZ + H_2O) are in good agreement with the experimental results, the AAD between the experimental and model results being about 6.8%.

It has been observed from the calculated concentration profiles in the film for absorption of CO_2 into (MDEA+PZ) that the concentrations of MDEA and PZ near the gas-liquid interface are lower by about 1.54 % and 36%, respectively, than their liquid bulk concentrations after a gas-liquid contact time of about 0.39s, showing substantial depletion of PZ at the gas-liquid interface.
The estimated k_{23} and k_{25} values obtained for CO_2 – (MDEA + PZ + H_2O) in this work have been correlated according to the following Arrhenius equations.

$$k_{23} = 1.75\times10^4 \exp\left(-\frac{8.75\times10^4}{R}\left(\frac{1}{T}-\frac{1}{298}\right)\right) \tag{19}$$

$$k_{25} = 1.55\times10^4 \exp\left(-\frac{8.75\times10^4}{R}\left(\frac{1}{T}-\frac{1}{298}\right)\right) \tag{20}$$

The estimated k_{23} and k_{25} values of this work have been found to be in good agreement with the results of Bishnoi and Rochelle[5].

5. Conclusions

The absorption of CO_2 into aqueous solutions of mixtures of small amounts of fast reacting PZ and much larger amounts of MDEA, were studied experimentally and theoretically. It has been found that the addition of small amounts of PZ to an aqueous solution of MDEA significantly enhances the rate of absorption and enhancement factor. New kinetic parameters, k_{23} and k_{25}, for the reactions of CO_2 with (MDEA + PZ) have been obtained using the mathematical model and the measured absorption data of this work. The rate constants presented in this work are in good agreement with those reported by Bishnoi and Rochelle[5].

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