Enrichment in CO₂ Absorption by 2-Methyl Piperazine-Activated Tertiary Amines, Physical Solvents, and Ionic Liquid Systems

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ABSTRACT: One of the ever-demanding research fields is the development of new solvents with better properties for mitigation of CO₂ compared to existing solvents. This work reports the measurement and modeling of CO₂ solubility in newly proposed aqueous solvent blends of 2-methyl piperazine with N-methyldiethanolamine (MDEA), sulfolane (TMSO₂), and 1-butyl-3-methyl-imidazolium acetate ([bmim] [Ac]). The operating temperature and CO₂ partial pressure conditions chosen were 303.2–323.2 K and 2–370 kPa, respectively. Along with this, qualitative ¹³C NMR and FTIR analysis were also performed to consider the proposed reaction scheme. The experimental vapor–liquid equilibrium data were modeled by a modified Kent–Eisenberg equilibrium model. The equilibrium constants associated with 2-methyl piperazine (2-MPZ) and [bmim] [Ac] deprotonation and carbamate formation reactions were regressed to fit the experimental CO₂ solubility data. In addition, the CO₂ cyclic capacity and heat of absorption were evaluated for the aq (MDEA + 2-MPZ) blend.

1. INTRODUCTION

The current requirement of mass absorption of various greenhouse gases is an essential controlling action for mitigating climate changes. Of the many greenhouse gases emitted into the atmosphere, CO₂ is the largest anthropogenic gas; hence, its control in the energy sector has been an ever-expanding issue for decades. Although post-combustion CO₂ capture is a mature technology, the method suggested in the literature over an extensive range of temperatures, pressures, and concentrations. Nevertheless, due to either low-equilibrium CO₂ solubility or low reaction rates of these amines, addition of activators is recommended by many researchers. Various activators such as piperazine and its derivatives blended with AMP, MDEA, MEA, and potassium carbonate (K₂CO₃) have been widely considered in the literature. Other amine activators which have been studied and proposed for the said purpose are bis (3-amino propyl) amine (APA), hexamethylenediamine, and triethylene tetramine. One of the PZ derivatives, viz., 2-methyl piperazine (2-MPZ), is explored in the present study for CO₂ absorption. A brief literature review of the selected solvents is discussed in the subsequent text.

The performance of CO₂ loading in potassium carbonate while increasing the concentration of amine additives such as 2-MPZ, potassium sarcosinate, and potassium lysinate has been investigated and reported in the literature. The inclusion of 2-MPZ and potassium lysinate has an affirmative influence on the CO₂ solubility. Nevertheless, the temperature 313.15 K and the pressure range 0–50 kPa were quite narrow in comparison to the horizon of CO₂
absorption applications. The highest CO2 loading found at 50 kPa with a molar fraction of 0.4 of 2-MPZ in K2CO3 solution was evaluated to be 0.89.

The simulation analysis of CO2 absorption in aqueous activator blends of PZ/2-MPZ for varying concentrations has also been reported over a wide range of temperatures and pressures using Aspen Plus. The blends were investigated for CO2 solubility where a meticulous analysis of speciation, kinetic parameters, and heat of absorption was done using the e-NRTL model.20 The highest CO2 loading capacity for (4 m piperazine + 4 m 2-MPZ) was found to be 0.84 mol of CO2/(kg amine + H2O), which is reasonably competitive with traditionally used aqueous amines. Similar studies of PZ/2-MPZ have also been reported elsewhere.21−24 The precipitation of piperazine at lower temperatures leads to the search for new activators that offer better absorption rates and cyclic capacity. The selection of the optimum concentration ratio of PZ/2-MPZ is also a huge concern since an increase in the concentration of 2-MPZ increases the viscosity of the overall system and thereby decreases the CO2 solubility due to less diffusion. 2-MPZ and PZ have also been investigated as promoters for K2CO3 and it was concluded that (15 wt % K2CO3 + 10 wt % 2-MPZ + 10 wt % PZ) at 313.15 K exhibits the highest CO2 loading and absorption rates.14

Pure physical solvents, such as sulfolane (TMSO2), Nmethylpyrrolidone (NMP), propylene carbonate (PC), etc., and their aqueous solvents have also been preferred over the years owing to the advantage of extremely low vapor pressure, leading to a low energy requirement in the regeneration step for acid gas separation systems.25−27 However, due to the low-equilibrium CO2 solubility and requirement of high pressures of the input streams for effective absorption, the blended solutions of physical solvents with amines have been reported in the literature.28 The thermodynamic analysis of the simultaneous removal of mercaptans and CO2 in aq (TMSO2 + DIPA) and aq (TMSO2 + MDEA) systems using PC-SAFT and e-NRTL models has also been reported.29 The results indicated that the studied solvents performed better than aq TMSO2 solutions. The effect of the increase in the PZ concentration in the blends of aq (MDEA + TMSO2) is also reported in the literature.12 The composition (42 wt % MDEA + 8 wt % PZ + 10 wt % TMSO2) is indicated to yield the highest CO2 solubility of αCO2 = 1.21163 mol of CO2/mol of (MDEA + PZ) at 303.15 K and 1236.604 kPa,12 which is comparable to traditionally used primary and secondary amines with PZ.

Recently, the simultaneous removal of CO2 and ethyl mercaptans has also been reported using aq (MDEA + TMSO2) solutions.30 The experimental results inferred that with increment in MDEA concentration from 30 to 40% at a constant total concentration of the solvent at 328.15 K, there was an increase in CO2 solubility of about 28.30%. Biphase solvent mixtures of H2O, diethylenetriamine, and TMSO2 have proved to be competitive with the blends of MDEA, TMSO2, and H2O under similar experimental conditions with respect to CO2 solubility and kinetics of the systems.31,32 Although a general conclusion states that most of the carbamate, dicarbamate, and tricarbamate are formed due to the amine phase rather than the TMSO2 phase.

In addition, another category of solvents that has been extensively studied over the past few decades is ionic liquids, owing to the better solvent properties they offer in comparison to amines. On the other hand, ILs also tend to exhibit lower CO2 absorption. Hence, blends of amines or amine activators with ILs may prove to increase the efficiency of the CO2 absorption/desorption process.33,34 Imidazolium-based ILs are well established in the literature,35−37 proving them to be more cost-competitive and having higher CO2 absorption in comparison to phosphonium- or pyridinium-based ILs. 1-Butyl-3-methylimidazolium acetate ([bmim] [Ac]) activated by amine activators 1-(2-aminoethyl) piperazine (AEP), and bis(3-aminopropyl)amine (APA), is also one of the promising solvents for CO2 capture, which was earlier reported by our group.38

Conclusively, aqueous blends of MDEA, TMSO2, and [bmim] [Ac], that is, a tertiary amine, a physical solvent, and an ionic liquid with 2-MPZ (amine activator), respectively, have been envisioned as potential solvents for CO2 capture. The concentration of the chemicals involved in the measurement of CO2 equilibrium solubility has been chosen rationally to get the desired optimum results. Subsequently, the vapor−liquid equilibrium (VLE) data have also been correlated using the Kent−Eisenberg model for CO2 solubility in aq (MDEA + 2-MPZ), aq (TMSO2 + 2-MPZ), and aq ([bmim] [Ac] + 2-MPZ). The efficacy of the studied solvents for CO2 absorption has been confirmed by COSMO-RS theoretical analysis and has been reported elsewhere.39

2. EXPERIMENTAL SECTION

2.1. Materials. CO2 gas (>99% pure) was procured from Linde India Ltd. and used without further purification. [bmim] [Ac] (≥95% pure), TMSO2 (99% pure), 2-MPZ (95% pure) and MDEA (≥99% pure) were purchased from Sigma-Aldrich. TMSO2, 2-MPZ, and MDEA were used with no auxiliary refinement for the CO2 solubility study. For solution preparation, the [bmim] [Ac] was first analyzed for its initial water content by the Karl Fischer method, which was found to be 1.7%. Then, the solvent was vacuum-dried for 48 h and analyzed again for water content, which was then calculated to be 0.04%. The solvent systems were prepared using double-distilled deionized water. Specification details of the chemicals used in this study were reported elsewhere.39

2.2. Experimental Method. 2.2.1. VLE Measurement. The schematic of the experimental setup, methodology, and validation of the assembly used to measure the VLE has been reported in detail by our research group.38,40,41 However, the measurement method and calculation of equilibrium data are briefly described here. The setup consists of two cells: a buffer (for storage of CO2 gas at a specific temperature and pressure) and an equilibrium cell (for reaction). Both the cells are equipped with temperature and pressure controllers and transducers in order to change and track the differences in temperature and pressure. The solvent introduced in the equilibrium cell is continuously stirred with the help of a magnetic stirrer. The total pressure (Pt) prevailing in the equilibrium vessel and solvent vapor pressure (Pv) can be used to evaluate the equilibrium partial pressure of CO2 (Pco2) at the respective temperature and liquid phase CO2 loading (α). The CO2 loading (αCO2) was further estimated as a function of temperature and Pco2. A similar method has been used in the literature for the measurement of CO2 equilibrium capacity.42−44 Other approaches such as the wetted wall column method45,46 and the Rubotherm magnetic suspension balance method47,48 have been reported in the literature for CO2 solubility. The wetted wall column method is primarily used for establishing the kinetics of the CO2 absorption
process. However, through the graphical method using the mass transfer coefficient and CO₂ partial pressure in the bulk phase, the CO₂ equilibrium partial pressure can be evaluated as function of CO₂ loading and temperature. Furthermore, the Rubotherm magnetic suspension balance method is quite costly. The approach is based on changes in weight calculations while CO₂ absorption takes place and is principally used for the screening of expensive solvents such as ionic liquids. Contrastingly, the equilibrium cell methodology adopted for the current work of CO₂ absorption is less cumbersome and reasonably priced.

The detailed equations required for calculations of $\alpha_{\text{CO}_2}$ and associated uncertainty are represented in Table S1. Nine solvents with the following compositions are studied in the present work at 303.2, 313.2, and 323.2 K (1) aq (3.509 m MDEA + 0.509 m 2-MPZ), (2) aq (3.017 m MDEA + 1.008 m 2-MPZ), (3) aq (2.502 m MDEA + 1.509 m 2-MPZ), (4) aq (3.501 m TMSO₂ + 0.509 m 2-MPZ), (5) aq (3.012 m TMSO₂ + 1.008 m 2-MPZ), (6) aq (2.500 m TMSO₂ + 1.509 m 2-MPZ), (7) aq (3.507 m [bmim] [Ac] + 0.509 m 2-MPZ), (8) aq (3.002 m [bmim] [Ac] + 1.008 m 2-MPZ), and (9) aq (2.510 m [bmim] [Ac] + 1.509 m 2-MPZ). Here, “m” represents mol/kg (molal unit).

2.2.2. FTIR and $^{13}$C NMR Analyses. The $^{13}$C NMR spectra of the CO₂ unloaded and loaded aq (3.017 m MDEA + 1.008 m 2-MPZ) blend were carried out using a 500 MHz NMR spectrophotometer in D₂O (model: Ascend, Bruker). The FTIR-ATR spectra (PerkinElmer Inc., Germany) has also been performed to qualify the system analysis in the range of 1800 to 600 cm⁻¹.

Qualitative $^{13}$C NMR and FTIR-ATR studies are performed to confirm various products of formation during the reaction of solvents under study with CO₂. The majority of new peaks formed due to CO₂ loading were observed in the up field of $^{13}$C NMR spectra (Figure 1). The peaks at 16.76—43.13 associated with several CH₂ groups of intermediate reactive species correspond to MDEA. However, on the other hand, peaks at 47.60—57.61 correspond to various mono- and secondary-carbamates formed in the system due to the presence of 2-MPZ.

The FTIR-ATR analysis of the aq (3.017 m MDEA + 1.008 m 2-MPZ) system under unloaded and under CO₂ loading conditions at 313.2 K is carried out (Figure 2). The characteristic peaks have been identified and apportioned as presented in Table 1 conclusive of which protonation of MDEA and different carbamate species formations have been inveterate.

3. PROPOSED CHEMICAL REACTION

Through the results obtained in $^{13}$C NMR and FTIR studies and literature for 2-MPZ, the equilibrium reactions for

![Figure 1. $^{13}$C NMR spectra of aq (3.017 m MDEA + 1.008 m 2-MPZ) solution (a) unloaded and (b) CO₂ loaded at 313.2 K.](image1)

![Figure 2. FTIR-ATR spectra of aq (3.017 m MDEA + 1.008 m 2-MPZ): red line, unloaded, and purple line, CO₂ loaded at 313.2 K.](image2)
The physical solubility of CO$_2$ is presented here by Henry’s law. Reversible reactions in the liquid phase are explained using chemical reaction equilibrium constants through the conceptualization of chemical equilibrium. The liquid phase reaction consists of protonation of both MDEA and 2-MPZ amine activators, carbamate formation by 2-MPZ and [bmim] [Ac], and several other reactions of formation of bicarbonate or carbonate species. The carbamate formation of 2-MPZ has not been reflected in the present study because at higher α$_{CO_2}$ bicarbonate is the key product of (2-MPZ-CO$_2$) reaction. The carbamate formation for the reaction between [bmim] [Ac] and CO$_2$ has been already reported in the literature. Since TMSO$_2$ is a physical solvent, it is assumed to exhibit negligible chemical interactions and only may have weak van der Waals forces of attraction with CO$_2$ and other species in the system. For all the systems considered in this work, the following reactions are in common: physical solubility, formation of bicarbonate ion, dissociation of bicarbonate ion, and dissociation of water. The chemical reactions pertaining to the [bmim] [Ac] + CO$_2$ + H$_2$O system have been reported by our research group elsewhere. It has also been confirmed through the experimental data, FTIR, and $^{13}$C NMR studies that [bmim] [Ac] having two active amino groups undergoes deprotonation and carbamate hydrolysis reaction. MDEA, being a tertiary amine and having one amino group, offers only deprotonation reaction in the MDEA + CO$_2$ + H$_2$O system. Furthermore, TMSO$_2$ is a well-known physical solvent used for solubilizing CO$_2$. Using the $^{13}$C NMR spectra, Chen et al. suggested the detailed reaction mechanism of the 2-MPZ + H$_2$O + CO$_2$ system. As per the published study, there are two amino groups in the 2-MPZ structure, out of which one of the amino groups stands in hindrance due to the presence of the neighboring methyl group. Both the amino groups form monocarbamate—one is hindered and the other unhindered. However, the electron-giving methyl group is anticipated to ease the positive charge on the adjoining amino group, so the protonation is likely to strike first on the hindered amino group. Both the 2-MPZ carbamates further can be either protonated and form zwitterions or react with one more CO$_2$ to form dicarbamate. Consequently, for the current work, two major reactions offered by 2-MPZ are considered: deprotonation and carbamate hydrolysis. Hence, the enhancement of CO$_2$ solubility is majorly due to the presence of 2-MPZ and the reactions offered by 2-MPZ, along with the base solvents of MDEA, [bmim] [Ac], and TMSO$_2$.

4. VLE MODELING

Efficient correlation of CO$_2$ solubility in solvents has been approached in different manners in the literature. Usually, if pure ionic liquids or physical solvents are utilized as CO$_2$ absorbents, the system is modeled using the equation of states, such as Peng–Robinson, Redlich–Kwong, and so forth, with different mixing rules, including cubic and group contribution methods. However, amines used for the CO$_2$ absorption process are usually modeled by complex models such as Clegg–Pitzer, e-NRTL, Deshmukh–Mather, and Kent–Eisenberg. Of the many available models, the Kent–Eisenberg model exhibits several advantages over other models in that it does not require various essential characteristics of the solvents, such as critical temperature, critical or reduced pressures, boiling point, binary interaction parameters, and acentric factors. Originally, in the KE model, equilibrium constants of the reactions participating in the system were considered to be a function of a single variable, that is, temperature. Later on, due to the complex behavior of the CO$_2$ solubility in any solvent system, the attributes of concentration of solvents and CO$_2$ partial pressure were also included as variables during the estimation of equilibrium constants. One of the major advantages of the modified KE model is that it allows the estimation of various species and pH in the system easily. Hence, more knowledge can be gained regarding the behavior of the system under study. In the present work, all the systems have been correlated using a modified KE model.

Henry’s law signifies the relationship between the CO$_2$ partial pressure $P_{CO_2}$ at equilibrium and the physically dissolved CO$_2$ concentration [$CO_2$] to describe the vapor phase equilibrium, which is presented in eq 1.

$$P_{CO_2} = H_{CO_2} \times [CO_2]$$

The modified KE model derivation for the ([bmim] [Ac] + H$_2$O + CO$_2$ + 2-MPZ) system is presented here. The model has already been presented for similar systems in our earlier work. For simplification, [bmim] [Ac] is renamed as $R_1$. The general mass and charge balance of various molecular and ionic species in the liquid phase is presented as follows

$$[bmim] [Ac] \text{ balance}$$

$$[R_1]_i = M_i = [R_1] + [R_1H^+] + [R_1COO^-]$$

2-MPZ balance

$$[2 - MPZ]_i = M_2 = [2 - MPZ] + [2 - MPZH^+] + [2 - MPZCOO^-]$$

CO$_2$ balance for the aq [bmim] [Ac] +2-MPZ system

$$a_{CO_2} \times (M_1 + M_2) = [CO_2] + [HCO_3^-] + [CO_3^{2-}] + [R_1COO^-] + [2 - MPZCOO^-]$$

Electroneutrality balance/charge balance for the aq ([bmim] [Ac] + 2-MPZ) system
The systems in eqs 1 and 2 can be utilized to calculate the association constants. The systems with MDEA and 2-MPZ can be given as follows:

$$\alpha_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n}$$

where $\alpha_{\text{CO}_2}$ is the CO$_2$ loading of the solvated solute, and $n$ and $n_{\text{CO}_2}$ are the molar concentrations of the solute and CO$_2$, respectively. The systems in eqs 1–5 and Table S2 can be utilized to develop a polynomial equation as a function of [H$^+$]. The equation hence formed for systems under consideration associated with the coefficients can be given as follows:

$$A_2 \times [H^+]^6 + B_2 \times [H^+]^6 + C_2 \times [H^+]^6 + D_2 \times [H^+]^6 = 0$$

where

$$A_2 = K_5 \times K_7$$

$$B_2 = K_5 \times K_7 \times (K_6 + K_4 + M_i + M_j)$$

where $K_5$ and $K_7$ are the molar concentrations of the solute and CO$_2$, respectively. The systems in eqs 1 and 2 can be utilized to calculate the association constants.

**Table 2. CO$_2$ Solubility Data inaq (MDEA + 2-MPZ) Solution**

| aq (MDEA + 2-MPZ) | $T = 303.2$ K | $T = 313.2$ K | $T = 323.2$ K |
|-------------------|---------------|---------------|---------------|
| molal (m) | $P_{\text{CO}_2}$/kPa | $\alpha_{\text{CO}_2}$ | $P_{\text{CO}_2}$/kPa | $\alpha_{\text{CO}_2}$ | $P_{\text{CO}_2}$/kPa | $\alpha_{\text{CO}_2}$ |
| 3.509 + 0.509 | 4.3 | 0.189 ± 0.002 | 5.7 | 0 | 6.6 | 0.139 ± 0.001 |
| 9.8 | 0.331 ± 0.002 | 15.2 | 0.335 ± 0.003 | 18.1 | 0.270 ± 0.002 |
| 21.2 | 0.462 ± 0.003 | 40.3 | 0.459 ± 0.004 | 33.8 | 0.376 ± 0.003 |
| 41.2 | 0.569 ± 0.004 | 72.7 | 0.546 ± 0.005 | 56.1 | 0.454 ± 0.004 |
| 65.1 | 0.644 ± 0.005 | 90.5 | 0.605 ± 0.005 | 73.6 | 0.513 ± 0.005 |
| 98.5 | 0.683 ± 0.006 | 114.3 | 0.642 ± 0.006 | 99.4 | 0.548 ± 0.005 |
| 119.1 | 0.708 ± 0.007 | 133.7 | 0.671 ± 0.007 | 114.2 | 0.578 ± 0.006 |
| 143.1 | 0.722 ± 0.007 | 157.8 | 0.761 ± 0.008 | | |
| 197.3 | 0.749 ± 0.009 | 199.3 | 0.775 ± 0.009 | | |
| 203.2 | 0.753 ± 0.009 | | | | |
| 3.017 + 1.008 | 2.3 | 0.183 ± 0.001 | 5.0 | 0.155 ± 0.001 | 5.0 | 0.141 ± 0.001 |
| 10.1 | 0.345 ± 0.002 | 11.5 | 0.303 ± 0.002 | 15.1 | 0.300 ± 0.002 |
| 20.0 | 0.506 ± 0.004 | 27.0 | 0.435 ± 0.003 | 34.5 | 0.422 ± 0.003 |
| 44.5 | 0.627 ± 0.005 | 57.9 | 0.534 ± 0.004 | 72.0 | 0.494 ± 0.004 |
| 86.5 | 0.706 ± 0.006 | 77.6 | 0.596 ± 0.005 | 82.9 | 0.554 ± 0.005 |
| 118.8 | 0.737 ± 0.007 | 99.2 | 0.638 ± 0.006 | 104.0 | 0.596 ± 0.006 |
| 146.2 | 0.759 ± 0.007 | 116.9 | 0.670 ± 0.006 | 129.6 | 0.624 ± 0.006 |
| 183.5 | 0.774 ± 0.008 | 157.4 | 0.760 ± 0.008 | 192.9 | 0.672 ± 0.008 |
| 235.7 | 0.786 ± 0.010 | 200.0 | 0.767 ± 0.009 | | |
| 279.9 | 0.873 ± 0.011 | | | | |
| 335.4 | 1.013 ± 0.013 | | | | |
| 2.502 + 1.509 | 3.0 | 0.171 ± 0.001 | 3.7 | 0.134 ± 0.001 | 5.5 | 0.119 ± 0.001 |
| 6.8 | 0.319 ± 0.002 | 7.9 | 0.284 ± 0.002 | 13.2 | 0.249 ± 0.002 |
| 24.3 | 0.443 ± 0.003 | 18.5 | 0.422 ± 0.003 | 26.5 | 0.377 ± 0.003 |
| 35.9 | 0.533 ± 0.004 | 44.2 | 0.524 ± 0.004 | 50.5 | 0.485 ± 0.004 |
| 77.6 | 0.617 ± 0.005 | 69.4 | 0.598 ± 0.005 | 75.4 | 0.550 ± 0.005 |
| 108.9 | 0.651 ± 0.006 | 97.1 | 0.646 ± 0.006 | 104.4 | 0.585 ± 0.006 |
| 127.6 | 0.669 ± 0.007 | 118.1 | 0.671 ± 0.006 | 126.9 | 0.609 ± 0.006 |
| 160.3 | 0.679 ± 0.007 | 136.4 | 0.723 ± 0.007 | 157.0 | 0.634 ± 0.007 |
| 241.1 | 0.706 ± 0.010 | 149.0 | 0.829 ± 0.008 | | |
| 251.2 | 0.797 ± 0.010 | 180.8 | 0.856 ± 0.009 | | |

**The standard uncertainties (u) associated with the measured quantity are u (T) = 0.1 K and u ($P_{\text{CO}_2}$) = 0.5 kPa. $\alpha_{\text{CO}_2}$ is the CO$_2$ loading of the solvent in mol of CO$_2$ per mol of solvent.**
The equilibrium parameters of the deprotonation of water and carbonate reactions are obtained from eq 6. In the modified KE model, the equilibrium constants $K_1$–$K_3$ and $K_8$ can be correlated as functions of temperature as given below

$$
\ln K = a_i + \frac{b_i}{T} + (c_i \times \ln(T))
$$

where, $a_i$, $b_i$, and $c_i$ are coefficients of the above equation, and the values of the same are taken from the literature. The resulting non-linear and linear simultaneous equations are further required to be solved using an optimization algorithm. The optimized equilibrium constants $K_D$, $K_3$, $K_{DP}$, $K_{PO}$, and $K_{MP}$ correspond to the deprotonation and carbonate hydrolysis reactions of various reactive species, are estimated as functions of $P_{CO2}$, $T$, and solvent concentration (MATLAB17). The solution of eq 6 results in multiple roots of $\left[H^+\right]$ but only a single value of $\left[H^+\right]$ that belongs in the array of $10^{-12}$–$10^{-3}$ kmol m$^{-3}$ has been used for $\alpha_{CO2}$ estimation. The accuracy of the KE toward prediction of the $CO_2$ loading is analyzed using % AAD as stated below

$$
\text{average absolute deviation: } \% \text{ AAD} = \frac{100}{N} \times \sum_{i=1}^{N} \left| \frac{Y_{\text{exp}} - Y_{\text{mod}}}{Y_{\text{exp}}} \right|
$$

where, $N$, $Y_{\text{exp}}$, and $Y_{\text{mod}}$ indicate the number of data points, the experimental value of $\alpha_{CO2}$, and the modified KE correlated value of $\alpha_{CO2}$, respectively.

## 5. RESULTS AND DISCUSSION

### 5.1. Influence of Various Reaction Factors on $\alpha_{CO2}$ and Modified Kent–Eisenberg Modeling of Vapor–Liquid Equilibrium Data.

The experimental data of $CO_2$


Table 4. CO₂ Solubility Data in aq ([bmim] [Ac] + 2-MPZ) Solution

| System | CO₂ (kPa) | a₀ | CO₂ (kPa) | a₀ | CO₂ (kPa) | a₀ |
|--------|-----------|----|-----------|----|-----------|----|
| G      | 3.507 + 0.509 | 64.4 | 0.085 ± 0.003 | 87.6 | 0.056 ± 0.003 | 62.7 | 0.047 ± 0.002 |
| H      | 3.002 + 1.008 | 22.2 | 0.144 ± 0.002 | 35.7 | 0.113 ± 0.002 | 23.0 | 0.107 ± 0.002 |
| K      | 2.510 + 1.509 | 3.5 | 0.183 ± 0.002 | 4.6 | 0.152 ± 0.002 | 5.0 | 0.122 ± 0.001 |
| L      | 6.755 × 10⁻¹² | 9.951 × 10⁶ | 0.273 ± 0.004 | 83.7 | 0.219 ± 0.004 | 59.7 | 0.194 ± 0.003 |
| N      | 7.655 × 10⁻¹¹ | 9.951 × 10⁶ | 0.283 ± 0.005 | 104.2 | 0.253 ± 0.004 | 98.1 | 0.225 ± 0.004 |
| P      | 2.168 × 10⁻¹⁰ | 5.933 × 10⁶ | 0.291 ± 0.006 | 125.4 | 0.269 ± 0.005 | 132.7 | 0.244 ± 0.005 |
| Q      | 2.728 × 10⁻⁹ | 5.933 × 10⁶ | 0.297 ± 0.007 | 156.4 | 0.276 ± 0.006 | 148.9 | 0.275 ± 0.005 |
| R      | 3.013 | 0.363 ± 0.010 | 370.1 | 0.299 ± 0.011 | 326.1 | 0.268 ± 0.010 |

The standard uncertainties (u) associated with the measured quantity are u (T) = 0.1 K and u (P_CO₂) = 0.5 kPa. a_CO₂ is the CO₂ loading of the solvent in mol of CO₂ per mol of solvent.

Table 5. Coefficients of Equilibrium Constants Estimated in the Present Work

| System | aq (MDEA + 2-MPZ) | aq ([bmim] [Ac] + 2-MPZ) | aq (TMSO₂ + 2-MPZ) |
|--------|-------------------|--------------------------|--------------------|
| K      | Kᵣ | K₃ | K₄ | K₅ | Kᵣ | K₃ | K₄ | K₅ | Kᵣ | K₃ | K₄ | K₅ |
| G      | 3.216 × 10⁻⁴ | 4.174 × 10⁴ | -9.782 × 10⁻⁷ | -2.485 × 10³ | -9.795 × 10⁻⁹ | -2.513 × 10⁴ | 2.586 × 10⁻¹ | -5.499 × 10⁴ |
| H      | 1.261 × 10⁻⁷ | 9.951 × 10⁶ | -4.366 × 10⁻⁷ | -4.820 × 10³ | -4.436 × 10⁻⁹ | -4.840 × 10⁴ | -3.299 × 10⁻⁵ | -5.814 × 10³ |
| K      | 1.024 × 10⁻¹⁰ | 5.933 × 10⁶ | 6.745 × 10⁻¹¹ | -5.974 × 10⁶ | 6.740 × 10⁻¹⁰ | -5.990 × 10⁶ | 2.492 × 10⁻¹⁰ | 5.817 × 10⁴ |
| L      | 6.755 × 10⁻¹¹ | 5.933 × 10⁶ | -3.979 × 10⁻² | -2.327 × 10⁻¹ | -1.627 × 10⁶ | -2.328 × 10⁻¹ | -7.333 × 10⁻⁹ | -4.496 × 10⁴ |
| N      | 2.168 × 10⁻¹⁰ | 5.933 × 10⁶ | 5.822 | 2.612 × 10⁻¹ | 5.822 | 2.612 × 10⁻¹ | -5.254 × 10⁻¹¹ | -1.541 × 10⁴ |
| P      | 7.655 × 10⁻¹¹ | 5.933 × 10⁶ | -3.410 × 10⁻² | 1.131 × 10⁻¹ | -5.177 × 10⁻² | 1.132 × 10⁻¹ | 9.969 × 10⁻¹⁰ | -2.062 × 10³ |
| Q      | 2.728 × 10⁻⁹ | 5.933 × 10⁶ | 1.555 × 10⁻²⁴ | 9.452 × 10⁴ | 1.563 × 10⁻二十四 | 9.453 × 10⁴ | -3.294 × 10⁻¹⁵ | 1.014 × 10⁹ |
| R      | 3.013 | 0.363 ± 0.010 | -1.799 × 10⁻¹⁴ | -1.388 × 10⁻³ | 22.49 | 7.522 | -3.897 | -7.680 × 10⁻² |

The competency of the modified KE model for prediction of CO₂ solubility is also presented in terms of residual plots for the aq (MDEA + 2-MPZ) system in Figure 3.

partial pressure with respect to each loading along with the associated uncertainty are presented in Tables 2–4. The standardization of the conceived methodology for the present work has been previously reported by our research group.38,40,41,67 The maximum evaluated uncertainty of CO₂ loading is 0.013.

The CO₂ solubility data have been associated using the modified KE model. The results of correlation were used to evaluate the coefficients of the equilibrium constants Kᵣ, K₃, K₄, and K₅ using non-linear regression analysis. A non-linear optimization method with the objective function as eq 9 was employed to reduce the imprecision between the experimental and predicted values. The evaluated equilibrium constants (Kᵣ, K₃, K₄, and K₅) in terms of concentration of solvents, T, and P_CO₂ can be expressed as follows:

\[ Kᵣ(or/Kₚ) = g + (h \times M) + (k \times T) + (l \times M \times T) + (n \times T^2) + (p \times P_CO₂) + (q \times P_CO₂^2) \]  

(10)

\[ K₃(or/Kₚ) = g + (h \times M) + (k \times T) + (l \times M^2) + (n \times M \times T) + (p \times T^2) + (q \times P_CO₂) + (r \times P_CO₂^2) \]  

(11)

where g, h, k, l, n, p, q, and r are the coefficients associated with the equilibrium constants and are found by optimization. The calculated values of equilibrium constants are given in Table 5. The equilibrium constants obtained through the KE model were in turn used to predict a_CO₂. The calculated % AAD for aq (MDEA + 2-MPZ), aq ([bmim] [Ac] + 2-MPZ), and aq (TMSO₂ + 2-MPZ) are presented in Table 6.
(TMSO₂ + 2-MPZ) systems is 7.53, 22.49, and 31.94, respectively.

CO₂ solubility is seen to decline with the increase in temperature for all systems under study (Tables 2−4). This decrease in αₐ₉ is due to the exothermic nature of reaction in proposed solvents and CO₂. With the increase in the 2-MPZ activator concentration in the blend keeping the overall concentration of the solvents unchanged, an increase in CO₂ solubility is also perceived in the aqueous blends. Additionally, with intensification in Pₐ₉, it is observed that αₐ₉ increases since an increase in system pressure results in the growth in kinetic energy associated with the gas molecules. This further leads to the improvement of the rate of diffusion up to a positive maximum limit. The number of collisions between gas molecules and the liquid surface increases when Pₐ₉ is increased. This subsequently results in higher CO₂ loading. However, after this limiting value of Pₐ₉ there is no remarkable increase in CO₂ loading. The experimental and modeled αₐ₉ values of aq (3.509 m MDEA + 0.509 m 2-MPZ) and aq (3.002 m [bmim] [Ac] + 1.008 m 2-MPZ) are studied as a function of temperature (Figure 4a,b). The results offer a decent covenant of the measured experimental data with the modeled αₐ₉. A contour analysis of the aq (TMSO₂ + 2-MPZ) system indicates that the system absorbed more CO₂ at low temperatures and high pressures (Figure 4c). The increase in concentration of 2-MPZ from 0.509 to 1.509 m in the aqueous solution of [bmim] [Ac] results in an increase in αₐ₉ at all temperatures, viz., (303.2, 313.2, and 323.2 K) (Figure 5a). It can be concluded that a 1.509 m concentration of 2-MPZ is highly appreciable and provides far better CO₂ solubility in comparison to the 0.509 m concentration of 2-MPZ in a blended system. The studies on the effect of the base solvent with the activator (2-MPZ) indicate that blends of MDEA with 2-MPZ provide superior αₐ₉ in comparison to [bmim] [Ac] or TMSO₂, at the same solvent concentration and temperature (Figure 5b). MDEA, being a tertiary amine, has an amino group that reacts chemically with CO₂, providing chemical absorption. Hence, in the aq (MDEA + 2-MPZ) solvent mixture, the amino groups present in both MDEA and 2-MPZ react only physically majorly, which is quite low at a low Pₐ₉ whereas MDEA majorly contributes through chemical absorption. Along with this, the ionic liquid blended with 2-MPZ shows better performance than that blended with TMSO₂. The total CO₂ solubility offered by any solvent is the sum effect of physical and chemical absorption. The former depends on the structure and is due to van der Waals forces of attraction, whereas the latter is due to the number of functional groups (majorly amino groups) available for chemical reaction. For the aq (MDEA + 2-MPZ) system the amino groups are present in both MDEA and 2-MPZ, and CO₂ solubility depends on both the solvents. The studied concentrations are (3.509 m MDEA + 0.509 m 2-MPZ), (3.017 m MDEA + 1.008 m 2-MPZ) and (2.502 m MDEA + 1.509 m 2-MPZ), where simultaneously, the activator 2-MPZ is increased and MDEA is decreased. Hence, it can be concluded that for the concentration of (2.502 m MDEA + 1.509 m 2-MPZ), the total number of amino groups present in the solution available to react with CO₂ is less compared to the (3.017 m MDEA + 1.008 m 2-MPZ) system. This behavior is also justified because in [bmim] [Ac] and TMSO₂ systems this does not occur. Both [bmim] [Ac] and TMSO₂ offer major physical absorption,
systems as a function of $\alpha_{\text{CO}_2}$. For the aq (2.500 m TMSO$_2$ + 1.509 m 2-MPZ) system, the maximum pH of 8.8 was observed at a low temperature of 303.2 K (Figure S1c). With the increase in $T$ and $\alpha_{\text{CO}_2}$, the pH was observed to decrease inevitably because of the fact that there were more $H^+$ ions in the systems in comparison to OH$^-$ ions at lower temperatures.

5.3. CO$_2$ Cyclic Capacity. The solvent transmission rates in the absorption—regeneration route is often taken as the performance indicator, which is directly a function of CO$_2$ cyclic capacity. In the present work, the CO$_2$ cyclic capacity has been estimated for the aq (MDEA + 2-MPZ) system using

$$\text{capacity} = \frac{\text{moles CO}_2}{\text{kgsolvent}}$$

where, $\alpha_{\text{PCO}_2,\text{rich}}$ is evaluated at 20, 30, and 40 kPa, and $\alpha_{\text{PCO}_2,\text{lean}}$ is calculated at 5 kPa. The CO$_2$ cyclic capacity of the system has been evaluated at 303.2 K with respect to MDEA and 2-MPZ concentration (Figure S2a,b). The total CO$_2$ cyclic capacity of the $\approx 4$ m (MDEA + 2-MPZ) system is observed to be 1.039. However, with respect to MDEA and 2-MPZ concentrations, the maximum of the parameters was observed to be 0.908 and 0.307 at 40 kPa, the highest partial pressure of the system. It indicates that owing to the much larger concentration of MDEA in comparison to 2-MPZ, the CO$_2$ cyclic capacity depends on MDEA rather than on 2-MPZ. The dependency of CO$_2$ cyclic capacity on temperature (Figure S2c) concludes that with the increase in temperature, the CO$_2$ cyclic capacity also tends to decrease, similar to $\alpha_{\text{CO}_2}$. Additionally, the CO$_2$ cyclic capacity estimated for the $\approx 4$ m (MDEA + 2-MPZ) system is found to be approximately 51.59% higher than 30 wt % MEA solution ($\approx 7$ m), hence indicating that the utilization of the proposed solvent blends will require a smaller equipment size for absorption and less re-circulation of the fresh solvent.

5.4. Heat of Absorption in the aq (MDEA + 2-MPZ) Solvent. CO$_2$ absorption in any solvent, whether amines or ionic liquids, results in generation of heat due to the usual exothermic nature of the reactions involved. This indicates that if the heat of absorption is higher, it will result in a high energy requirement during regeneration. Hence, the energy requirements for any solvent desorption process are dictated by the heat of CO$_2$ absorption. The latter can either be measured experimentally using instruments such as a reaction calorimeter or can be evaluated from VLE data using the Gibbs–Helmholtz equation. The equation is presented as follows:

$$\frac{d(\ln P_{\text{CO}_2})}{d\left(\frac{1}{T}\right)} = \frac{\Delta H_r}{R}$$

The heat of absorption in aq (3.509 m MDEA + 0.509 m 2-MPZ) is obtained by eq 13 using the slope of the plot of ln($P_{\text{CO}_2}$) versus (1/$T$). As revealed in Figure S2d, plots were made with $\alpha_{\text{CO}_2} = 0.37$, 0.47, and 0.57, corresponding to which the obtained slopes were $-4783.69$, $-4675.13$, and $-4873.65$, respectively. The obtained heat of absorption is presented in Table 6. In comparison to activated aq MEA or DEA systems, that is, primary or secondary amines, tertiary amines exhibit a

Figure 5. (a) Effect on CO$_2$ solubility with addition of 2-MPZ in aq [bmim] [Ac] at 303.2 K. (b) CO$_2$ solubility comparison in TMSO$_2$, MDEA, and [bmim] [Ac] added with 2-MPZ at 303.2 K ("m" signifies "mol/kg").
Table 6. Heat of Absorption in aq (3.509 m MDEA + 0.509 m 2-MPZ) at Various Compositions within the Temperature Range of 303.2–333.2 K

| α_{CO2}  | ΔH_{a} (kJ/mol) |
|---------|----------------|
| 0.37    | −39.77         |
| 0.47    | −38.87         |
| 0.57    | −40.52         |

lower heat of absorption. This is owing to the reason that primary amines form carbamate and dicarbamate, which result in high heat of absorption, whereas bicarbonate formation, which is one of the principal reactions occurring in tertiary amine systems, is an endothermic reaction. Comparable interpretations have also been reported in the literature. The uncertainty associated with pH and heat of absorption is found using the equation given in serial number 6 in Table S1. Both the variables are found to depend on four major parameters of the system, that is, temperature, CO2 partial pressure, CO2 loading, and concentration of the solvent. Hence, the uncertainty associated with each of these variables is considered in order to evaluate the uncertainty in pH and heat of absorption calculations. The maximum uncertainty associated with pH and heat of absorption was found to be: aq (MDEA + 2-MPZ): 0.1126, aq ([bmim] [Ac] + 2-MPZ): 0.1123, and aq (TMSO2 + 2-MPZ): 0.1122.

5.5. Comparison with Literature CO2 Solubility. An assessment of the studied solvents is done with the available literature. However, due to the lack of literature in the studied range of composition, the nearest available literature was considered. CO2 solubility in the blend of aq (3.017 m MDEA + 1.008 m 2-MPZ) solution is quite competitive to literature available data (Figure 6). In addition, a comparison of CO2 solubility in aq MDEA, TMSO2, and [bmim] [Ac] enhanced by the PZ-based amine activator, viz., 2-MPZ was studied over inclusive variations in experimental conditions. Qualitative analysis through FTIR and 13C NMR of the unloaded and loaded solvents indicated carbamate formation by 2-MPZ reacting with CO2. The results evidently specify that CO2 solubility increases with respect to an increase in both P_{CO2} and concentrations of activators in solvent blends. A modified KE model was developed to correlate the CO2 solubility data. Results indicated that an increase in 2-MPZ in blends of aq, MDEA, TMSO2, or [bmim] [Ac] improved the CO2 solubility tremendously. The optimized equilibrium constants associated with various reactions as functions of P_{CO2} solvent concentration, and T of absorption have been estimated using regression analysis. The speciation and pH data as a function of α_{CO2} have been estimated by means of the modified KE model. The CO2 cyclic capacity and low heat of absorption of the aq (MDEA + 2-MPZ) solvent indicated it to be a prospective solvent for CO2 capture. In addition, an assessment of CO2 solubility data of solvent blends with the literature reveals that the considered solvents have good potential for post-combustion CO2 capture applications.

6. CONCLUSIONS

CO2 solubility in aq MDEA, TMSO2, and [bmim] [Ac] enhanced by the PZ-based amine activator, viz., 2-MPZ was studied over inclusive variations in experimental conditions. Qualitative analysis through FTIR and 13C NMR of the unloaded and loaded solvents indicated carbamate formation by 2-MPZ reacting with CO2. The results evidently specify that CO2 solubility increases with respect to an increase in both P_{CO2} and concentrations of activators in solvent blends. A modified KE model was developed to correlate the CO2 solubility data. Results indicated that an increase in 2-MPZ in blends of aq, MDEA, TMSO2, or [bmim] [Ac] improved the CO2 solubility tremendously. The optimized equilibrium constants associated with various reactions as functions of P_{CO2} solvent concentration, and T of absorption have been estimated using regression analysis. The speciation and pH data as a function of α_{CO2} have been estimated by means of the modified KE model. The CO2 cyclic capacity and low heat of absorption of the aq (MDEA + 2-MPZ) solvent indicated it to be a prospective solvent for CO2 capture. In addition, an assessment of CO2 solubility data of solvent blends with the literature reveals that the considered solvents have good potential for post-combustion CO2 capture applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02217.

Table S1 Details of equations for calculation of α_{CO2} and associated uncertainty; Table S2 Reaction, reaction mechanism, and equilibrium constants associated with reactions in the system; Figure S1 Modified KE model-predicted equilibrium liquid phase concentration of various species in CO2-loaded aq (3.509 m MDEA + 0.509 m 2-MPZ) at T = 303.2 K and aq (3.002 m [bmim] [Ac] + 1.008 m 2-MPZ) at T = 313.2 K and pH as a function of CO2 loading in aq (2.500 m TMSO2 + 1.509 m 2-MPZ); CO2 cyclic capacity of the aq (MDEA + 2-MPZ) system at 303.2 K with P_{CO2,leak}= 5 kPa as functions of MDEA concentration and 2-MPZ concentration; Figure S2 CO2 cyclic capacity of the aq (3.509 m MDEA + 0.509 m 2-MPZ) system with P_{CO2,leak}=5 kPa as a function of temperature; and plot of ln(P_{CO2}) with 1/T for calculation of heat of absorption for the aq (MDEA + 2-MPZ) system (PDF).

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Figure 6. Comparison of CO2 solubility in aq (3.017 m MDEA + 1.008 m 2-MPZ) with the literature at 303.2 K ("m" signifies "mol/ kg").
Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c02217

Notes

The authors declare no competing financial interest.

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