PREDICTION OF CARBON DIOXIDE SOLUBILITY IN BLENDS OF AQUEOUS POTASSIUM LYSINATE AND PIPERAZINE USING THERMODYNAMIC MODELING

Afaf Syalsabila¹, Abdulhalim Shah Maulud², Humbul Suleman³
Nik Abdul Hadi Md Nordin⁴

¹CO₂ Research Centre, Universiti Teknologi PETRONAS, Bandar Seri Iskandar 32610 Perak, Malaysia;
²Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar 32610 Perak, Malaysia;
³Department of Chemical and Biochemical Engineering, Technical University of Denmark, SoltoftsPlads, Building 229, room 240, 2800 Kgs. Lyngby;
⁴Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar 32610 Perak, Malaysia;
¹norafaf.syalsabila@gmail.com, ²halims@utp.edu.my, ³hsul@kt.dtu.dk, ⁴nahadi.sapiah@utp.edu.my

Corresponding Author: Afaf Syalsabila

https://doi.org/10.26782/jmcms.spl.9/2020.05.00023

Abstract

In the present study, a thermodynamic modeling using explicit model is performed for the determination of carbon dioxide solubility in blends of aqueous potassium lysinate with piperazine at a wide range of pressure from 500 to 4100 kPa, temperature within 303.15-343.15 K, and solvent concentrations of 1, 2 and 3 M. The model has suitably predicted the carbon dioxide thermodynamics of the solutions. The average absolute deviation from the correlation of the explicit model is found to be 8.5%.

Keywords: vapor-liquid equilibrium, carbon dioxide, thermodynamic modeling, amino acid, alkanolamine

I. Introduction

Removal of carbon dioxide has become an exigency in post-combustion capture (PCC) technology for its largest anthropogenic contributor to global warming. Several techniques are used for removal of carbon dioxide. These include membrane, chemical absorption and adsorption, physical absorption, and cryogenic processes. However, the leading technology to capture and remove carbon dioxide in the PCC is...
chemical absorption. In this technique, a chemical solvent or absorbent reacts reversibly with carbon dioxide in flue gas, to release a cleaned gas to atmosphere[VI].

Salt solutions based amino acid are the new type of solvents emerged as possible alternatives to the conventional alkanolamine solutions. Being functionally similar to alkanolamine (amine group), this amino acid salt is regarded as low vapor pressures, thermally stable and environmentally friendly [IX, I]). Usually, a strong base such as potassium hydroxide (KOH) of sodium hydroxide (NaOH) is mixed with amino acid salt, producing an aqueous potassium/sodium salt of amino acid solutions [IV]. Addition of such base neutralizes the carboxylic group thus producing a salt function. This salt function is to ensure non-volatility of the substance which eventually leads to a better economic feasibility, mostly at stripping column as it prevents solvent loses [VIII].

Previously, carbon dioxide absorption using amino acid salt solutions have been extensively examined (XVII-XVI). One of the works was performed by Benedicte[X], as part of his study to examine various types of amino acids (taurine, glycine, L-alanine, L-proline and L-lysine) to capture carbon dioxide. Using analytical semi-flow and synthetic methods, it was found that all of the tested amino acids were comparable to the conventional alkanolamines and L-lysine possessed the best properties amongst others.

However, recently, blends of amine are introduced as an idea to combine the advantages from different classes of amine to produce absorbents with better performance for carbon dioxide capture. Chung et al [III] examined carbon dioxide absorption capacity in a blend of triethanolamine (TEA) and piperazine (PZ) and observed that TEA+PZ solutions has higher capacity than pure TEA. Moreover, small amount addition of PZ has also improved the carbon dioxide solubility of potassium alaninate in the work of Kang et al [VIII]. Majority studies on absorption of carbon dioxide in solvent blend systems have experienced improvements in several ways; including better thermodynamic efficiency, higher absorption rate, lower energy requirement during regeneration and better resistance to degradation and corrosion[XIII-XV].

This paper presents a correlation of our previous study on the VLE of carbon dioxide solubility in novel blends of aqueous potassium lysinate with piperazine (LysK+PZ)[XIX]. From our published work (Table 1), the carbon dioxide solubility data increased with the increase of pressure, whereas decreased with the increase of temperature and concentration. This trend of inverse relationship is congruent with literature published elsewhere [XVII, XI-XX]. Moreover, explicit model established by Suleman et al[XVIII], is further used in this present study for the correlation of the said experimental data. Being computationally simple, this model combines only a single correction parameter and subsequently regressed to process parameters. It is basically derived from equilibrium thermodynamic theory with an abridged set of reaction equations that has successfully correlated carbon dioxide solubility data in various blends of amino acid salt solutions with alkanolamines for the first time in the work of Suleman et al[XVIII]. Furthermore, the detail of its thermodynamic framework is shown in the next section.

Copyright reserved © J. Mech. Cont.& Math. Sci.
Afaf Syalsabila et al
| Concentration (M) | Temperature (K) | Table 1: Experimental carbon dioxide solubility in blends of aqueous potassium lysinate and piperazine |
|-------------------|-----------------|--------------------------------------------------|
|                   | 303.15          | 323.15                                           |
|                   |                 | 343.15                                           |
| P (kPa)           | α (mol/mol)     | P (kPa)                      | α (mol/mol)     | P (kPa)                      |
| 1                 |                 | 2                               |                 |
| 581.30            | 0.7204          | 558.80                          | 0.2591          |
| 1131.3            | 0.7711          | 1156.3                          | 0.3685          |
| 1618.8            | 0.9187          | 1650.0                          | 0.5417          |
| 2125.0            | 0.9305          | 2087.5                          | 0.6636          |
| 2668.8            | 0.9337          | 2508.8                          | 0.7552          |
| 2968.8            | 0.9854          | 3050.0                          | 0.8183          |
| 3438.8            | 1.0020          | 3493.8                          | 0.9195          |
| 3912.5            | 1.4860          | 4062.5                          | 0.9499          |
| 2                 |                 | 3                               |                 |
| 556.30            | 0.5117          | 500.00                          | 0.1475          |
| 1071.3            | 0.5606          | 1018.8                          | 0.1735          |
| 1569.4            | 0.6284          | 1500.0                          | 0.1976          |
| 2021.3            | 0.6926          | 2006.3                          | 0.2218          |
| 2443.8            | 0.7300          | 2493.8                          | 0.2352          |
| 2993.8            | 0.7831          | 3056.3                          | 0.2512          |
| 3450.0            | 0.8372          | 3512.5                          | 0.2668          |
| 4075.0            | 0.8684          | 4043.8                          | 0.3184          |
| 3                 |                 | 4                               |                 |
| 556.30            | 0.2573          | 500.00                          | 0.1148          |
| 1050.0            | 0.2724          | 1100.0                          | 0.1307          |
| 1506.3            | 0.2791          | 1512.5                          | 0.1556          |
| 2025.0            | 0.3790          | 2062.5                          | 0.1878          |
| 2481.3            | 0.4007          | 2581.3                          | 0.1962          |
| 3000.0            | 0.4149          | 3050.0                          | 0.2194          |
| 3525.0            | 0.4305          | 3493.8                          | 0.2656          |
| 4056.3            | 0.4785          | 4050.0                          | 0.3034          |

Copyright reserved © J. Mech. Cont.& Math. Sci.
Afaf Syalsabila et al
Thermodynamic Framework

The simplified reaction mechanisms of carbon dioxide solubility in aqueous blends of potassium lysinate with piperazine can be generally represented by following equations (19).

\[ RR^-NH + H^+ \rightleftharpoons RR^-NH_2^+ \]  
\[ CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \]  
\[ KOH \rightleftharpoons K^+ + OH^- \]  
\[ RNH + H^+ \rightleftharpoons RNH_2^+ \]  

Equations above can be jointly written as below, yielding a combined equilibrium constant, \( k_c \) for the blend solutions of LysK+PZ.

\[ RR^-NH + CO_2 + H_2O + KOH + RNH + H^+ \rightleftharpoons RR^-NH_2^+ + HCO_3^- + K^+ + OH^- + RNH_2^+ \]  

\[ k_c = \frac{[RR^-NH_2^+][HCO_3^-][K^+][OH^-][RNH_2^+]}{[RR^-NH][CO_2][KOH][RNH][H^+]} \]  

Mathematical simplification and rearrangement results to an equation as follows.

\[ \frac{k_c}{k_2k_3} = \frac{[RR^-NH_2^+][RNH_2^+]}{[RR^-NH][RNH][H^+]} \]  

The amino acids protonation was presumed to be dependent upon the free amino acid concentration available at any instant and the carbon dioxide loading, \( \alpha \).

\[ [RR^-NH_2^+] = \alpha [RR^-NH] \]  
\[ [RNH_2^+] = \alpha [RNH] \]  

Hence simplification and rearrangement of Equation 5 yields the following equation;

\[ \frac{k_c}{k_2k_3} \]
All the carbon dioxide species from liquid sides are assumed to be represented by bicarbonate ion hence, the carbon dioxide balance is:

\[ \alpha([A_{MT}]+[A_{LK}])=\left[HCO_3^-\right] \]  

(11)

Based on the equilibrium constant of bicarbonate ion in Equation 2, Equation 11 above can be re-modified, yielding Equation 12.

\[ \alpha^2([A_{MT}]+[A_{LK}])=\left[CO_2\right] \sqrt{\frac{k_2 k_3}{k_c}} \]  

(12)

Combining all equilibrium constants into a common equilibrium constant \(k_{mix}\) and definition of Henry’s law, \(\alpha\) can be calculated by using Equation 13 below.

\[ \alpha=\frac{P_{CO_2}k_{mix}}{H_{CO_2}([A_{MT}]+[A_{LK}])} \]  

(13)

Moreover, the Henry’s constant can be obtained by using Equation 14 (20).

\[ H_{CO_2} = \exp \left( \frac{6789.04}{T} - 11.4519 \ln T \right) - 0.0104547 + 94.4914 \]  

(14)

Equation shown below (see Equation 15) is the \(k_{mix}\) for the explicit model of carbon dioxide absorption in blend solutions of LysK+PZ. And, its value was calculated by objective function, OF (see Equation 16), provided in MATLAB environment.

\[ \ln k_{mix} = A + B[A_{MT}] + C[A_{LK}] + D P_{CO_2} + ET \]  

(15)

\[ OF=\frac{1}{N} \sum_{N=1}^{N} \left( a_{calc}-a_{expt} \right)^2 \]  

(16)

Table 2 presents the values for regressed parameters of \(k_{mix}\) denoted as A, B, C, D and E for carbon dioxide solubility in blend solutions of LysK+PZ.
Table 2: Value of constants for $k_{mix}$ (Equation 15)

| Parameter | Value   |
|-----------|---------|
| A         | 62.4930 |
| B         | -1.1710 |
| C         | 0.6631  |
| D         | -0.1721 |
| E         | -10.5726|

Results and Discussions

Figure 1 presents the correlated data of 1 molar aqueous blend of potassium lysinate solutions with piperazine against our previously reported data. The relationship of the model was slightly over predicted in high temperature (343.15K) whereas a trend of under prediction was seen in low temperature (< 323.15K). However, the correlation of explicit model in 2 molar potassium lysinate and 2 molar piperazine solutions was improved (see Fig. 2). The model results especially in higher pressure region (> 2000kPa) and at temperature 323.15K were considerably good with correlation flagging at low pressures (< 1500kPa). This is due to the disregard of activity coefficient effect possessed from the behavior of semi-empirical models. Contrarily, over predicted data were observed in lower pressure region (< 1500kPa) and at higher temperature of 343.15K. It is prominent that the slight increase in the deviation caused by the high concentrations of solvent used. Nevertheless, the overall trend of under prediction was followed in correlation of 2 molar concentrations.

Figure 3 explicates the relationship between model predicted data and experimental data of carbon dioxide solubility in aqueous blends of 3 molar potassium lysinate and 3 molar piperazine solutions. It is understood from these plots that, the equilibrium carbon dioxide loading predicted by the explicit model are in good conformance with the experimental carbon dioxide loading data particularly at lower pressure region of less than 2000kPa, for all temperature conditions (303.15, 323.15 and 343.15K). Meanwhile, the relationship was slightly debilitated in the higher-pressure region (> 2000kPa) mainly at temperature 323.15K. Above all, the square root relationship of carbon dioxide loading with pressure in the model equation resulted in a trend of under prediction in Fig.3.

The average absolute deviation (AAD), between the model predicted and experimental results was found to be 8.5%. Considering all the experimental data points, it is interesting to note that our newly developed explicit model presented a high-quality prediction in carbon dioxide solubility of aqueous potassium lysinate blended with piperazine. Our model is potentially capable of maintaining acceptable
correlation providing a set of theoretically justified experimental data, with the outliers deemed consistent.

**Fig. 1:** Model results for carbon dioxide solubility in 1 molar of LysK+PZ solutions

**Fig. 2:** Model results for carbon dioxide solubility in 2 molar of LysK+PZ solutions
Conclusions

A semi-empirical thermodynamic framework has been presented for the prediction of carbon dioxide solubility in mixture of amino acid salts and alkanolamine solutions. This explicit model is based on simplified mathematical equation from the derivation of basic equilibrium thermodynamics. The calculated data exemplified good conformance with the experimental data of aqueous LysK+PZ solutions with satisfactorily overall correlation (majority > 90% of the data points). Moreover, the explicit model exhibited an AAD% of 8.5%. The model can be used extensively in correlation of new mixture of aqueous amino acid salt solutions and alkanolamines, pertaining to the stated reaction mechanisms.

Acknowledgment

Funding by FRGS grant scheme (0153AB-L24, 2016-2018) from Ministry of Higher Education (MOHE) Malaysia is appreciated.

List of Symbols

- $A$ - $E$: Adjustable parameters
- $A_{MT}$: Total amino acid salt concentration, mole/litre
- $A_{LK}$: Total amino alkanolamine concentration, mole/litre
- $CO_{2}$: Carbon dioxide
- $H_{2}O$: Water
| Symbol | Definition |
|--------|------------|
| $H^+$  | Hydrogen ion |
| $HCO_3^-$ | Bicarbonate |
| $HCO_2^-$ | Henry’s constant for carbon dioxide, atm litre/mole |
| $P_{CO_2}$ | Partial pressure of carbon dioxide, kPa |
| $KOH$  | Potassium hydroxide |
| $K^+$  | Potassium ion |
| $k_1$  | Equilibrium constant of protonation of amino acid |
| $k_2$  | Equilibrium constant of bicarbonate formation |
| $k_3$  | Equilibrium constant of dissociation of potassium hydroxide |
| $k_4$  | Equilibrium constant of dissociation of alkanolamine |
| $OH^-$ | Hydroxide ion |
| $P_{CO_2}$ | Pressure of carbon dioxide in vapor phase, kPa |
| $RNH$  | Free alkanolamine |
| $RNH_2^+$ | Protonated alkanolamine |
| $RR^-NH$ | Free amino acid |
| $RR^-NH_2^+$ | Protonated amino acid |
| $\alpha$ | Carbon dioxide loading |
| $\alpha_{calc}$ | Calculated carbon dioxide loading, mole of CO$_2$/mole of amine |
exp

Experimental carbon dioxide loading, mole of CO₂/mole of amine

Reference

I. Aronu UE, Hessen ET, Haug-Warberg T, Hoff KA, Svendsen HF. Equilibrium absorption of carbon dioxide by amino acid salt and amine amino acid salt solutions. Energy procedia. 2011;4:109-16.

II. Bougie F, Iliuta MC. Sterically hindered amine-based absorbents for the removal of CO₂ from gas streams. J ChemEng Data. 2012;57(3):635-69.

III. Chung P-Y, Soriano AN, Leron RB, Li M-H. Equilibrium solubility of carbon dioxide in the amine solvent system of (triethanolamine+ piperazine+ water). J ChemThermodyn. 2010;42(6):802-7.

IV. Donaldson TL, Nguyen YN. Carbon dioxide reaction kinetics and transport in aqueous amine membranes. IndEngChemFundam. 1980;19(3):260-6.

V. Edwards T, Maurer G, Newman J, Prausnitz J. Vapor-liquid equilibria in multicomponent aqueous solutions of volatile weak electrolytes. AIChE J. 1978;24(6):966-76.

VI. Gabrielsen J. CO₂ capture from coal fired power plants. Graduate Schools Yearbook 2005.2005:61.

VII. Hamzehie ME, Najibi H. Carbon dioxide absorption in aqueous solution of potassium glycinate+ 2-amino-2-methyl-1-propanol as new absorbents. RSC Advances. 2016;6(67):62612-23.

VIII. Kang D, Park S, Jo H, Min J, Park J. Solubility of CO₂ in amino-acid-based solutions of (potassium sarcosinate),(potassium alaninate+ piperazine), and (potassium serinate+ piperazine). J ChemEng Data. 2013;58(6):1787-91.

IX. Kumar P, Hogendoorn J, Feron P, Versteeg G. Equilibrium solubility of CO₂ in aqueous potassium taurate solutions: Part 1. Crystallization in carbon dioxide loaded aqueous salt solutions of amino acids. IndEngChem Res. 2003;42(12):2832-40.

X. Lerche BM, Stenby EH, Thomsen K. CO₂ capture from flue gas using amino acid salt solutions: Technical University of DenmarkDanmarksTekniskeUniversitet, Department of ChemistryInstitut for Kemi; 2012.

Copyright reserved © J. Mech. Cont.& Math. Sci.
Afaf Syalsabila et al
XI. Mondal MK, Balsora HK, Varshney P. Progress and trends in CO2 capture/separation technologies: a review. Energy. 2012;46(1):431-41.

XII. Muñoz DM, Portugal AF, Lozano AE, José G, de Abajo J. New liquid absorbents for the removal of CO2 from gas mixtures. Energy & Environmental Science. 2009;2(8):883-91.

XIII. Nainar M, Veawab A. Corrosion in CO2 capture process using blended monoethanolamine and piperazine. IndEngChem Res. 2009;48(20):9299-306.

XIV. Portugal A, Sousa J, Magalhães F, Mendes A. Solubility of carbon dioxide in aqueous solutions of amino acid salts. ChemEng Sci. 2009;64(9):1993-2002.

XV. Sakwattanapong R, Aroonwilas A, Veawab A. Behavior of reboiler heat duty for CO2 capture plants using regenerable single and blended alkanolamines. IndEngChem Res. 2005;44(12):4465-73.

XVI. Song H-J, Lee S, Maken S, Park J-J, Park J-W. Solubilities of carbon dioxide in aqueous solutions of sodium glycinate. Fluid Phase Equilib. 2006;246(1):1-5.

XVII. Suleman H, Maulud AS, Man Z. Carbon Dioxide Solubility in Aqueous Potassium Lysinate Solutions: High Pressure Data and Thermodynamic Modeling. Procedia Engineering. 2016;148:1303-11.

XVIII. Suleman H, Maulud AS, Syalsabila A. Thermodynamic modelling of carbon dioxide solubility in aqueous amino acid salt solutions and their blends with alkanolamines. Journal of CO2 Utilization. 2018;26:336-49.

XIX. Syalsabila A, Maulud AS, Nordin NAHM, Suleman H, editors. VLE of carbon dioxide loaded aqueous potassium lysinate with separate blends of piperazine and 2-amino-2-methyl-1-propanol. AIP Conference Proceedings; 2018: AIP Publishing.

XX. Van Holst J, Politiek PP, Niederer JP, Versteeg GF, editors. CO2 capture from flue gas using amino acid salt solutions. Proceedings of 8th International Conference on Greenhouse Gas Control Technologies; 2006.