Modeling of CO_2 Removal from Gas Mixture by 2-amino-2-methyl-1-propanol (AMP) Using the Modified Kent Eisenberg Model

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Abstract—In this paper, the solubility of CO_2 in AMP solution have been measured at temperature range of (293, 303 ,313,323) K.The amine concentration ranges studied are (2.0, 2.8, and 3.4) M. A solubility apparatus was used to measure the solubility of CO_2 in AMP solution on samples of flue gases from Thermal and Central Power Plants of Esfahan Steel Company. The modified Kent Eisenberg model was used to correlate and predict the vapor-liquid equilibria of the (CO_2 + AMP + H_2O) system. The model predicted results are in good agreement with the experimental vapor-liquid equilibrium measurements.

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Keywords—AMP, Carbon dioxide; loading, Flue gases, Modified Kent Eisenberg model

I. INTRODUCTION

AT the Kyoto Conference, many countries agreed to reduce the emissions of greenhouse gases into the atmosphere or at least to keep them at the current level. Since CO_2 is regarded as a major greenhouse gas, contributing to global warming, there is a growing interest in developing technologies for capturing and sequestering large quantities of CO_2 produced from industrial sources such as fossil-fuel electric power generation facilities [1,2]. Many CO_2 separation methods such as gas absorption and membrane separation are now being developed to recover and concentrate CO_2 in flue gases. Gas absorption by chemical solvents such as aqueous solutions of alkanolamines is one of the most effective methods for CO_2 removal .The absorption process is associated with chemical reactions between the basic amine and the acid gas. Depending on the type of amine being used, carbon dioxide would react with alkanolamine, either directly or through an acid-base buffer mechanism, to form nonvolatile ionic species such as carbonate, bicarbonate and carbamate. There are several different alkanolamines that are suitable for this purpose. However, the most popular ones used in the industries are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA).

A recent advancement in gas treating technology is the application of sterically hindered amine e.g., 2-amino-2-methyl-1-propanol (AMP), which offer absorption capacity, absorption rate, selectivity and degradation resistance advantages over conventional amines for CO_2 removal from gases.[3,4]

Design of gas treating processes with alkanolamine-based aqueous solvents requires knowledge of the vapor-liquid equilibrium (VLE) of the CO_2-alkanolamine water system. Different models for the correlation and the prediction of the phase equilibria were developed using solubility data. The models are based on a system of equations for the chemical and phase equilibria, the neutrality and the mass balance. The simplest models consider the system as ideal and the amine as non-volatile. According to these approximations Kent and Eisenberg provide empirical expressions for evaluating the equilibrium and the Henry's law constants as a function of temperature, amine concentration and gas solubility for (CO_2 +H_2O + amine) systems [5]. Tontiwachwuthikul et al.[6], Posey et al [7]., Park et al [8], and Gabrielsen et al [9]. have derived this model in order to optimize it. More sophisticated models taking into account the non-ideality were developed as for example, the Deshmukh-Mather model [10] , the electrolyte-NRTL model , The Chen and Evans model[11] and UNIQUAC-NRF model.[12]

In this research, theoretical and experimental investigation for solubility of CO_2 in AMP has been done. The experimental data were used to estimate the modified Kent and Eisenberg model parameters using an optimization method.

Process selection for Esfahan Steel Company CO_2 recovery plant:

Esfahan Steel Company is located in Esfahan, Iran. Table 1 shows the composition and molar flow rate of Esfahan Steel Company flue gases from thermal and central power plants. Flue gases and engine exhausts have very low CO_2 partial pressures because they are typically available at or near atmospheric pressure with CO_2 concentrations of typically 3–13 vol%.

TABLE I MASS FLOW AND MOLAR COMPOSITION OF FLUE GASES

Central power plant		Thermal power plant	
Composition	Mole(%)	Composition	Mole(%)
CO2	10	CO_2	5.3
O_2	3.5	O_2	11
N_2	~86.5	N_2	~83.7

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CO	34ppm	CO	0 ppm
NO	40ppm	NO	54ppm
NO_2	40ppm	NO_2	0 ppm
SO_2	0 ppm	SO_2	0 ppm

Sampling Procedure:

Sample of the flue gas using a small compressor was transferred into the capsule. To prevent gas leakage and acidic vapor entrance into the compressor, all necessary fittings for gas transfer were chosen from compressed hoses and also the steam trap was used

II. EXPERIMENTAL

Apparatus
In this study, the solubility measurement apparatus is similar to the one used by Pahlevanzadeh et al [13,14].This apparatus is presented in Fig. 1.
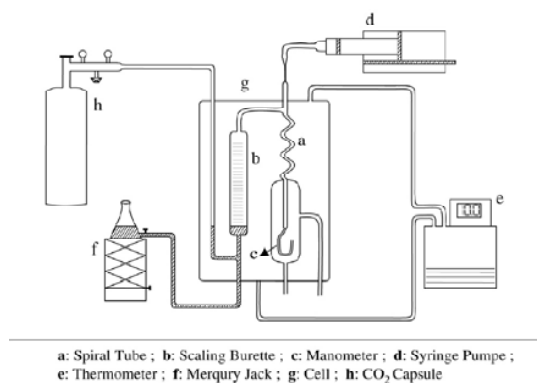

a: Spiral Tube ; b: Scaling Burette ; c: Manometer ; d: Syringe Pumpe ;
e: Thermometer ; f: Merqury Jack ; g: Cell ; h: CO_2 Capsule

Fig. 1. The apparatus for measuring the solubility of gases in liquid

Procedures
For measurement of the gas solubility, the equilibrium cell was allowed to reach thermal equilibrium at the desired temperature and then first the solvents were put into a vacuum flask for degassing. Vacuum was then applied and the degassing process was continued for 10 min. Next, the degassing solvent was mixed to prepare a solution containing a certain percentage.

The cell was then purged with the desired mixture of flue gases for time of 10 min and quickly with used a water drop close of the U-shaped tube and then freshly prepared amine solution of desired concentration was slowly injected in the cell as The flow rate and time of the injection were 5 cc/min and 5 min. the cell was fully sealed It took about (20 to 22) hr to reach equilibrium for each run

The solvent became saturated with the gas while flowing down the spiral tube. As the gas dissolved in the solvent, the

pressure inside dropped. The gas pressure in the apparatus was adjusted by elevating the mercury vessel and with the help of the U-shaped tube at the end of the spiral tube. The volume of mercury displaced was equal to the solute gas dissolved in the solvent. In order to estimate the solubility of gas in the solvent, the volume of solute gas is measured at experimental conditions and the molar volume of solute gas is calculated by an equation of state.

Each experiment was repeated at least 2 times, and the average results were considered. The results for each concentration and temperature of the solution are presented in Table 2 and Table 3.

TABLE II CO_2 SOLUBILITY IN AQUEOUS AMP SOLUTION BASED ON THERMAL POWER PLANT SAMPLES

C=2M		C=2.8		C=3.4	
T(K)	α (moleCO2/ mole AMP)	T(K)	α (moleCO2/ mole AMP)	T(K)	α (moleCO2/ mole AMP)
293	0.769	303	0.6443	303	0.666
303	0.6372	313	0.5509	313	0.5743
313	0.5141	323	0.4269	323	0.4519

TABLE III CO_2 SOLUBILITY IN AQUEOUS AMP SOLUTION BASED ON CENTRAL POWER PLANT SAMPLES

C=2M		C=2.8		C=3.4	
T(K)	α (moleCO2/ mole AMP)	T(K)	α (moleCO2/ mole AMP)	T(K)	α (moleCO2/ mole AMP)
293	0.8239	303	0.7201	303	0.758
303	0.7428	313	0.6244	313	0.646
313	0.617	323	0.4981	323	0.5215

Modified Kent Eisenberg model:

At Modified Kent Eisenberg model no trace of activity coefficient is detected apparently, but this parameter occurs in equilibrium and Henry constants and no ideal hypothetical is considered for liquid phase in this model. Therefore, for liquid phase the Modified Kent Eisenberg model is used and also the gas phase is considered ideal

Chemical Equilibria.

An equilibrium solution for the AMP + CO2 + H2O system is governed by the following set of equations:

$$AMPH^+ \xrightarrow{K_1} H^+ + AMP \qquad K_1 = \frac{[H^+][AMP]}{[AMPH^+]} \qquad (1)$$

$$CO_2 + H_2O \xrightarrow{K_3} HCO_3^- + H^+ \qquad K_3 = \frac{[H^+][HCO_3^-]}{[CO_2]} \qquad (2)$$

$$H_2O \xrightarrow{K_4} OH^- + H^+ \qquad K_4 = \frac{[H^+][OH^-]}{[H_2O]} \qquad (3)$$

$$HCO_3^- \xrightarrow{K_5} CO_3^{2-} + H^+ \qquad K_5 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \qquad (4)$$

Equation (1) represents the protonation of amine and Equations (2)-(4) are the ionization reactions for the different species in the solutions

These reactions, along with total mole balances and a charge balance, were used to arrive at an equilibrium solution composition.

Amine balance:

$$[AMP]_t = [AMP] + [AMPH^+]$$ (5)

CO_2 balance:

$$\alpha[AMP]_t = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$ (6)

Charge balance:

$$[H^+] + [AMPH^+] - [HCO_3^-] - 2[CO_3^{2-}] - [OH^-] = 0$$ (7)

Where α is the gas loading. The concentration of carbon dioxide in the liquid phase can be estimated from Henry's law, i.e.

$$p_{co2}\varphi_{co2} = H_{CO2}[CO_2]$$ (8)

Henry's constant for CO2 in an aqueous solution was estimated using the method of Danckwerts [15].

The apparent equilibrium constant, K_1, for reaction (1) as defined in terms of the concentration of the corresponding species, are taken to be dependent on the partial pressure of CO_2 and the gas loading in the solution. Since the equilibrium constant at infinite dilution, K_1, is only a function of temperature, a factor F_1 is introduced which takes into account the effects of CO_2 partial pressure and the gas loading. Thus

$$K_1' = K_1 F_1$$ (9)

The dependency of the equilibrium constant, K_i, as well as the Henry's constant, H, with temperature is expressed as

$$K_i \text{ or } H_{CO_2} = \exp(\frac{A}{T} + B\ln T + CT + D)$$ (10)

where $A_i - D_i$ are constants. Values of these constants for all of the reactions (1)-(4) and that for the Henry's constant are taken from the literature, as given in Table 4.

TABLE IV VALUES OF THE CONSTANTS USED IN EQUATION [17]

parameter	A	B	C	D	Range of validity (°C)
K_2	-12092.1	-36.7816	0	235.482	0-225
K_3	-12431.7	-35.4819	0	220.067	0-225
K_4	-13445.9	-22.4773	0	140.932	0-225
$H CO_2$	-6789.04	-11.4519	-0.01454	94.4914	0-225

In this work, F_1 is defined in a general form as

$$F_1 = a + b\ln(p_{co_2}) + c\alpha + d(\ln(p_{co_2}))^2 + e\alpha \ln(p_{co_2})$$ (11)

Similarly, a-e are constants which are to be regressed. For reactions (2)-(4) only the equilibrium constants at infinite dilution, K_i, were used.

Above equations contains eight unknown. Which are :

$$[AMPH^+], [AMP], [H^+], [HCO_3^-], [CO_3^{2-}], [OH^-], [CO_2], K_1'$$

In order to determine the above unknowns, eight equations are needed which are achieved from chemical equations, balance of neutrality and mass and Henry's law. Equations (1)-(8) can be reduced, for aqueous solution of AMP, to a single polynomial equation in terms of the concentrations of hydrogen ions, H+,

$$A[H^+]^2 + B[H^+] + C = 0$$ (12)

$$A = \alpha[AMP]_t - \frac{P_{CO_2}}{H_{CO_2}}$$

$$B = -K_3 \frac{P_{CO_2}}{H_{CO_2}}$$

$$C = -K_3 K_4 \frac{P_{CO_2}}{H_{CO_2}}$$

Solving equation (12) and calculating the amount of [H+], value of K_1' is obtained from the following equations

$$[CO_2] = \frac{P_{CO_2}}{H_{CO_2}} \qquad (13)$$

$$[OH^-] = \frac{K_5}{\left[H^+\right]} \qquad (14)$$

$$[HCO_3^-] = K_3 \frac{P_{CO_2}}{H_{CO_2}} \frac{1}{\left[H^+\right]} \qquad (15)$$

$$[CO_3^{-2}] = K_3 K_4 \frac{P_{CO_2}}{H_{CO_2}} \frac{1}{\left[H^+\right]^2} \qquad (16)$$

$$[AMPH^+] = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-] - \left[H^+\right] \qquad (17)$$

$$[AMP] = [AMP]_t - [AMPH^+] \qquad (18)$$

$$K_1' = \frac{[AMP][H^+]}{[AMPH^+]} \qquad (19)$$

Values of K_1' in different experimental conditions are achieved and parameters of equation (19) with using MATLAB software is optimized.

When the function K_1' was achieved, Equation (1) to (8) is solved again.

Unknowns at this stage as follows:

$$[AMPH^+],[AMP],[H^+],[HCO_3^-],[CO_3^{2-}],[OH^-],[CO_2],\alpha_{calc}$$

Similarly, Equations (1)-(8) can be reduced, to a single polynomial equation in terms of the concentrations of hydrogen ions, H^+,

$$A\left[H^+\right]^4 + B\left[H^+\right]^3 + C\left[H^+\right]^2 + D\left[H^+\right] + E = 0 \qquad (20)$$

$$A = 1$$

$$B = [AMP] + K_1'$$

$$C = -(K_3 \frac{P_{CO_2}}{H_{CO_2}} + K_5)$$

$$D = -\left(2K_3 K_4 \frac{P_{CO_2}}{H_{CO_2}} + K_1' K_5 + K_1' K_3 \frac{P_{CO_2}}{H_{CO_2}} \right)$$

$$E = -2K_1' K_3 K_4 \frac{P_{CO_2}}{H_{CO_2}}$$

$$\alpha_{calc} = \frac{[CO2] + [HCO_3^-] + [CO_3^{-2}]}{[AMP]} \qquad (21)$$

With comparing the α_{exp} and α_{calc} values and calculating the relative error, accuracy of model is analyzed

$$f = \frac{\alpha_{cal} - \alpha_{exp}}{\alpha_{cal}} \qquad (22)$$

III. RESULTS AND DISCUSSION

To ensure the reliability of the experimental data it is important that the concentration of amine in the solution is maintained throughout each run. Analysis on the concentration of amine before and at the end of each experiment showed that in most cases the variations between the readings were less than 10%. However, slightly higher variations of about were obtained for experiments with very low CO2 partial pressures which normally required 18-24 hours to reach equilibrium where evaporation of water is likely to occur. The measured variations also included errors in the analysis, thus, without introducing any significant errors, it can be concluded that the concentration of amine in the solution remained constant throughout each set of experimental run.

Fig. 2-5, shows the effect of both temperature and CO2 partial pressure and concentration on the ultimate CO2 loading. As expected, the loading increases with the CO2 partial pressure and with decreasing temperature and increasing concentration. Despite being a primary amine, AMP showed a high loading at low partial pressure. This value of ultimate loading is similar to the one that can be obtained using tertiary amines such as MDEA [18]. This result can be explained by the absence of carbamate in the system. The structure of AMP induces steric hindrance that is unfavorable for carbamate formation.
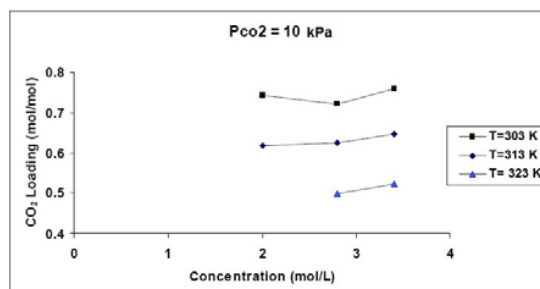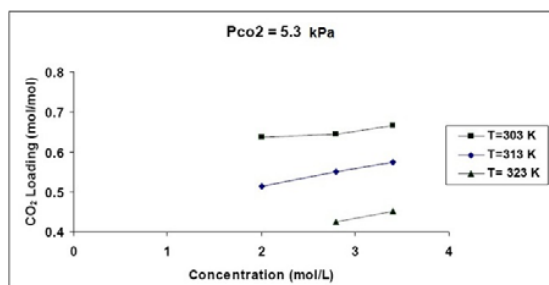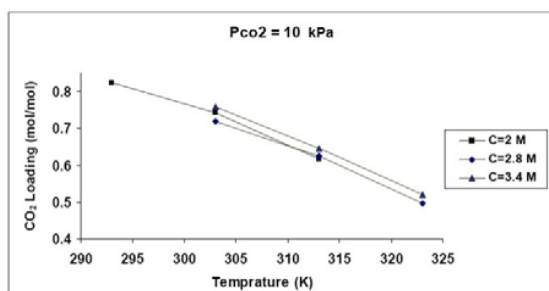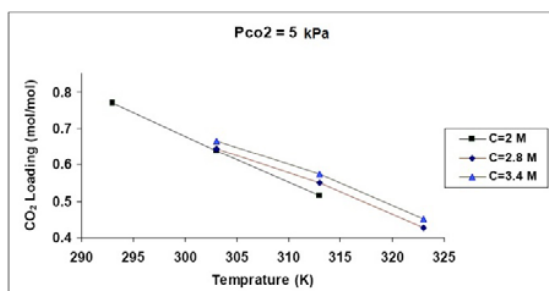

Fig. 2 CO$_2$ loading (mol CO$_2$ /mol amine) in AMP solution

Fig. 3 CO_2 loading (mol CO_2 /mol amine) in AMP solution

Fig. 4 CO_2 loading (mol CO_2 /mol amine) in AMP solution

Fig. 5 CO2 loading (mol CO2 /mol amine) in AMP solution

A Comparison of experimental and calculated data for CO2 loading at different amine concentrations, temperatures and CO2 partial pressures as given in Table 5 was fitted simultaneously.

TABLE V EXPERIMENTAL AND CALCULATED DATA FOR CO_2 LOADING IN AQUEOUS AMP SOLUTION

f (error %)	α_{cal} (mol CO_2 /mol amine)	$_{exp}$(mol CO_2 /mol αamine)
-28.337	1.0731	0.769
-21.794	0.8147	0.6372
-25.161	0.992	0.7428
-19.862	0.6416	0.5141
-16.135	0.7357	0.617
10.656	0.5822	0.6443
-8.387	0.786	0.7201
20.152	0.4585	0.5509
-27.710	0.8637	0.6244
14.442	0.373	0.4269
-29.102	0.7026	0.4981
11.359	0.598	0.666
-16.1206	0.9037	0.7578
13.352	0.5066	0.5743
-9.201	0.7115	0.646
12.582	0.4014	0.4519
-9.883	0.5787	0.5215

The predictions of CO2 solubility in aqueous AMP solution for various relative amine compositions in the temperature range (293 to 323) K are in good agreement as shown in Table 5

Equation (20) is very sensitive to the initial guess. However, by limiting the possible root within the range of pH for loaded and fresh solutions which lies between 7 and 11, the equation converged to a final solution within a few iterations. In all cases, the relative error between the predicted and experimental data never exceeded 28%.

For modeling of the vapor liquid equilibrium of CO2 + alkanolamine + water systems, average deviations in the range of 15 to 30% have been reported by previous workers [10, 17] who used deterministic techniques for modeling. In this work, the optimization toolbox in Matlab software was employed in order to achieve better VLE prediction accuracy. The Generated parameters for equation 11 in the AMP + CO2 + H2O system by the the optimization toolbox is summarized in Table 6, respectively

TABLE VI GENERATED PARAMETERS FOR EQUATION 11

a	b	c	d	e
−0.156301	0.422210	−0.10566	0.029302	0.134542

According to the above results, the following factors lead to differences among the results of experimental and theoretical values:

1. Experiments in low CO2 partial pressure were performed. Therefore, caused error in experiments.

2. In this model, all effects of non-ideal were only considered in the function F. While the protonation reaction of amine was considered the main reaction in order to make non-ideal liquid phase

3. Weak relationship between K1' and partial pressure of carbon dioxide and CO2 loading causes lackage for a suitable initial proposing equation for the function K1'

4. These results may be due to the fact that during the regression process, only the liquid phase interaction parameters are considered

IV. CONCLUSIONS

The equilibrium solubility of CO2 in aqueous solutions of AMP was measured in the temperature range of (293 to323) K for a CO2 partial pressure (5.3 and 10) kPa The modified Kent Eisenberg model which takes into account the effects of CO2 partial pressure and loading on the apparent equilibrium constant for the protonation of amine is able to give relatively good predictions on the total CO2 loading in solutions of AMP. The model has been validated with the experimental results for various relative amine compositions in the temperature range (303 to 323) K. The predictions of CO2 solubility in aqueous AMP solutions have been found to be in good agreement with the experimental results of this study.

NOTATION

[AMP] concentration of 2-amino-2-methyl-1-propanol in the aqueous solution

[AMP]$_{initial}$ initial liquid bulk concentration

a, b, c,d,e   parameters in Eq. (11)

H   Henry's constant

K   equilibrium constant

P   Pressure

R   gas constant

T   temperature

v   molar volume

x, y   liquid and vapor compositions

M   molarity

Greek letters

α   CO$_2$ loading of the aqueous amine solution

Subscripts

t   Total, reacted as well as unreacted

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