Absorption of Carbon Dioxide into Piperazine Activated Aqueous N-Methyldiethanolamine

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Presented by

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Global Warming and CO_2 Capture: The Perspective

- One of the most serious problems facing the human civilization today is global warming, climate change and consequential threat to the environment of this planet.
- Hence, one of the most challenging issues confronting the international community is how to attain economic growth, poverty mitigation and energy security without deteriorating earth's environment further.

Global Warming and CO_2 Capture: The Perspective

- As world population multiplies to about 9 billion in 2050 and demand for energy to sustain economic growth increases exponentially, energy supply projections point to the fact that abundant, affordable fossil fuels will have to be used to fuel economic growth well beyond 2020.

- Production and use of fossil fuels contribute to 64% of global anthropogenic greenhouse gas (GHG) emission, and fossil fuel based power generation currently accounts for one third of annual global CO_2 emission.

Global Warming and CO_2 Capture: The Perspective

- Although among the GHGs CO_2 is the least potent on molecular basis, given its massive emission levels, the threat of global warming is the highest from emission of CO_2

- The global concern for this is well reflected in the deep global engagements that continue from the Rio Earth Summit in 1992 through the 1997 Kyoto Protocol of United Nations Framework Convention on Climate Change (UNFCCC) to the UN Climate Change Conference in Copenhagen in December 2009.

Global Warming and CO_2 Capture: The Perspective

- CO_2 capture from large point sources of CO_2 emission, such as coal based power plants, natural and synthesis gas processing plants and cement plants and its sequestration is identified as a major option to address the problem of global warming and climate change. However, the main focus of CCS today is coal based power plants.
- Amine based regenerative chemical absorption processes have been widely practiced for several years for CO_2 capture from gas streams in natural gas and synthesis gas processing.

Global Warming and CO_2 Capture: The Perspective

- The gas streams in these processes are at a high pressure of about 30 to 100 atmosphere. But the major challenges for CO_2 capture from 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.
- The presence of SO_x, NO_X and significant oxygen partial pressure in the flue gas put up further problems for implementation of amine absorption process for CO_2 capture from power plant flue gas streams

Global Warming and CO_2 Capture: The Perspective

- The state of the art process uses 15 – 30 mass % aqueous monoethanolamine (MEA) for regenerative absorption of CO_2 However, this process is highly energy intensive due to the high regeneration energy requirement. Besides, high degradation and high corrosiveness of MEA contribute to increasing the cost of electricity by about 70 – 80%.

- This fact reduces the motivation of implementing MEA process for CO_2 capture from the flue gas of coal based power plants.

Present Work

- Based on our experience of working with mixed amine solvents for higher reaction rate and higher equilibrium capacity for CO_2 and on the basis of literature information, we have taken up investigation to explore the efficacy of two piperzine (PZ) activated amine solvents, (AMP + PZ +H_2O) and (MDEA + PZ + H_2O) for CO_2 capture.

- PZ activated AMP is the preferred solvent for Kansai Electric Power Company and Mitsubishi Heavy Industries, while PZ activated MDEA is introduced by BASF for absorption of CO_2.

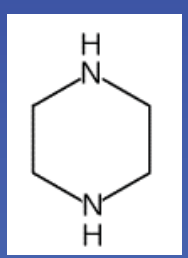
Present Work

- Our work on (AMP + PZ +H_2O) is published elsewhere (Samanta and Bandyopadhyay, Chem. Eng. Sci, 64, 1185 – 1194, 2009).
- This work presents an experimental and theoretical investigation on the absorption of CO_2 into PZ activated aqueous MDEA solvent.

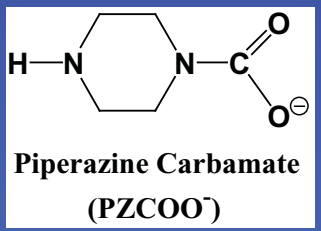
Model Development

Basic Chemistry

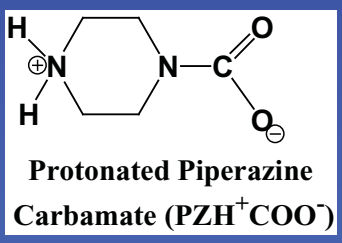
- Spectroscopic investigations by Bishnoi and Rochelle (2002), Ermatchkov et al. (2003) and Kamps et. al. (2003) on aqueous solutions of CO2 and PZ establish the formation of the following piperazine species in the liquid phase:



Piperazine (PZ)



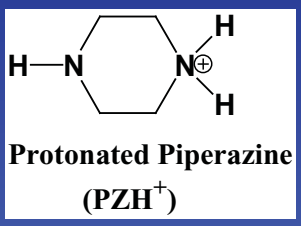
Piperazine Carbamate ($PZCOO^-$)



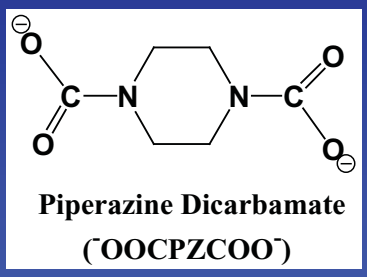
Protonated Piperazine Carbamate (PZH^+COO^-)

Model Development

Basic Chemistry



Protonated Piperazine
(PZH^+)



Piperazine Dicarbamate
($^-OOCPZCOO^-$)

Model Development

Reaction Schemes

- When CO_2 is absorbed into PZ activated aqueous MDEA the following reactions may occur:

$$CO_2 + R'R''R'''N + H_2O \xleftrightarrow{K_1, k_{21}} R'R''R'''NH^+ + HCO_3^- \quad (1)$$

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

$$CO_2 + R'R''R'''N + PZ \xleftrightarrow{K_3, k_{23}} PZCOO^- + R'R''R'''NH^+ \quad (3)$$

Model Development

Reaction Schemes

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

$$CO_2 + R'R''R''N + PZCOO^- \xleftrightarrow{K_5, k_{25}} PZ(COO^-)_2 + R'R''R''NH^+ \quad (5)$$

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

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

Model Development

Reaction Schemes

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

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

$$R'R''R''N + H_3O^+ \xleftrightarrow{K_{10}} R'R''R''NH^+ + H_2O \quad (10)$$

$$2H_2O \xleftrightarrow{K_{11}} H_3O^+ + OH^- \quad (11)$$

Model Development

BULK LIQUID EQUILIBRIUM MODEL

- An equilibrium model has been developed to estimate the initial liquid bulk concentrations of all chemical species from the initial concentration of PZ and MDEA and CO_2 loading.
- It is assumed that all reactions are at equilibrium.

Overall R/R//R//N (MDEA/AMP) balance:

$$u_2^0 + u_3^0 = \left[R^{/}R^{//}R^{//}N\right]_{initial} \quad (12)$$

Overall PZ balance:

$$u_8^0 + u_9^0 + u_{10}^0 + u_{11}^0 + u_{12}^0 = \left[PZ\right]_{initial} \quad (13)$$

Model Development

BULK LIQUID EQUILIBRIUM MODEL

Overall CO_2 balance:

$$u_1^0 + u_4^0 + u_6^0 + u_{10}^0 + u_{11}^0 + 2u_{12}^0 = \alpha_1 \left\{\left[R^{/}R^{//}R^{//}N\right]_{initial} + \left[PZ\right]_{initial}\right\} \quad (14)$$

Electroneutrality balance:

$$u_3^0 + u_7^0 + u_9^0 - u_4^0 - u_5^0 - 2u_6^0 - u_{10}^0 - 2u_{12}^0 = \alpha_1 \left\{\left[R^{/}R^{//}R^{//}N\right]_{initial} + \left[PZ\right]_{initial}\right\} \quad (15)$$

Model Development

BULK LIQUID EQUILIBRIUM MODEL

All reactions are in equilibrium:

$$K_2 = \frac{u_7^0 u_{10}^0}{u_1^0 u_8^0} \quad (16)$$

$$K_4 = \frac{u_7^0 u_{12}^0}{u_1^0 u_{10}^0} \quad (17)$$

$$K_6 = \frac{u_4^0}{u_1^0 u_5^0} \quad (18)$$

$$K_7 = \frac{u_6^0 u_7^0}{u_4^0} \quad (19)$$

Model Development

BULK LIQUID EQUILIBRIUM MODEL

$$K_8 = \frac{u_9^0}{u_7^0 u_8^0} \quad (20)$$

$$K_9 = \frac{u_{11}^0}{u_7^0 u_{10}^0} \quad (21)$$

$$K_{10} = \frac{u_3^0}{u_2^0 u_7^0} \quad (22)$$

$$K_{11} = u_5^0 u_7^0 \quad (23)$$

Model Development

BULK LIQUID EQUILIBRIUM MODEL

- where, u_1 = $[CO_2]$, u_2 = $[R_1R_2R_3N]$, u_3 = $[R_1R_2R_3NH+]$, 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} = $[PZ\ (COO^–)_2]$ and superscript '0' denotes initial liquid bulk concentration of species i.

- The twelve simultaneous nonlinear algebraic equations (equations (12)-(23)) have been solved using IMSL Math/Library in FORTRAN 90 for the twelve unknowns $u_1^0, \ldots\ldots\ldots\ldots, u_{12}^0$ of the liquid bulk concentrations.

Model Development

DIFFUSION-REACTION MODEL

- Reactions (1) - (6) having finite reaction rates are given by:

$$R_1 = -k_{21}u_1u_2 + \frac{k_{21}}{K_1}u_3u_4 \qquad (24)$$

$$R_2 = -k_{22}u_1u_8 + \frac{k_{22}}{K_2}u_{10}u_7 \qquad (25)$$

$$R_3 = -k_{23}u_1u_2u_8 + \frac{k_{23}}{K_3}u_{10}u_3 \qquad (26)$$

$$R_4 = -k_{24}u_1u_{10} + \frac{k_{24}}{K_4}u_7u_{12} \qquad (27)$$

Model Development

DIFFUSION-REACTION MODEL

- Reactions (1) - (6) having finite reaction rates are given by:

$$R_5 = -k_{25} u_1 u_2 u_{10} + \frac{k_{25}}{K_5} u_3 u_{12} \qquad (28)$$

$$R_6 = -k_{26} u_1 u_5 + \frac{k_{26}}{K_6} u_4 \qquad (29)$$

Model Development

DIFFUSION-REACTION MODEL

- Equations describing the diffusion-reaction process :
- CO_2 balance:

$$\frac{\partial u_1}{\partial t} = D_1 \frac{\partial^2 u_1}{\partial x^2} + \sum_{i=1}^{6} R_i \qquad (30)$$

- Total carbon (from CO_2) balance:

$$\frac{\partial u_1}{\partial t} + \frac{\partial u_4}{\partial t} + \frac{\partial u_6}{\partial t} + \frac{\partial u_{10}}{\partial t} + \frac{\partial u_{11}}{\partial t} + 2\frac{\partial u_{12}}{\partial t} = D_1 \frac{\partial^2 u_1}{\partial x^2} + D_4 \frac{\partial^2 u_4}{\partial x^2} + D_6 \frac{\partial^2 u_6}{\partial x^2} + D_8 \frac{\partial^2 u_{10}}{\partial x^2} + D_9 \frac{\partial^2 u_{11}}{\partial x^2} + 2D_{10} \frac{\partial^2 u_{12}}{\partial x^2} \qquad (31)$$

Model Development

DIFFUSION-REACTION MODEL

- Equations describing the diffusion-reaction process:

- Total MDEA/AMP balance:

$$\frac{\partial u_2}{\partial t}+\frac{\partial u_3}{\partial t}=D_2\frac{\partial^2 u_2}{\partial x^2}+D_3\frac{\partial^2 u_3}{\partial x^2} \quad (32)$$

- Total PZ balance:

$$\frac{\partial u_8}{\partial t}+\frac{\partial u_9}{\partial t}+\frac{\partial u_{10}}{\partial t}+\frac{\partial u_{11}}{\partial t}+\frac{\partial u_{12}}{\partial t}=D_8\frac{\partial^2 u_8}{\partial x^2}+D_9\frac{\partial^2 u_9}{\partial x^2}+D_{10}\frac{\partial^2 u_{10}}{\partial x^2}+D_{11}\frac{\partial^2 u_{11}}{\partial x^2}+2D_{10}\frac{\partial^2 u_{12}}{\partial x^2} \quad (33)$$

Model Development

DIFFUSION-REACTION MODEL

- Carbamate balance:

$$\frac{\partial u_{10}}{\partial t}+\frac{\partial u_{11}}{\partial t}=D_{10}\frac{\partial^2 u_{10}}{\partial x^2}+D_{11}\frac{\partial^2 u_{11}}{\partial x^2}-R_2-R_3+R_4+R_5 \quad (34)$$

- Dicarbamate balance:

$$\frac{\partial u_{12}}{\partial t}=D_{12}\frac{\partial^2 u_{12}}{\partial x^2}-R_4-R_5 \quad (35)$$

- Electroneutrality Balance:

$$\frac{\partial u_3}{\partial t}+\frac{\partial u_7}{\partial t}+\frac{\partial u_9}{\partial t}-\frac{\partial u_4}{\partial t}-\frac{\partial u_5}{\partial t}-2\frac{\partial u_6}{\partial t}-\frac{\partial u_{10}}{\partial t}-2\frac{\partial u_{12}}{\partial t}=D_3\frac{\partial^2 u_3}{\partial x^2}+D_7\frac{\partial^2 u_7}{\partial x^2}+D_9\frac{\partial^2 u_9}{\partial x^2}-D_4\frac{\partial^2 u_4}{\partial x^2}-D_5\frac{\partial^2 u_5}{\partial x^2}-2D_6\frac{\partial^2 u_6}{\partial x^2}-D_{10}\frac{\partial^2 u_{10}}{\partial x^2}-2D_{12}\frac{\partial^2 u_{12}}{\partial x^2} \quad (36)$$

Model Development

DIFFUSION-REACTION MODEL

- **Instantaneous reactions at equilibrium:**

$$K_7 = \frac{u_6 u_7}{u_4} \qquad (37)$$

$$K_8 = \frac{u_9}{u_8 u_7} \qquad (38)$$

$$K_9 = \frac{u_{11}}{u_{10} u_7} \qquad (39)$$

$$K_{10} = \frac{u_3}{u_2 u_7} \qquad (40)$$

Model Development

DIFFUSION-REACTION MODEL

- **Instantaneous reactions at equilibrium:**

$$K_{10} = \frac{u_3}{u_2 u_7} \qquad (40)$$

$$K_{11} = u_5 u_7 \qquad (41)$$

- **Thus there are 12 partial differential-algebraic equations.**
- **Equations are solved for the concentration profiles of the chemical present in the aqueous solutions of MDEA/PZ.**

Model Development

DIFFUSION-REACTION MODEL

- **Initial and boundary conditions at x = ∞ :**

At t = 0 (for all x ≥ 0) and at x = ∞ (for all t ≥ 0), the concentration of chemical species are equal to their liquid bulk concentrations, i.e.,

$$u_i = u_i^0, \quad i = 1,.....12 \tag{42}$$

- **Boundary conditions at gas-liquid interface (x =0):**

$$\frac{\partial u_i}{dx} = 0\,, \quad i = 2,3.....,12 \qquad \text{at } x = 0 \text{ and } t > 0 \tag{43}$$

Model Development

DIFFUSION-REACTION MODEL

For volatile component CO_2, the mass-transfer rate in the gas near the interface is equal to the rate in the liquid near the interface:

$$-D_1 \frac{\partial u_1}{dx} = k_g(p_1 - H_1 u_1(0,t)) \qquad \text{at } x = 0 \text{ and } t > 0 \tag{44}$$

Model Development

Method of Solution

- The Method-of-Lines is used to transform each PDE into a set of ODEs in t by discretizing the spatial variable x.

- The following finite difference expression is used to approximate the spatial derivatives.

$$\frac{\partial^2 u_i}{\partial x^2} = \frac{\left[u_{i+1} - 2u_i + u_{i-1}\right]}{h^2} \qquad (48)$$

Model Development

Method of Solution

- The resulting equations are solved by using subroutine DDASSL (Petzold, 1983) in double precision FORTRAN 90.

- Equally spaced nodes are used to discretize the x.

- The typical no. of nodes used in this work is 400-425.

- Nodal spacings used are of the order of 10^{-8} m.

Model Development

Physicochemical Properties & Model Parameters

- The density and viscosity of aqueous solutions of PZ and PZ activated aqueous MDEA have been measured.
- Nitrous oxide (N_2O) is used as a surrogate to CO_2 in estimating the physical solubility and diffusivity of CO_2 in these solvents.

Model Development

Physicochemical Properties & Model Parameters

- Physical solubility and diffusivity of N_2O in aqueous PZ and PZ activated MDEA solutions at various temperatures and various relative compositions of PZ and MDEA have been measured.
- "N_2O analogy" is then adopted to estimate the solubilities and diffusivities of CO_2 in (PZ + H_2O) and (MDEA + PZ + H_2O) solutions (Samanta et al., 2007).

Model Development

Physicochemical Properties & Model Parameters

Equilibrium and forward rate constant	Correlation	Reference
K_2	$\ln K_2 = -29.31 - \frac{5615}{T}$	Bishnoi (2000)
K_4	$\ln K_4 = -30.78 - \frac{5615}{T}$	Bishnoi (2000)
K_7	$\log_{10} K_7 = 6.498 - 0.0238T - \frac{2902.4}{T}$	Danckwerts and Sharma (1996)
K_8	$\ln(\frac{1}{K_8}) = -11.91 - \frac{4351}{T}$	Pagano *et al.* (1961)
K_{11}	$\ln K_{11} = 132.899 - \frac{13445.9}{T} - 22.4773 \ln T$	Posey (1996)
K_6	$\log_{10}(K_6 K_{11}) = 179.648 + 0.019244\,T - 67.341 \log_{10} T - \frac{7495.441}{T}$	Read (1975)
K_9	$\ln\left(\frac{1}{K_9}\right) = -8.21 - \frac{5286}{T}$	Bishnoi (2000)

Model Development

Model Parameters

K_{10}	$\ln(\frac{1}{K_{10}}) = -9.4165 - \frac{4234.98}{T}$	Austgen (1989)
k_{21}	$k_{21} = 2.91 \times 10^7 \exp\left(-\frac{4579}{T}\right)$	Rinker *et al.* (1995)
k_{22}	$k_{22} = 5.8 \times 10^4 \exp\left[-\frac{3.5 \times 10^4}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right]$	Samanta and Bandyopadhyay (2007)
k_{24}	$k_{24} = 5.95 \times 10^4 \exp\left[-\frac{3.55 \times 10^4}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right]$	Samanta and Bandyopadhyay (2007)
k_{26}	$\log_{10} k_{26} = 13.635 - \frac{2895}{T}$	Pinsent *et al.* (1956)

Experimental

- The physical solubility measurements presented here were carried out in a Corning glass equilibrium cell.
- The temperature of the equilibrium cell and jacketed eudiometer was controlled within ± 0.1 K of the desired level with a circulator temperature controller (JULABO FP 55, FRG).

Experimental

- A precise manometric device was used to maintain the atmospheric pressure in the cell throughout the experiment. All solubility measurements were carried out at atmospheric pressure.
- Same wetted wall contactor used for absorption rate measurement were used to measure the diffusivity of CO_2 in water and of N_2O in water and aqueous amine solutions.

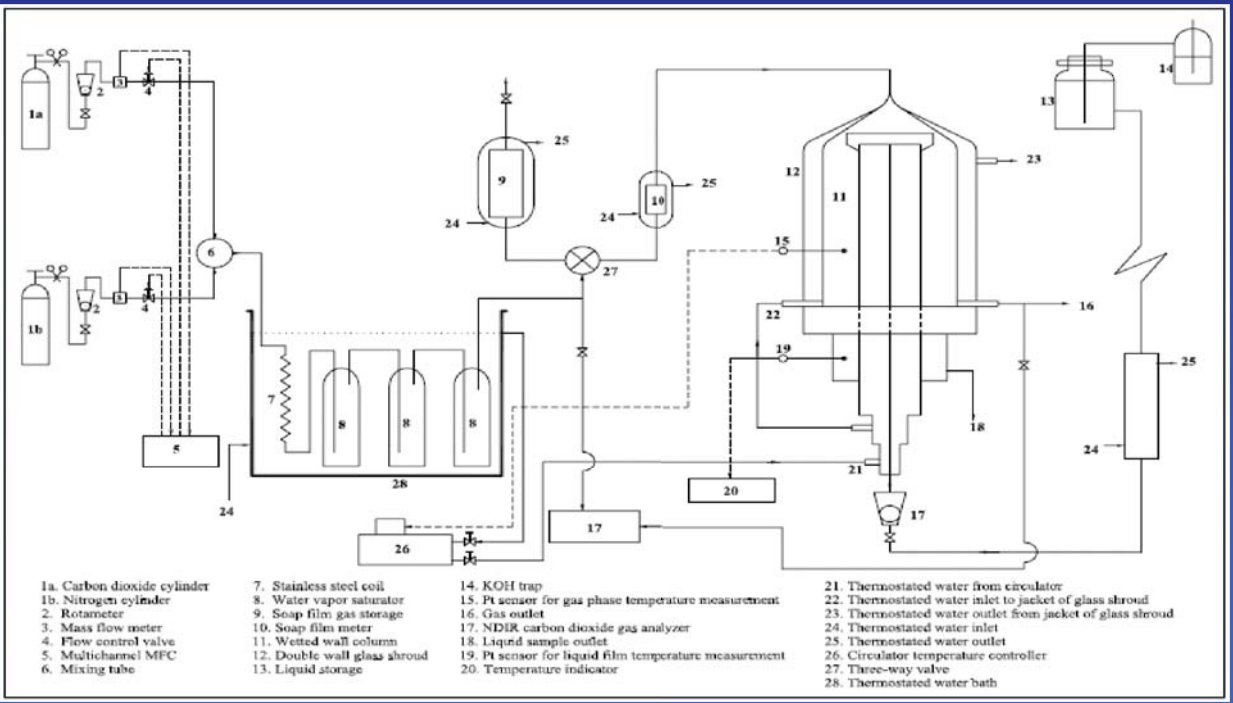
Experimental

- Absorption measurements were done at steady state using a 2.81 10^{-2} m o.d. stainless steel wetted wall column.
- The rates of absorption of CO_2 in aqueous solutions of MDEA/PZ were measured over the temperature range of 298 – 313 K.
- For CO_2 - (MDEA +PZ) total amine concentration were kept at 30 wt % and PZ is used with concentration ranging from 2 to 8 wt %.
- The initial CO_2 loading of the solutions was equal to zero (solute free solvent).

Experimental

- Volumetric gas flow rate of about 1.8 x 10^{-4} $m^3.s^{-1}$ was used throughout all runs using mass flow controller (Sierra Instruments) for CO_2 and N_2.
- The liquid flow rate was maintained at about 2 10^{-6} $m^3.s^{-1}$ by a precalibrated rotameter.
- The CO_2 concentration at the inlet and outlet of the column was determined with precalibrated HORIBA NDIR gas analyzer (Model: VA 3000).
- The total CO_2 content of each liquid sample was determined by acidulating and measuring the volume of evolved gas by precision gas burette.

Experimental



Results and Discussion

Physicochemical Properties

mass % MDEA	mass % PZ	[MDEA] $\left(\frac{kmol}{m^3}\right)$	[PZ] $\left(\frac{kmol}{m^3}\right)$	T (K)	ρ $\left(\frac{kg}{m^3}\right)$	$\mu \times 10^3$ $\left(\frac{kg}{ms}\right)$	H_{CO_2} $\left(\frac{kPa\,m^3}{kmol}\right)$	$D_{CO_2} \times 10^9$ $\left(\frac{m^2}{s}\right)$
28	2	2.41	0.24	298	1025.4	3.183	3441	0.84
28	2	2.41	0.24	303	1023.1	2.692	3838	1.04
28	2	2.41	0.24	308	1020.8	2.251	4267	1.16
28	2	2.41	0.24	313	1018.2	1.925	4661	1.30
25	5	2.51	0.60	298	1024.5	3.341	3303*	0.70
25	5	2.51	0.60	303	1022.3	2.778	3660*	0.88
25	5	2.51	0.60	308	1019.9	2.317	3926*	0.94
25	5	2.51	0.60	313	1017.5	1.965	4203*	1.09
22	8	1.89	0.95	298	1023.2	3.481	3259	0.62
22	8	1.89	0.95	303	1021.5	2.891	3651	0.74
22	8	1.89	0.95	308	1019.3	2.413	4090	0.85
22	8	1.89	0.95	313	1016.9	2.028	4454	0.95
30	0	0	2.56	313	1019.3	1.843	4254*	1.37

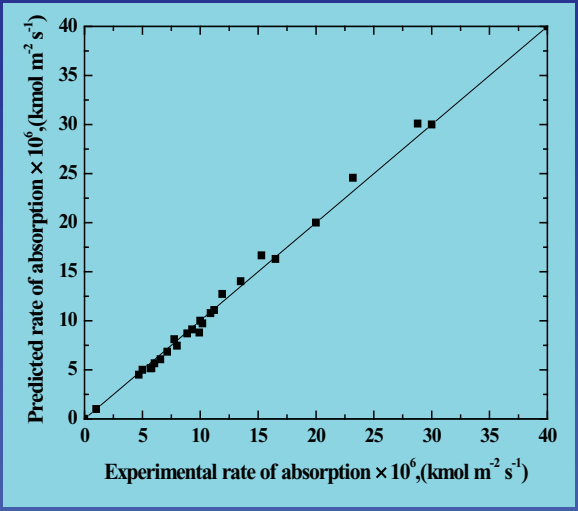
Results and Discussion

Absorption of CO_2 into Aqueous (MDEA + PZ)

[PZ] = 0.238 kmol.m^{-3} [MDEA] = 2.409 kmol.m^{-3}
$V_G = 180 \times 10^{-6}$ m^3.s^{-1} h = 6.5$\times 10^{-2}$ m
Total pressure = 101.3 kPa

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
298	4.8	0.53	4.5	6.05	96.5	5.65	90.1
303	4.89	0.49	5.17	6.57	99.7	6.07	92.1
308	4.95	0.43	5.85	7.16	105.5	6.83	100.6
313	4.84	0.42	6.28	7.75	118.8	8.11	124.3
313	1.69	0.43	6.18	4.69	209.4	4.51	201.4
313	6.67	0.40	6.39	9.30	101.8	9.11	99.7
313	13.83	0.43	6.17	16.5	90.1	16.3	88.9

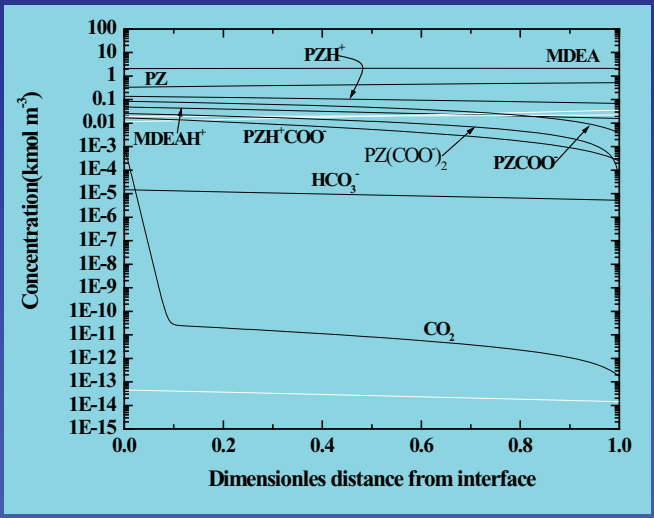
Results and Discussion



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

AAD between the experimental and model results is about 6.8 %.

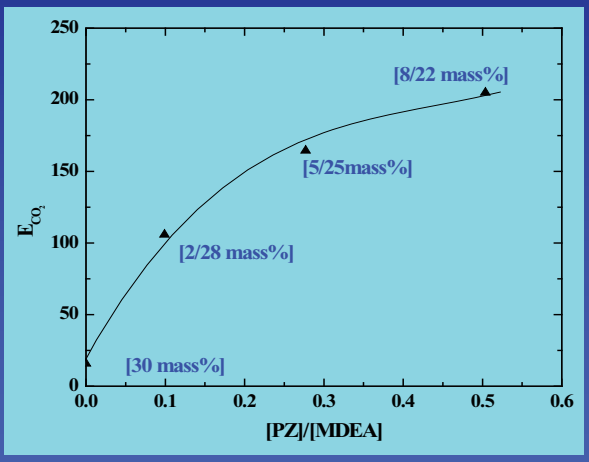
Results and Discussion



Calculated concentration profile of species in the liquid film near the gas-liquid interface at the end of the absorption length. [MDEA] = 2.1513 kmol m-3, [PZ] = 0.596 kmol m-3, T = 313 K, pco2 = 4.66 kPa and θ = 0.39 s.

Conc. of MDEA & PZ are lowered by about 1.5 % &36 %, respectively.

Results and Discussion

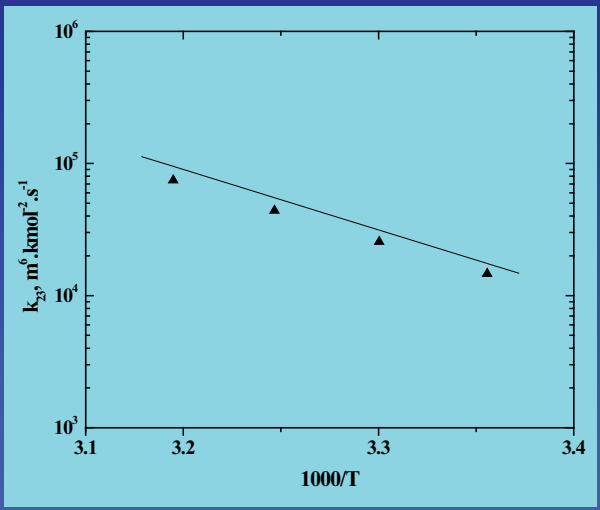


30 mass% MDEA	E_{CO2} = 15.8
2 mass% PZ + 28 mass% MDEA	E_{CO2}= 118.8
5 mass% PZ + 25 mass% MDEA	E_{CO2} = 164.5
8 mass% PZ and 28 mass% MDEA	E_{CO2} = 202.4

T = 313K & $p_{CO2} \approx$ 5kPa

Effect of molar ratio of PZ/MDEA on the enhancement of CO2 absorption into aqueous solution of (PZ + MDEA). ▲, T = 313 K.

Results and Discussion



Arrhenius plot for k_{23} for (CO2 + PZ + MDEA). ▲, Bishnoi and Rochelle (2002); calculated (this work).

$$CO_2 + R'R''R''N + PZ \xleftrightarrow{K_3, k_{23}} PZCOO^- + R'R''R''NH^+$$

Results and Discussion

- 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.

Results and Discussion

- 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%.

Results and Discussion

- As shown in the figure the addition of small amounts of PZ to an aqueous solution of MDEA results in significant increase in the specific rate of absorption and enhancement factor.
- 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.

Results and Discussion

- 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%.

- Similar improvement in the specific rate of absorption and enhancement factor with the addition of small amounts of PZ in aqueous AMP has been observed by Samanta and Bandyopadhyay (2009) for absorption of CO_2 in aqueous (AMP+PZ).

Results and Discussion

- The estimated k_{23} and k_{25} values obtained for CO_2 – (MDEA + PZ + H2O) in this work have been correlated according to the following Arrhenius equations.

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

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

- The estimates of k_{23} of this work have been found to be in good agreement with the result of Bishnoi and Rochelle (2002).

Conclusions

- The absorption of CO_2 into aqueous solutions of mixtures small amounts of fast reacting PZ and much larger amount of MDEA, were studied experimentally and theoretically.

- New kinetic parameters, k_{23} and k_{25}, for the reactions of CO_2 with aqueous (MDEA + PZ) have been obtained using the mathematical model and the measured absorption data of this work. The rate constants are in good agreement with those reported by Bishnoi and Rochelle (2002).

Conclusions

- It has also 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.

- On the basis of rate enhancement both PZ activated solvents, (MDEA + PZ + H_2O) (This work) and (AMP + PZ + H_2O) (Previous work of present authors), appear to be potential candidates for CO_2 removal from power plant flue gas streams.

Conclusions

- The average heat of absorption of PZ activated MEA has been found to be about 71 kJ/mol (Schafer *et. al,* 2002) and that of PZ activated AMP has been found to be about 65 kJ/mol (computed from ENRTL model by these authors), which are lower than the average heat of absorption of about 84 kJ/mol of MEA

- The degradation resistance of both MDEA and AMP is higher than that of MEA. Besides, the overall degradation resistance of both MDEA and AMP further improves with addition of PZ.

Conclusions

- Both MDEA and AMP are much less corrosive than MEA, while corrosiveness of PZ is high. However, since as an activator PZ concentration in AMP and MDEA is not likely to be above 5 mass % in a total amine concentration of 30 mass %, the overall corrosiveness of (MDEA +PZ) and (AMP+PZ) is likely to remain much lower than that of MEA.

- The other important points to be considered are all these amines, PZ, MDEA and AMP have very low biodegradability and the prices of PZ ($ 3.48/lb), MDEA ($ 2.51/lb) and AMP ($ 5.6/lb) are much higher than the price of MEA ($ 0.65/lb)

Thank you !