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Kundu is presently working with National Institute of Technology Rourkela

Modelling Vapour-liquid Equilibria Of CO_2 Over Aqueous PZ Solution

[1]C. Anil and [2]Kundu, M.*

[1]Chemical Engineering Department, MVGR College of Engineering, Vizianagaram. India
[2]Chemical Engineering Group, Birla Institute of Technology and Science, Pilani, Rajasthan, India.

ABSTRACT

Regenerative chemical absorption of the acid gases into solutions of alkanolamines is widely used for gas treating. Nowadays the addition of an accelerator like piperazine (PZ), to aqueous N-methyldiethanol amine (MDEA) has found widespread application in the removal and absorption of CO_2 from process gases. Representation of the experimental data with a model is required, so that one can systematically correlate and predict the vapor-liquid equilibria (VLE) of these systems. Present study is focused on modeling the solubility of CO_2 over aqueous PZ solution following the approach of Kent and Eisenberg, considering apparent equilibrium constants for the chemical reactions. The develop model has been validated with CO_2 solubility over 0.2 M and 0.6 M piperazine solutions in the temperature range 298-343 K. The model predictions of the VLE of CO_2 in 2 and 4 M aqueous piperazine solutions over the temperature range 313- 393 K are in excellent agreement with the experimental results from open literature.

INTRODUCTION

Selective and bulk removal of removal of acid gas impurities, such as CO_2 and H_2S, from gas mixtures is very   important in natural gas processing, hydrogen purification, treating refinery off gases and synthesis gas for ammonia manufacture. For the rational design of gas treating equipments, a model describing thermodynamic equlilibrium is needed, as deviation from the equilibrium provides the driving force in a kinetically controlled process.

Aqueous solutions of *N*-methyldiethanolamine (MDEA) were found to be the attractive solution for the higher equilibrium loading capacity and lower regeneration energy. However, a slow reaction with CO_2 limits the use of MDEA. Satori and Savage (1983) suggested that the sterically hindered amines such as 2-amino-2-methyl-1-proponal (AMP) have higher cyclic capacities of CO_2 than conventional primary and secondary amines such as MEA, diethanolamine (DEA), and diisopropanolamine (DIPA) and appreciable rates of absorption. The BASF activated MDEA technology used piperazine as an activator in order to accelerate the absorption or desorption rate. Appl et al. (1982) reported that piperazine would be more effective than the conventional absorption accelerators. Bishnoi and Rochelle (2000) found that the piperazine could directly react with carbon dioxide to form the piperazine carbamate. The rate constant of piperazine has been found to be a factor of 10 higher than that of conventional alkanolamines such as MEA.

  Corresponding author, E-mail: mkundu@bits-pilani.ac.in, madhushreek@yahoo.com
Fax: 01596-244183

Aroua and Salleh (2003) correlated the CO_2 solubility in PZ using Kent Eisenberg approach and measured the solubilities of CO_2 aqueous PZ solutions in the temperature range 293-323 K, with CO_2 partial pressures ranging from 0.4-95 kPa. Kamps et al. (2003) presented a thermodynamic model to describe VLE of CO_2 in (PZ+H_2O) and in (PZ+MDEA+H_2O) solution. They also reported CO_2 solubility in 2 and 4 M aqueous piperazine solutions over the temperature range 313- 393 K. Bishnoi and Rochelle (2000) measured the solubility of CO_2 in 0.6 M PZ solution in the temperature range 313-343 K, and in the CO_2 loading range 0.16-0.96. Derks et al. (2005) presented new solubility data of CO_2 in aqueous PZ solution of concentrations 0.2 and 0.6 M in the temperature range 298-343 K. They also correlated all the available data in the open literature including their own using a model based on the electrolyte equation of state, as originally proposed by Fürst and Renon (1993).

The thermodynamic models applied so far for representing CO_2 solubility in amine solutions are mainly of three classes. They are empirical approach as introduced by Kent and Eisenberg , excess Gibbs energy based models, and a comparatively new one, application of equation of state model. The application of the latter two types of rigorous models requires substantial computing time to solve large number of simultaneous equations. Moreover, it is difficult to apply these models when interaction parameters for all pairs of species are not readily available. Also, failure to provide a good estimate of the initial values may cause convergence problems in the calculation (Li and Shen, 1993).

MODEL DEVELOPMENT

In the aqueous phase for the $\left(CO_2 + PIPH_2 + H_2O\right)$ system, the following chemical equilibria are involved,
The autoprotolysis of water:

$$H_2O \quad \overset{K_1}{\rightleftharpoons} \quad H^+ + OH^- \tag{1}$$

Formation of bicarbonate:

$$CO_2 + H_2O \quad \overset{K_2}{\rightleftharpoons} \quad HCO_3^- + H^+ \tag{2}$$

The dissociation of bicarbonate:

$$HCO_3^- \quad \overset{K_3}{\rightleftharpoons} \quad CO_3^{2-} + H^+ \tag{3}$$

The protonation of piperazine:

$$PIPH_2 + H^+ \quad \overset{K_4}{\rightleftharpoons} \quad PIPH_3^+ \tag{4}$$

The diprotonation of piperazine:

$$PIPH_3^+ + H^+ \quad \overset{K_5}{\rightleftharpoons} \quad PIPH_4^{2+} \tag{5}$$

Formation of piperazine carbamate

$$PIPH_2 + HCO_3^- \quad \overset{K_6}{\rightleftharpoons} \quad PIPHCOO^- + H_2O \tag{6}$$
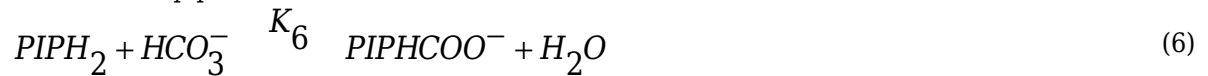
Formation of piperazine dicarbamate

$$PIPHCOO^- + HCO_3^- \quad \overset{K_7}{\rightleftharpoons} \quad PIP\left(COO^-\right)_2 + H_2O \tag{7}$$
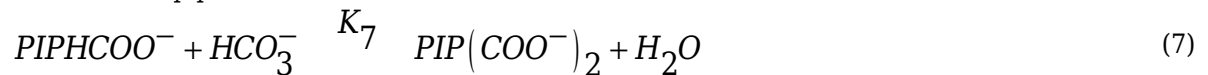
Formation of protonated piperazine carbamate

$$PIPHCOO^- + H^+ \quad \overset{K_8}{\rightleftharpoons} \quad PIPH_2^+\left(COO^-\right) \tag{8}$$
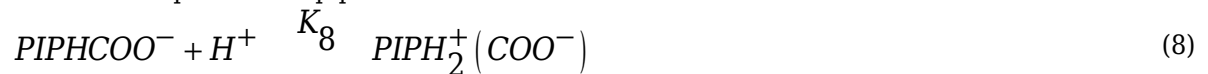
Due to chemical reactions in the liquid phase, carbon dioxide is dissolved predominantly in non-volatile, ionic form. Henry's law relates acid-gas partial pressures to physically dissolved acid-gas concentration in the solvent.

$$p_{CO_2} = H_{CO_2}[CO_2]$$

(9)

The chemical equilibrium constants for reactions (1-8) and Henrys constant (H_{CO_2}) are taken from Kamps et al. (2003), based on molality scale and are presented in Table 1. The total aminel balance, carbon dioxide balance, and equation of electroneutrality are as follows,

$$m = [PIPH_2] + PIPH_3^+ + PIPH_4^{2+} + PIPHCOO^- + PIP(COO^-)_2 + PIPH_2^+COO^-$$

(10)

$$m\alpha = [CO_2] + [HCO_3^-] + [CO_3^{2-}] + [PIPHCOO^-] + [PIP(COO^-)_2] + [PIPH_2^+COO^-]$$

(11)

$$[H^+] + [PIPH_3^+] + 2[PIPH_4^{2+}] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [PIPHCOO^-] + 2[PIP(COO^-)_2]$$

(12)

Table1: Chemical Equilibrium Constants (On Molality Scale) And Henry's Constant

$$\ln K_R = A + \frac{B}{T} + C\ln(T) + DT + \frac{E}{T^2}$$

$$\ln H = A + \frac{B}{T} + C\ln(T) + DT + \frac{E}{T^2}$$

Reaction	A	B	C	D	E
R1	140.932	-13445.9	-22.4773	---	---
R2	-1203.01	68359.6	188.444	-0.206424	$-4.71291 \cdot 10^6$
R3	175.360	-7230.6	-30.6509	0.0131478	$-3.72805 \cdot 10^6$
R4	14.119	3814.4	---	-0.015096	---
R5	10.113	2192.3	---	-0.017396	---
R6	-8.635	3616.1	---	---	---
R7	-3.655	1322.3	---	---	---
R8	10.026	3493.1	---	---	---
H (Mpa)	192.876	-9624.41	-28.7488	0.0144074	---

For the known concentration of piperazine m (molality/molarity) and carbon dioxide loading α, there are eleven equations (1) -(8) and (10)-(12) and eleven unknowns to be solved. equations Expressing all the unknown species concentration in equilibrium in terms of [H⁺], [HCO₃⁻] and [PIPH₃⁺], we can reduce the number of equations, hence, simplify our model. The three resulting non-linear equations are solved using Newton Raphson method. The expressions for equilibrium concentration of different species are as follows,

$$[OH^-] = \frac{K_1}{[H^+]}$$

(13)

$$[CO_3^{2-}] = \frac{K_3[HCO_3^-]}{[H^+]} \tag{14}$$

$$[PIPH_2] = \frac{[PIPH_3^+]}{K_4[H^+]} \tag{15}$$

$$[PIPH_4^{2+}] = K_5[H^+][PIPH_3^+] \tag{16}$$

$$[PIPHCOO^-] = \frac{K_6[HCO_3^-][PIPH_3^+]}{K_4[H^+]} \tag{17}$$

$$[PIP(COO^-)_2] = \frac{K_6 K_7[HCO_3^-]^2[PIPH_3^+]}{K_4[H^+]} \tag{18}$$

$$[PIPH_2^+(COO^-)] = \frac{K_6 K_8[HCO_3^-][PIPH_3^+]}{K_4} \tag{19}$$

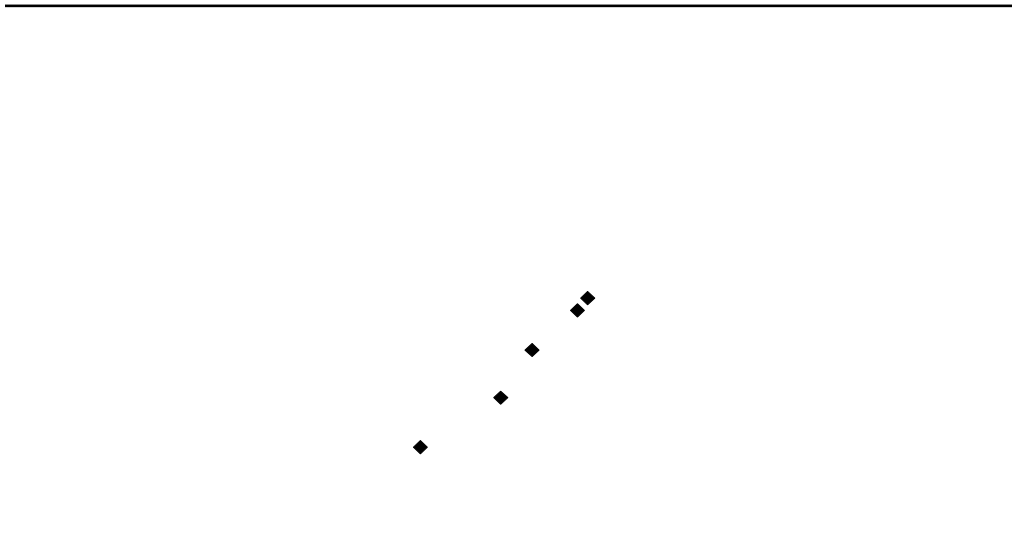$$[CO_2] = \frac{[H^+][HCO_3^-]}{K_2} \tag{20}$$

RESULTS AND DISCUSSION

The model predictions for the equilibrium partial pressure of CO_2 over aqueous piperazine solutions are in good agreement with the experimental data available in the literature over a temperature range of 298-393 K, and $PIPH_2$ concentration range of 0.2 – 4.0 M. A summary of the results is presented in Table 2. Figure 1 shows a typical parity plot.

Table 2: Prediction Of Equilibrium Solubility Of CO₂ In Aqueous Piperazine Solution

Piperazine concentration	Temperature(^{0}C)	No. of data points	*AAD%* of Prediction	Reference
0.2 molarity	25-70	21	25.06	[6]
0.6 molarity	25-70	30	31.72	[6]
2 molality	40-120	48	27.33	[5]
4 molality	40-120	37	20.08	[5]

$$AAD\% = \left[\sum_n \left(p_{cal} - p_{exp}\right)/p_{exp}\right]/n \times 100$$

Figure1: Comparison Of Model Predicted And Experimentally Measured CO_2 Equilibrium Partial Pressure Over Aqueous Piperizine Solutions In The Temperature Range 298-393 K. Reference (Concentration M-molarity, m-molality)

CONCLUSIONS

In this work, Solubility of CO_2 in PZ has been correlated over a temperature range 298-393 K, and concentration ranging from 0.2-4 M solution of PZ using Kent and Eisenberg approach. The model predictions are in reasonable agreement with the experimental data available in the open literature. The concentrations of eleven species present in the equilibriated liquid phase can be determined; hence generation of concentration profile is possible with the present model.

ACKNOWLEDGEMENT

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