Research Article

VLE of Carbon Dioxide-Loaded Aqueous Potassium Salt of *L*-Histidine Solutions as a Green Solvent for Carbon Dioxide Capture: Experimental Data and Modelling

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In this study, vapour-liquid equilibrium of CO₂-loaded aqueous potassium salt of *L*-histidine was studied for a wide range of temperature (313.15–353.15 K), pressure (150–4000 kPa), and solvent concentrations (1–2.5 molar). The experimental results show that *L*-histidine has an excellent absorptive capacity for carbon dioxide. When compared to conventional solvent (monoethanolamine) and amino acid salt (potassium *L*-lysinate) at similar process conditions, *L*-histidine has superior absorption capacity. Moreover, modified Kent–Eisenberg model was used to correlate the VLE of the studied system with excellent agreement between the model and experimental values. The model exhibited an AARE% of 7.87%, which shows that it can satisfactorily predict carbon dioxide solubilities in aqueous potassium salt of *L*-histidine at other process conditions. Being a biological component in origin, almost negligibly volatile, and highly resistant to oxidative degradation, *L*-histidine offers certain operational advantages over other solvents used and has a promising potential for carbon dioxide capture.

1. Introduction

The consent of environmental protocols has resulted to the increase of efforts in research toward reducing the carbon dioxide emissions. In this effort, the main step is to separate the carbon dioxide from process flue and fuel streams. There are various techniques which have been applied for this purpose [1]. Of these techniques, removal of carbon dioxide (CO₂) by chemical absorption technique is regarded a standout amongst the most industrial process, technologically and commercially. The process has been broadly received in power plant industry. This involves a chemical reaction between the CO₂ containing industrial gas streams and a solvent which then results to a greener and cleaner gas released to the atmosphere. Aqueous alkanolamines such as monoethanolamine (MEA) are commonly used. However,

this class of solvents has a few downsides like limiting the cyclic CO₂ loading capacity and causing an implication in regeneration economically. Aside from being corrosive, they also add to formation of toxic degradation products and solvent losses due to evaporation [2]. The fugitive losses in the environment have been shown to be directly associated with occurrences of cancer and other medical complexities, apart from their adverse contribution in destroying marine and atmospheric ecology [3].

In the current years, research on using amino acid salt-based solvents as another alternative has been centred for carbon dioxide separation related technology. Interestingly, these amino acid salts have similar functional group to the conventional alkanolamines. Hence, it is expected that their reactivity toward carbon dioxide is as good as alkanolamines-based solvents. Apart from that, they possess

high resistance to thermal and oxidative degradation as well as low in volatility for they are naturally ionic compounds, potentially are a greener solvent for capturing carbon dioxide [4, 5]. Their application shall result in a much cleaner and environmentally friendly process. Few studies on these systems are presently available in the literature. Majority of these already scant works are oriented toward the provision of precursor vapour-liquid equilibrium (VLE) data for studies, pertaining to kinetics and transport property-based investigations. The VLE data form the base for all design and simulation studies, which eventually leads to proper equipment sizing and better selection of operational parameters, resulting in optimal production.

One of the initial works was performed by Muñoz et al. [6] as part of their study on structure/function relationship in various solutions of amino acid salts, namely, proline, serine, taurine, ornithine, and arginine. They examined that the carbon dioxide capacity in these aforementioned solvents at concentration of 1 molar was comparable to the conventional MEA [6]. Recently, the carbon dioxide solubility in aqueous potassium lysinate solutions has been studied at temperature (313.15–353.15 K), concentration (1–2.5 M), and pressure (150–4040 kPa). It was discovered that lysine offered good absorptive capacity for carbon dioxide, and model results developed based on the Kent–Eisenberg model are coherent with experimental findings [7]. A comprehensive literature review of the similar studies was conducted in the field. Table 1 provides exhaustive summary about the recent studies in the discussed field.

However, it was interesting to note that VLE data for carbon dioxide-loaded aqueous potassium histidinate (HisK) are absent. Although there was a reported literature on physical properties and kinetics of CO₂ absorption into this HisK solution from the work of Shen et al. [30], the VLE data for the said system are fictional. Hence, in this study, CO₂ solubility of aqueous potassium histidinate solution was measured at pressure ranging from 150 to 4000 kPa, temperature from 313.15 to 353.15 K, and solvent concentrations of 1 and 2.5 molar. A reliable high-pressure vapour-liquid equilibrium apparatus was used to perform this experimental study.

VLE data on this said system are likely the most essential ancestor data for the development of mathematical models particularly at predicting the CO₂ loading values. For this reason, a mathematical model based on the modified Kent and Eisenberg approach is extended to correlate the equilibrium solubility data of the aforementioned system, with satisfactory results. Although there are several models available for the prediction of CO₂ equilibrium data, the thermodynamic modeling efforts for the aqueous amino acid salt solutions have been limited to modified Kent–Eisenberg model [31, 32]. Being computationally simple, this model has been preferably and broadly used by previous researchers with good correlation of their experimental data [7, 25, 29]. Usually, all the nonidealities of the process system are combined in a single/dual correction parameter(s) of the model, that is a function of amine concentration, carbon dioxide loadings, and/or pressure [33], yielding a good relationship between the model's results and the experimental

data. Hence, a study on the modeling of CO₂ solubility using the Kent and Eisenberg approach appears desirable.

2. Materials and Methods

The chemicals used throughout the experimentation are tabulated in Table 2. All chemicals were of sufficient purity and used without further purification. Samples were weighed using a mass balance Sartorius BSA224S-CW ($u=0.1$ mg). Separate aqueous solutions of 1.0 and 2.5 molar of potassium hydroxide and *L*-histidine were prepared in 250 ml volumetric flasks ($u=0.1$ ml) using deionized water and micropipettes (Duran). Both solutions were then mixed in equal volumes to create 1.0 molar and 2.5 molar aqueous potassium salt of *L*-histidine. The results of the study were reiterated thrice to ensure the repeatability of the results, using freshly prepared sample of aqueous potassium salt of *L*-histidine, each time.

Pressurized reactor system (PRS) was used to measure the carbon dioxide solubility in the solvent and is shown in Figure 1. The apparatus has two vessels primarily made up of stainless steel and designed as 600 ml and 200 ml for feed cell and solubility cell, respectively. Each vessel is jacketed with electrically operated heaters. The apparatus has been used previously at various instances to reaffirm the carbon dioxide solubility in various alkanolamines with good reliability [7, 34, 35]. The feed vessel and reactor cell are equipped with a temperature (type: Autonics TK-4S) and pressure (type: Keyence GP-100M) gauge each. The digital temperature and pressure gauges extract data from the system and transfer it to computer data acquisition system. The computer uses a USB data link with LAB View software for data storage and utilization.

In a usual run, the solubility cell was filled with 40 ml of freshly prepared solvent. The system was purged with low-pressure nitrogen (0.1 kPa) for two minutes to ensure the removal of air/oxygen present in the solubility cell. While purging, the feed cell was filled initially with a known quantity of carbon dioxide, n_{IQ} . After completion of nitrogen flush, carbon dioxide gas was then transported to the solubility cell and n_{FQ} is introduced as CO₂ number of moles in the feed tank after transferring to the solubility cell. Thus, the number of moles of CO₂ being fed to the solubility cell is calculated as follows:

$$n_{FD} = n_{IQ} - n_{FQ}. \quad (1)$$

In the solubility cell, the pressure of CO₂ gas dropped by times as the gas chemically reacts and dissolves in the solvent which then brought to an equilibrium state. The residual number of moles of CO₂ or undissolved gas were calculated by the tmPR-LCVM-UNIFAC equation of state/excess Gibbs energy model [36], using partial pressure of carbon dioxide, P_{RS} at equilibrium, using

$$P_{RS} = P_{PT} - P_{NT} - P_{WT} - P_{AA}, \quad (2)$$

where P_{PT} is denoted as the total pressure in solubility cell at equilibrium whilst P_{NT} , P_{WT} , and P_{AA} are the equilibrium partial pressures of nitrogen, water, and amino acid in the solubility cell, respectively. The value of P_{RS} was then further

TABLE 1: Sources of experimental data for carbon dioxide solubility in various aqueous amino acid salt solutions.

Amino acid	Counterion	<i>P</i> (kPa)	<i>T</i> (K)	<i>C</i> (M)	Source
<i>L</i> -lysine	Potassium	150–4040	313.15–353.15	1.0–2.5	[7]
	Potassium	10	298.15–323.15	2.0–8.0	[8]
	Potassium	0.1–100	298.15–348.15	0.2–3.0	[9]
	Potassium	0–45	298.15–313.15	0.5–2.5	[10]
	Potassium	0.21–20.52	323.15–343.15	2.317	[11]
	Potassium	0.47–115.26	298.15–353.15	0.50–2.50	[12]
	Potassium	0.21–20.81	313.15–343.15	1.08–2.28	[13]
	Potassium	10	298.15–323.15	2.0–8.0	[8]
<i>L</i> -proline	Potassium	0.1–100	298.15–348.15	0.2–3.0	[9]
	Potassium		298.15–313.15	2.5	[14]
	Potassium	70	285.15–323.15	0.5–3.0	[15]
	Potassium	2.90–928.60	313.15–353.15	0.50–2.00	[16]
<i>L</i> -alanine	Potassium	5.20–2583.90	293.15–323.15	0.07–0.066	[17]
	3-(methylamino)propylamine	10	313.15–353.15	2.5	[18]
<i>L</i> -taurine	Potassium	0.20–1041.70	313.15–353.15	1.50	[19]
	Potassium	1–1000	313.15–353.15	2.0–6.0	[20]
<i>L</i> -glycine	Potassium	10	298.15–323.15	2.0–8.0	[8]
	Sodium	100–2500	298.15–313.15	1.0–3.0	[21]
	Sodium	0.1–200	303.15–323.15	1.0–3.0	[22]
	Potassium	0.1–60	293.15–351.15	0.1–3.0	[23]
	Sodium	0.10–213.50	303.15–323.15	1.0–3.5	[22]
	Sodium	92.00–2505.00	313.15	1.0	[24]
	Sodium	0.59–773.50	313.15–333.15	0.5–2.8	[25]
	Potassium	5.10–2508.70	293.15–323.15	0.1–0.9	[26]
<i>L</i> -threonine	Potassium	0.10–42.00	313.15	1.00	[23]
<i>L</i> -aspartate	Potassium	7.20–951.20	313.15–353.15	0.5–2.0	[27]
<i>L</i> -glutamate	Potassium	5.10–871.40	313.15–353.15	0.5–2.0	[27]
<i>L</i> -amino-butyric acid	Potassium	4.60–977.60	313.15–353.15	0.5–2.0	[28]
<i>L</i> -sarcosine	Potassium	0.20–938.40	313.15–353.15	4.0	[19]
<i>L</i> -phenyl alanine	Sodium	1.35–23.11	303.15–333.15	0.5–1.3	[29]

TABLE 2: List of materials used.

Materials	Abbreviation	CAS	Purity	MW (g/mol)	Source	Purification method
Histidine	His	71-00-1	0.995 (mass fraction)	155.15	Merck Malaysia (Pvt.) Ltd.	None
Potassium hydroxide	KOH	1310-58-3	0.850 (mass fraction)	56.11	Merck Malaysia (Pvt.) Ltd	None
Carbon dioxide	CO ₂	124-38-9	0.999 (mass fraction)	44.01	Gas Walker (Pvt.) Ltd	None
Nitrogen	N ₂	7727-37-9	0.999 (mass fraction)	28.01	Gas Walker (Pvt.) Ltd	None

used to determine the value of n_{RS} . This n_{RS} is important for determination of CO₂ number of moles absorbed in the solvent, as demonstrated in the following equation:

$$n_{AB} = n_{FD} - n_{RS}. \quad (3)$$

The number of moles in each case (n_{IQ} , n_{FQ} , and n_{RS}) were determined by translated modified Peng–Robinson equation of state [37] and Span and Wagner EoS [38] for pressures lower and higher than 3000 kPa, respectively. Hence, the carbon dioxide loading was determined as follows:

$$\alpha = \frac{n_{AB}}{n_{AA}}, \quad (4)$$

where n_{AA} is the number of moles of unloaded amino acid initially fed to the solubility cell.

3. Thermodynamic Framework

3.1. Modified Kent–Eisenberg Model for Absorption of Carbon Dioxide in Aqueous Potassium Histidinate Solution (HisK).

The chemical reaction between carbon dioxide and amino acid salt like histidine is best explained by the zwitterion mechanism which broadly recognized for the development of model for CO₂ absorption in the aqueous solutions of alkanolamines and amino acid salts [39]. The equations describing the equilibrium of CO₂ with HisK are as follows [30]:

FIGURE 1: Pressurized reactor system.

The equilibrium constants, k_a – k_f , for reactions (5)–(10) are given as

$$k_a = \frac{[\text{RR}^-\text{NH}][\text{H}^+]}{[\text{RR}^-\text{NH}_2^+]}, \quad (11)$$

$$k_b = \frac{[\text{RR}^-\text{NH}][\text{HCO}_3^-]}{[\text{RR}^-\text{NCOO}^-]}, \quad (12)$$

$$k_c = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2]}, \quad (13)$$

$$k_d = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}, \quad (14)$$

$$k_e = [\text{OH}^-][\text{H}^+], \quad (15)$$

$$k_f = \frac{[\text{OH}^-][\text{K}^+]}{[\text{KOH}]}. \quad (16)$$

Moreover, balances for reactions given in (5)–(10) are given as follows:

Amino acid balance:

$$[A_{\text{MT}}] = [\text{RR}^-\text{NH}] + [\text{RR}^-\text{NH}_2^+] + [\text{RR}^-\text{NCOO}^-] \quad (17)$$

CO₂ balance:

$$\alpha[A_{\text{MT}}] = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{RR}^-\text{NCOO}^-] \quad (18)$$

Electroneutrality balance:

$$[\text{H}^+] + [\text{K}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + 2[\text{RR}^-\text{NCOO}^-] + [\text{RR}^-\text{NH}] \quad (19)$$

The potassium hydroxide value of equilibrium constant is assumed to be very high as compared to other equilibrium constants, k_a to k_e , and the strength of molar for potassium ion, $[\text{K}^+]$, is presumed to be equal to the strength of molar for potassium hydroxide $[\text{KOH}]$. Therefore, value of $[\text{K}^+]$ is known. The solution and rearrangement of equations (11)–(17) and (19) yield the equation of polynomial given below:

$$A[\text{H}^+]^5 + B[\text{H}^+]^4 + C[\text{H}^+]^3 + D[\text{H}^+]^2 + E[\text{H}^+] + F = 0, \quad (20)$$

where

$$A = k_{bx},$$

$$B = k_{bx}[\text{K}^+] + k_{ax}k_{bx},$$

$$C = k_{ax}k_{bx}[\text{K}^+] + k_{ax}k_c[\text{CO}_2] - k_{bx}k_c[\text{CO}_2] - k_{bx}k_e - k_{ax}k_{bx}[A_{\text{MT}}],$$

$$D = k_{ax}k_c[\text{CO}_2][\text{K}^+] - 2k_{ax}k_c[\text{CO}_2][A_{\text{MT}}] - k_{ax}k_{bx}k_c k_{bx}k_e - 2k_{bx}k_c k_d[\text{CO}_2], \quad (21)$$

$$E = -k_{ax}k_c^2[\text{CO}_2]^2 - k_{ax}k_c k_e[\text{CO}_2]$$

$$-2k_{ax}k_{bx}k_c k_d[\text{CO}_2],$$

$$F = -2k_{ax}k_c^2 k_d[\text{CO}_2]^2.$$

The value of hydrogen ion concentration, $[H^+]$, was determined within the range of 10^{-5} to 10^{-12} , according to the relevancy of pH value of HisK solutions and solved by

$$\alpha = \frac{([CO_2] + (k_c[CO_2]/[H^+]) + (k_c k_d[CO_2]/[H^+]^2) + [RR^-NCOO^-])}{[A_{MT}]}, \quad (22)$$

where the value of $[RR^-NCOO^-]$ is governed by the equation as follows:

$$RR^-NCOO^- = \frac{\{k_c[K^+][CO_2][H^+]^2 + k_c[CO_2][H^+]^3 - k_c^2[CO_2]^2[H^+] - k_c k_e[CO_2][H^+] - 2k_c^2 k_d[CO_2]^2\}}{k_{bx}[H^+]^3 + 2k_c[CO_2][H^+]^2}. \quad (23)$$

3.2. Modified Kent–Eisenberg Model Parameters for Absorption of Carbon Dioxide in Aqueous Potassium Histidine Solution (HisK). Henry's law equation given below is used in the model of modified Kent and Eisenberg for determination of carbon dioxide value in the liquid phase:

$$[CO_2] = \frac{P_{CO_2}}{H_{CO_2}}. \quad (24)$$

On the other hand, the values of equilibrium constants in equations (7)–(10) are obtained from published literatures and calculated based on

$$k_i = \exp\left(\frac{a_i}{T + b_i \ln T + c_i}\right). \quad (25)$$

From the equation above, the value of factors from a_i to c_i is tabulated in Table 3. The values of apparent equilibrium constants for amino acid, k_{ax} and k_{bx} , are regressed to the experimental data.

The regressed values of k_a and k_b in this work are represented by a set of apparent equilibrium constants given in [41]:

$$k_{ax} = k_a f_a, \quad (26)$$

$$k_{bx} = k_b f_b, \quad (27)$$

where the values of k_a and k_b are determined similarly as equilibrium constants given in Table 3, on the basis of equation (25). The regressed parameters for both k_a and k_b are tabulated in Table 4.

Moreover, the values of correction factors, f_a and f_b , are determined by

$$f_a = \exp(s_1[A_{MT}] + s_2 P_{CO_2} + s_3[A_{MT}]^2), \quad (28)$$

$$f_b = \exp(s_4[A_{MT}] + s_5 P_{CO_2} + s_6[A_{MT}]^2). \quad (29)$$

The values of correction parameters for f_a and f_b are given in Table 5.

4. Results and Discussion

The experimental equilibrium CO_2 loadings in 1 M and 2.5 M aqueous HisK solutions are presented in Table 6.

equation (20). The carbon dioxide loading in the aqueous HisK solution thereby can be calculated based on the following equation:

With increase in pressure, the solubility of carbon dioxide increases, whereas increase in temperature leads to decrease in loading values. An overall increase in carbon dioxide solubility is seen with increase of the HisK solvent concentration. However, the individual values of gas loading are reduced with increase in solvent concentration, since the HisK concentration appears in the denominator of loading equation as defined in equation (4). Moreover, the trend of the carbon dioxide loadings with respect to pressure, temperature, and concentration was congruent with the common understanding [7, 10, 29, 34, 42, 43]. Additionally, the exothermic reaction of CO_2 with HisK creates a further increase in temperature, leading to a lower loading of CO_2 [44]. From the table below, it can also be seen that carbon dioxide loadings in HisK solutions were significant with maximum values reaching 2.399 moles of CO_2 per mole of HisK solvent at equilibrium partial pressure of CO_2 (3901 kPa).

Additionally, the behaviour of experimental equilibrium CO_2 loading data and literature data of monoethanolamine (MEA) are studied and observed. Figure 2 shows the behaviour of carbon dioxide loadings in 1 molar MEA and 1 molar HisK solutions. Similarly, Figure 3 presents the behaviour of carbon dioxide loadings in 2.5 molar MEA and 2.5 molar HisK solutions. Graphical analysis based on Figures 2 and 3 shows that the CO_2 loading of HisK is superior to that of MEA. As seen in Figure 2, HisK exhibits very high absorptive capacity than that of MEA at lower temperature (313.15 K). Contrarily, the carbon dioxide loadings at 353.15 K are similar to MEA. This means that HisK solutions can absorb more carbon dioxide per mole of solvent. Hence, more carbon dioxide is taken up the absorber section of the carbon dioxide separation system and can be stripped easily in the stripper section with same equilibrium loading. Additionally, based on Figure 3, HisK shows better CO_2 absorption at high temperature (353.15 K) than MEA, which further strengthens its potential for carbon dioxide absorption and stripping in respective sections. This provides a larger window of absorptive potential (the amount of carbon dioxide transferred from absorption section to a stripping section of a carbon dioxide capture plant), where the HisK solutions are capable of carrying more carbon dioxide gas per cycle of carbon dioxide removal system than MEA, provided that the kinetics of both systems are deemed equal.

TABLE 3: Values of constants for equation (25).

Equilibrium constant	a	b	c	Reference
k_c	-12092.1	-36.7816	235.482	[40]
k_d	-1243.7	-35.4819	220.067	[40]
k_e	-13445.9	-22.4773	140.932	[40]

TABLE 4: Values of constants k_a and k_b for equations (25) and (26).

Amino acid salt	Equilibrium constant for deprotonation, k_a		Equilibrium constant for carbamate reversion, k_b	
	a_i	c_i	a_i	c_i
HisK	-20325.2711	-29.5371	-8306.3479	-46.2272

TABLE 5: Values of constants f_a and f_b for equations (28) and (29).

Amino acid salt	Correction parameter for deprotonation, f_a			Correction parameter for carbamate reversion, f_b		
	s_1	s_2	s_3	s_4	s_5	s_6
HisK	1.1343	-0.0900	-0.0139	-0.5817	0.0013	-0.0402

TABLE 6: Experimental carbon dioxide solubility in aqueous potassium salt of *L*-histidine.

Concentration (M)	Temperature (K)					
	313.15		333.15		353.15	
	P (kPa)	α (mol. (mol-HisK ⁻¹))	P (kPa)	α (mol. (mol-HisK ⁻¹))	P (kPa)	α (mol. (mol-HisK ⁻¹))
1.0	154.00	1.1007	392.60	0.8512	360.30	0.6319
	511.00	1.2621	623.90	1.0293	621.60	0.7239
	1001.0	1.5029	1011.7	1.1899	1023.4	0.7924
	1499.0	1.7222	1448.9	1.2419	1434.9	0.9988
	2055.0	1.8000	1923.9	1.2533	2021.6	1.1379
	2418.0	1.9153	2605.1	1.3601	2641.1	1.1405
	2801.0	2.0897	2992.6	1.4968	3123.5	1.2897
	3450.0	2.2356	3523.9	1.6111	3555.8	1.4457
	3901.0	2.3990	4192.6	1.8089	4078.9	1.5379
2.5	205.10	0.6782	352.60	0.5996	230.10	0.4279
	502.60	0.6990	523.90	0.6665	455.10	0.4659
	911.40	0.8031	942.60	0.7865	1136.4	0.5843
	1432.6	0.9276	1861.4	0.8991	1436.4	0.6076
	1972.6	1.1050	2286.4	0.9115	1905.10	0.7687
	2423.9	1.1330	2792.6	0.9672	2361.4	0.7968
	2837.5	1.1626	3155.1	0.9803	2917.6	0.8400
	3398.9	1.2898	3448.9	1.0000	3598.9	0.9025
	3930.1	1.3554	3905.1	1.1464	3923.9	0.9982

The standard uncertainties: $u(T) = 0.1$ K; $u(P) = 1.25$ kPa; $u(M)$ for 1 and 2.5 molar concentration is 0.010 M and 0.004 M, respectively, whereas $u_c(\alpha) = 0.082$.

For example, the carbon dioxide loading for 1 molar aqueous potassium salt of *L*-histidine at 313.15 K and a pressure of 1000 kPa is 1.503 mol/mol, whereas the carbon dioxide loading in 1 molar MEA at similar process conditions is 1.143 mol/mol. This means that HisK solutions can pick 0.36 more moles of carbon dioxide than MEA at absorber conditions. Similarly, the carbon dioxide loading for 1 molar aqueous potassium salt of *L*-histidine at 353.15 K and a pressure of 360 kPa is 0.632 mol/mol, whereas the carbon dioxide loading in 1 molar MEA at almost similar process conditions (316 kPa than 360 kPa) is 0.772 mol/mol. This means that, at stripping conditions (assuming that stripper operates at 353.15 K), HisK solutions will be less loaded at equilibrium than the MEA (quantitatively by a difference of

0.14 mol/mol). Eventually, HisK solutions can separate 0.871 moles of carbon dioxide per mole of solvent per cycle, whereas MEA can only transfer 0.371 moles at similar process conditions.

Furthermore, better absorptive potential also allows the stripping section to be operated at lower temperature (353.15 K) as compared to MEA (>373.15 K), resulting in lower energy penalty, reducing thermal degradation of solvent, and reducing the fugitive emission of the solvent.

On the other hand, Figure 4 illustrates the behaviour of carbon dioxide loadings in 1 molar potassium salt of lysine (LysK) with 1 molar HisK solutions, whereas Figure 5 presents the behaviour of carbon dioxide loadings in 2.5 molar LysK and 2.5 molar HisK solutions. It can be seen

FIGURE 2: Experimental solubility behaviour of carbon dioxide in 1 M aqueous potassium salt of *L*-histidine and data of 1 M monoethanolamine [45].

FIGURE 4: Experimental solubility behaviour of carbon dioxide in 1 M aqueous potassium salt of *L*-histidine and data of 1 M aqueous potassium salt of lysinate [7].

FIGURE 3: Experimental solubility behaviour of carbon dioxide in 2.5 M aqueous potassium salt of *L*-histidine and data of 2.5 monoethanolamine [45].

FIGURE 5: Experimental solubility behaviour of carbon dioxide in 2.5 M aqueous potassium salt of *L*-histidine and data of 2.5 M aqueous potassium salt of lysinate [7].

from these figures that carbon dioxide solubility in HisK solutions is higher when compared to LysK solutions at 313.15 K and almost similar at 353.15 K. Although amino acid salt of lysine was previously observed to have higher CO_2 absorption capacity than others in the group [7, 9, 46–48], it is explicated in this study that amino acid salt of histidine offered a comparable absorption capacity with the lysine. This can be attributed to the presence of an amide bond in the R-structure of *L*-histidine that presumably allows great capture of the carbon dioxide molecule. This means that *L*-histidine has comparatively high absorptive

potential with lysine, allowing great separation of carbon dioxide in the carbon dioxide removal system. It is expected that the presence of amide bond shall also contribute to better kinetic rate for HisK solutions, since its structure resembles with piperazine-type promoters.

The modified Kent–Eisenberg model was used to correlate the experimental results of this study. Figure 6 shows the correlated CO_2 loading against the experimental results for carbon dioxide solubility in 1 molar HisK solutions. Similarly, Figure 7 illustrates the correlated CO_2 loading

FIGURE 6: Correlation of modified Kent–Eisenberg model against the experimental solubility of carbon dioxide in 1 M aqueous potassium salt of *L*-histidine (HisK).

FIGURE 7: Correlation of modified Kent–Eisenberg model against the experimental solubility of carbon dioxide in 2.5 M aqueous potassium salt of *L*-histidine (HisK).

against the experimental results for carbon dioxide solubility in 2.5 molar HisK solutions. The carbon dioxide loadings correlated by the model are slightly underpredicted at the low temperature (313.15 K) and overpredicted at the high temperature (353.15 K). This is attributed to the regression of temperature-dependent correction parameters (a_i and c_i) for equilibrium constants for deprotonation and carbamate formation and can be further improved by adding more correction factors by taking the square of temperature as the correction value. However, this will induce greater complexity in the model and tend to override the contribution of

concentration and pressure-based correction factors. With respect to pressure, the model results are satisfactory as all the values along the pressure curve are well correlated. Similarly, the effect of concentration on the correlated values is well within the nonideality level assumed for the application of the Kent–Eisenberg model. Overall, the model results are in good agreement with the experimental CO_2 loading data. The results of the model are within the experimental errors of this study. The average absolute relative error (AARE%) was determined by

$$\text{AARE\%} = \left(\frac{\alpha_{\text{calc}} - \alpha_{\text{expt}}}{\alpha_{\text{expt}}} \right) \cdot 100\%. \quad (30)$$

The AARE% between the model predicted and experimental results was found to be 7.87%, indicating that the modified Kent–Eisenberg model shows satisfactory results and able to accurately predict the solubility of carbon dioxide at a wide range of process conditions with minimum computational complicity.

5. Conclusions

In this study, the VLE data of carbon dioxide-loaded aqueous solutions of potassium salt of *L*-histidine were measured using the HP-VLE apparatus. The experimental study was performed for a wide range of process parameters (temperature of 313.15 to 353.15 K, pressure of 150 to 4000 kPa, and solvent concentration of 1 and 2.5 molar). The experimental results show that the HisK solutions exhibited high absorption capacity of carbon dioxide, with intrinsic advantages of being negligibly volatile, resistant to degradation, and environmentally friendly. Moreover, a high carbon dioxide solubility will limit the amount of solvent needed to capture a certain amount of carbon dioxide, thus reducing the amount of used pump power as well as decrease the heat requirements for regeneration [49, 50].

On the other hand, the HisK solutions also offered comparatively better carbon dioxide absorption potential than conventional solvent like MEA and potential amino acid salt solution like potassium lysinate. The experimental results provided a unique insight into the phase equilibrium behaviour of the studied $\text{CO}_2 + L\text{-histidine} + \text{H}_2\text{O}$ systems. The tested system has the ability to capture carbon dioxide and is a promising green solvent that can replace conventional alkanolamines. Moreover, the vapour-liquid equilibrium data for aqueous HisK solutions were correlated by a modified Kent–Eisenberg model. Remarkably, AARE% of 7.87% was generated. The model results were in excellent agreement with the experimental data of this study and indicate that the model can be effectually used for accurate prediction of VLE of the said system at other process conditions in simulation studies.

Abbreviations

n_{fed} :	Number of moles of carbon dioxide fed to the solubility cell
n_1 :	Number of moles of carbon dioxide initially in the feed tank

n_2 :	Number of moles of carbon dioxide after feeding to the solubility cell
n_{abs} :	Number of moles of carbon dioxide absorbed in the amino acid solution
n_{res} :	Residual number of moles of carbon dioxide in the solubility cell
$n_{\text{aminoacid}}$:	Unreacted number of moles of amino acid solution fed to the solubility cell
P_{resCO_2} :	Partial pressure of carbon dioxide in the solubility cell at equilibrium
P_T :	Total residual pressure in the solubility cell at equilibrium
P_N :	Partial pressure of nitrogen in the solubility cell at equilibrium
P_W :	Partial pressure of water in the solubility cell at equilibrium
P_A :	Partial pressure of amino acid in the solubility cell at equilibrium
A_{MT} :	Total amino acid salt concentration (mole/litre)
CO_2 :	Carbon dioxide
CO_3^{2-} :	Carbonate
f_a, f_b :	Correction parameters for the modified KE model
H_2O :	Water
H^+ :	Hydrogen ion
HCO_3^- :	Bicarbonate
H_{CO_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_a :	Equilibrium constant of deprotonation of amino acid for the modified KE model
k_b :	Equilibrium constant of carbamate hydrolysis of amino acid for the modified KE model
k_{ax} :	Apparent equilibrium constant of deprotonation of amino acid for the modified KE model
k_{bx} :	Apparent equilibrium constant of carbamate hydrolysis of amino acid for the modified KE model
k_c :	Equilibrium constant of dissociation of carbon dioxide for the modified KE model
k_d :	Equilibrium constant of dissociation of carbon bicarbonate for the modified KE model
k_e :	Equilibrium constant of dissociation of water for the modified KE model
k_f :	Equilibrium constant of dissociation of potassium hydroxide for the modified KE model
OH^- :	Hydroxide ion
P_{CO_2} :	Pressure of carbon dioxide in vapour phase (kPa)
RR^-NH :	Free amino acid
RR^-NH_2^+ :	Protonated amino acid
RR^-NCOO^- :	Carbamate ion of amino acid

s_1-s_6 :	Adjustable parameters for the modified KE model based upon process parameters
α :	Carbon dioxide loading, mole of CO_2 /mole of amine
α_{calc} :	Calculated carbon dioxide loading, mole of CO_2 /mole of amine
$u(T)$:	The temperature uncertainty
$u(P)$:	The pressure uncertainty
$u(M)$:	The concentration uncertainty
$u_c(\alpha)$:	The combined expanded uncertainty.

Data Availability

The data are available upon request from Nor Afaf Syalsabila, Universiti Teknologi PETRONAS, Seri Iskandar, Perak, Malaysia, norafafsyalsabila@gmail.com, +60 011-19637178.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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