4th International Conference on Process Engineering and Advanced Materials

Carbon Dioxide Solubility in Aqueous Potassium Lysinate Solutions: High Pressure Data and Thermodynamic Modeling

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Abstract

In present study, the solubility of carbon dioxide has been determined in aqueous potassium lysinate solutions for a wide range of pressure (150 – 4040 KPa), temperature (313.15 – 353.15K) and concentration (1 – 2.5 M). It was found that lysine has good absorptive capacity for carbon dioxide and is comparable to conventional alkanolamines. An enhanced Kent Eisenberg model developed for high pressure vapor-liquid equilibrium data has been used to correlate carbon dioxide solubility in aqueous potassium lysinate solutions. The model results are coherent with experimental findings.

Keywords: Thermodynamic modelling; Vapor – liquid equilibrium; Carbon dioxide; Amino acid

1. Introduction

Carbon dioxide removal via absorption is regarded one of the most technologically and commercially proven process. The process has been widely adopted in chemical and power generation industry. Alkanolamines are the solvents of choice, due to their good absorptive capacity, fast kinetics, low cost and operational.

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A variety of alkanolamines and their mixtures has been introduced. However, this class of solvents entails various drawbacks, like high energy penalty, corrosiveness and environmental degradation issues [1, 2]. This has instigated research in alternatives to alkanolamines.

Alkaline salts of amino acids have been proposed as an alternative to alkanolamines [3-6]. As they contain an amine group, amino acid salts are known to be a good absorber of carbon dioxide with fast reactivity. Moreover, they are thermally stable, minutely volatile and environmental friendly [7-10]. A number of amino-acid salts have been investigated. Recently, Mazinani et al. [11] has investigated the potassium salts of lysine at low pressure. Since Lysine contains two amine groups in its structure, it can absorb more carbon dioxide theoretically. Similarly, Shen et al. [12] has shown that potassium salts of lysine are comparatively better in absorptive capacity when compared to conventional alkanolamines. However, no data of carbon dioxide absorption in aqueous potassium based lysinate salt solutions are available in moderate and high pressure region. Moreover, none of the published study presents a thermodynamic model for the aforementioned system.

In this work, carbon dioxide solubility has been studied in potassium salts of lysine for wide range of pressure (150 – 4040 KPa), temperature (313.15 – 353.15K) and concentration (1 – 2.5 M). Moreover, an enhanced form of Kent-Eisenberg model has been developed by incorporation of equation of state/excess Gibbs energy model for the satisfactory correlation of high pressure VLE experimental results.

2. Materials and Methods

Amino acids are naturally amphoteric in nature, due to co-existence of carboxylic and amine functional groups. When dissolved in water, the following behavior is seen.
Thus, a zwitterion of an amino acid can act both as an acid or a base. Addition of a base removes a proton from the ammonium group, leaving the molecule with a net negative charge. This anion form of amino acid, with a deprotonated amine group can readily react with an acid gas (carbon dioxide or hydrogen sulphide). Potassium or sodium hydroxides are used for this purpose. The following equation explains the phenomenon.

\[
\text{OOC} - R - \text{NH}^+ + \text{KOH} \rightarrow \text{K}^+ + \text{OOC} - R - \text{NH}_2 + \text{H}_2\text{O}
\]  

The neutralization of the amine group by the base effectively enhances the solubility of carbon dioxide in potassium based amino-acid salts. They react with carbon dioxide in similar way as of conventional alkanolamines [13].

L-Lysine monohydrate (purity >99.5%) and potassium hydroxide were obtained from Merck Malaysia (Pvt.) Ltd. Sample solutions of 1 and 2.5 molar were prepared by adding the L-lysine to an equimolar amount of potassium hydroxide in a volumetric flask, along with de-ionized water. Solutions were prepared using a mass balance (Sartorius BSA224S-CW) with an accuracy of ±0.1 mg, 250 ml volumetric flasks and micropipettes (Duran). Carbon dioxide gas (purity >99.99%) was supplied by Gas Walker (Pvt.) Ltd.

Vapor–liquid equilibrium for the CO₂ loaded aqueous potassium lysinate solutions was measured at 303.15K, 323.15K and 343.15K for various pressures. The apparatus used a high pressure dual cell (feed-reactor) mechanism and is given in Figure 1.

Gas was fed from carbon dioxide cylinder to a thermostatted feed cell, having a volume of 600 ml and allowed to be equilibrated. The pressure of the gas was measured by digital pressure gauge (Keyence GP-100M), with an accuracy of ±0.625KPa. Similarly, gas temperature was measured by digital temperature gauge (Autonics TK-4S), with an accuracy of ±0.1K. One hundred (100) ml of prepared potassium lysinate solution was fed to thermostatted reactor/solubility cell, having a volume of 200 ml. The solution was heated up to desired temperature and flushed with nitrogen gas. Carbon dioxide gas was fed from the feed cell in increments of 500 KPa. The remaining gas in feed cell was allowed to equilibrate for two hours and then pressure and temperature readings were noted. Initially, two or more gas bleeds were needed for registering a residual pressure. The gas bleeds were continued until the feed cell pressure remained higher than the solubility cell pressure. For pressures above 3000 KPa, the feed cell had to be refilled accordingly.

Figure 1: High pressure vapor-liquid equilibrium apparatus
Hence, the gas fed to solubility cell for each reading was determined by Eq. (3).

$$n_{\text{fed}} = n_1 - n_2$$  \hspace{1cm} (3)

The number of moles in each case for Eq. (3) was determined by translated modified Peng-Robinson equation of state (tmPR EoS) \[14\] and Span and Wagner EoS \[15\], for pressures less and greater than 3 MPa, respectively.

The solution mixture was stirred by a magnetic stirrer for two hours initially and switched off. The stagnant system was allowed to achieve equilibrium. The readings were digitally noted at intervals of 30 seconds by LABVIEW data acquisition system, until the pressure readings stabilized at a constant temperature, set initially. The stirrer was switched on again for at least 15 minutes to shake off any gas pockets in liquid region and even more, if variation in pressure values was again observed. The process was repeated until the effect of switching on the stirrer on pressure was nullified at equilibrium. The pressure readings for residual gas at equilibrium were then recorded.

The system was then washed (both by distilled water and acetone), dried and refilled with new solution for next reading. The number of moles of carbon dioxide absorbed in aqueous alkanolamine solution was determined by Eq. (4).

$$n_{\text{abs}} = n_{\text{fed}} - n_{\text{res}}$$  \hspace{1cm} (4)

The partial pressure of amino acid solution in Eq. (5) was neglected due to low volatility. The carbon dioxide loading was determined by Eq. (6).

$$\alpha = \frac{n_{\text{abs}}}{n_{\text{amino acid}}}$$  \hspace{1cm} (6)

3. Thermodynamic Framework

Following equilibrium reactions occur in the chemical absorption of carbon dioxide in potassium lysinate solutions \[11\].

$$RNH_3^+ \leftrightarrow k_1 RNH_2 + H^+$$  \hspace{1cm} (7)

$$RNHCOO^- + H_2O \leftrightarrow RNH_2 + HCO_3^-$$  \hspace{1cm} (8)

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$$  \hspace{1cm} (9)

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$  \hspace{1cm} (10)

$$H_2O \leftrightarrow OH^- + H^+$$  \hspace{1cm} (11)

where R denotes the L-lysine amino acid. The equilibrium constants, \(k_1\)-\(k_5\) for the carbon dioxide-alkanolamine-water system can be taken from Eq. (7) to (11) and are given below.

$$k_1 = \frac{[RNH_2][H^+]}{[RNH_3^+]}; k_2 = \frac{[RNH_2][HCO_3^-]}{[RNHCOO^-]}; k_3 = \frac{[HCO_3^-][H^+]}{[CO_2]}; k_4 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}; k_5 = \frac{[OH^-][H^+]}{[H_2O]}$$

The balance equations for reactions are given as follows:

Potassium Lysinate Balance:

$$[AA_{\text{total}}] = [RNH_2] + [RNH_3^+] + [RNHCOO^-]$$  \hspace{1cm} (12)

CO₂ Balance:
\[ \alpha = [AA_{\text{total}}] = [CO_2] + [HCO_3^-] + [CO_3^{2-}] + [RNHCOO^-] \]  

(13)

Electro-neutrality Balance:

\[ [H^+] + [RNH_3^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [RNHCOO^-] \]  

(14)

Since the Henry’s law is limitedly applicable to pressures below 1000 KPa \cite{17}, the concentration of carbon dioxide in liquid phase is determined by an equation of state/ excess Gibbs energy model developed recently for high pressure carbon dioxide and water equilibrium systems \cite{18}.

\[ \Lambda = \left( \frac{\lambda}{A_v} + 1 \right) \frac{G^e}{RT} + \frac{1 - \lambda}{A_m} \sum_i x_i \ln \left( \frac{b_i}{b_j} \right) + \sum_i x_i \Lambda_i \]  

(15)

Eq. (15) is called the Linear Combination of Vidal and Michelsen (LCVM) mixing rule\cite{19}. LCVM combines translated modified Peng Robinson equation of state\cite{14} with original Universal Functional Activity Coefficients (UNIFAC)\cite{20} for evaluation of physical forces (\( \Lambda_i \)) and activity coefficients. The EoS/G\( ^E \) model predicts the vapor liquid equilibria of carbon dioxide-water system. Hence, it is superior to Henry’s law, which assumes ideal fugacity in vapor phase. The resulting model equation by rearrangement of Eq. (12), (13) and (14), is as follows.

\[ \Lambda[H^+] + B[H^+] + C[H^+] + D[H^+] + E[H^+] + F = 0 \]  

(16)

where

\[ A = 1; B = [AA_{\text{total}}] + k_1; C = -k_1[C\text{O}_2^-] - k_1 + \frac{k_1 k_2 [CO_2]}{k_2}; \]

\[ D = \frac{-k_1 k_2 [CO_2][AA_{\text{total}}]}{k_2} - 2k_1 k_4 [CO_2] - 2k_1 k_3 [CO_3^-] - k_1 k_4; \]

\[ E = -2k_1 k_4 [CO_2] - k_1 k_4 [CO_3^-] - \frac{k_2 k_4 [CO_2]}{k_3} - \frac{k_2 k_4 [CO_3^-]}{k_3}; \]

\[ F = \frac{-2k_1 k_4 [CO_2]}{k_2} \]

where values of \( k_1 \) and \( k_2 \) are regressed to experimental data \cite{9,17}. The values of equilibrium constants from \( k_3 \) to \( k_5 \) were taken from Edwards et al. \cite{21}. The roots of the Eq. (16) are determined and the concentration of hydrogen ion is selected between the range \( 10^{-5} \) and \( 10^{-12} \) (corresponding to the pH value of 5 and 12 for potassium lysinate solutions). Hence, the value of acid gas loading, \( \alpha \) for potassium lysinate solutions is determined using the modified form of Eq. (13).

\[ \alpha = \left( \frac{[CO_2] + k_2 [CO_2]}{[H^+] + k_4 [CO_2]} \right) + \frac{k_2 k_4 [CO_2]}{[H^+]^2} \left( \frac{2k_1 k_4 [CO_2] + k_2 [CO_3^-] [H^+] + k_4 [H^+] - [H^+]^3}{[H^+]^2 - \frac{k_2 [CO_2]}{k_4}} \right) \left( [AA_{\text{total}}] \right) \]  

(17)

3.1. Regression of Model Parameters

As stated earlier, the protonation and carboxylation equilibrium constants of potassium lysinate solutions are regressed to experimental data. The minimization objective function, \( OF \) was optimized using “fminsearch” algorithm in MATLAB environment, using experimental data generated in this study.
\[ \text{OF} = \arg \min_{NDP} \frac{1}{NDP} \sum_{i=1}^{NDP} (x_{\text{calc}} - x_{\text{exp}})^2 \]  

(18)

The regressed values of equilibrium constants for amino-acid protonation and amino-acid carbamate formation are given as follows.

\[ \ln k_1 = -5857.05 / T - 0.1213 [\text{AA}_{\text{total}}] \]  

(19)

\[ \ln k_2 = 950.583 / T \]  

(20)

4. Results and Discussion

Table 1 presents the experimental carbon dioxide solubility in aqueous potassium lysinate solutions.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Concentration (Molar)</th>
<th>313.15</th>
<th>333.15</th>
<th>353.15</th>
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<td></td>
<td>( P ) (kPa)</td>
<td>( a ) (mol/mol)</td>
<td>( P ) (kPa)</td>
<td>( a ) (mol/mol)</td>
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Figures 2 and 3 represent the correlation of enhanced Kent-Eisenberg model for CO2-Potassium Lysinate-H2O system with experimental data, given in Table 1.

As shown, the model shows satisfactory results with average deviation of 17.55%, for a wide range of temperature and pressure for potassium lysinate concentrations. The model can be further improved by incorporating the effect of potassium hydroxide in activation of amine functional group of amino acid. Moreover, the results are compared to monoethanolamine (MEA) data of Lee et al. [22] with concurrent temperature and concentration values. Graphical analysis shows that at high pressures, potassium lysinate solutions have better absorptive capacity, at lower temperatures. L-lysine is superior in absorption capacity at normal operating temperatures applied in absorption section of carbon capture plants (<323.15K). Similarly, L-lysine exhibits lower absorption capacity at high temperature (353.15K) when compared to MEA. Hence, the absorptive potential (the amount of carbon dioxide transferred from absorption section to a stripping section of a carbon dioxide capture plant) is greater than conventional alkanolamine. Moreover, with better absorptive potential, the stripping section can be operated at lower temperature (353.15K) as compared to MEA (>373.15K), resulting in lower energy penalty, reducing thermal degradation of solvent and reducing the fugitive emission of the solvent.
5. Conclusions

The vapour–liquid equilibrium of carbon dioxide-potassium lysinate-water system has been studied for a high pressure region at various temperatures and potassium lysinate concentrations. The experimental results show that potassium lysinate is a good option for the replacement of conventional alkanolamines solvents, in terms of comparable absorptive capacity in addition to environmental benefits. An enhanced form of Kent-Eisenberg model has been used for correlation of experimental data values and results are in good agreement.

References


