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Experimental data and modeling of the CO$_2$ solubility in 2-methylimidazole aqueous solution

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- CO$_2$
- Solubility

**ABSTRACT**

CO$_2$ capture plays a critical role in reducing carbon emissions. Novel chemical absorption media, such as imidazole aqueous solutions, have been extensively studied as potential candidates. In this work, new experimental data of CO$_2$ solubility in 5–30 wt% 2-methylimidazole (2-Melm) aqueous solutions at 293.15–313.15 K were measured. The Cubic-Plus-Association equation of state (CPA EoS) with the pseudo chemical reaction approach has been proposed to model the CO$_2$ solubility in the 2-Melm aqueous solutions. The CPA model can describe well the saturated vapor pressure (1.1%), liquid density (0.5%) and vapor-liquid equilibrium data (14%) of 2-Melm aqueous solutions. Temperature dependent binary interaction parameters between 2-Melm and CO$_2$ are needed in order to satisfactorily represent the phase equilibrium data of the 2-Melm-H$_2$O-CO$_2$ ternary systems (11%) in the temperature range of 293.15–393.15 K, which covers all the decarbonization process operation conditions. With the pseudo chemical reaction approach within CPA EoS, it is possible to distinguish the physical and chemical effects of CO$_2$ solubility in chemical absorbents. This work provides the experimental and model basis for further research and application of the novel imidazole-based separation media for CO$_2$ capture.

**1. Introduction**

The increasingly severe problem of global warming has become one of the main factors threatening the sustainable development of mankind, and the reduction of greenhouse gas emissions to mitigate climate change has attracted the attention of the international community [1,2]. Governments around the world have been committed to intensifying scientific research and technological development to enhance the ability to deal with climate change [3–6]. CO$_2$ is the most important anthropogenic greenhouse gas, and increasing its level in the atmosphere will have a serious impact on the natural environment and human health [7,8]. Carbon capture, utilization and storage (CCUS) [9–11] is recognized as one of the most promising technologies to reduce CO$_2$ emissions. CCUS is the capture and separation of CO$_2$ generated in the chemical plants, such as power, steel, and ammonia plants, oil refineries [12,13], to realize the resource utilization or storage of CO$_2$ [14]. Numerous methods have been proposed to capture CO$_2$, including physical absorption [15], chemical absorption [16,17], membrane separation [18,19], and adsorption [20]. Compared with other separation media, chemical absorbents [21] have the advantages of high solubility and low viscosity, which also makes it a relatively mature CO$_2$ capture technology currently used in industry [22]. The gas–liquid contact between the absorbent aqueous solution and CO$_2$ produces a reversible chemical reaction to capture CO$_2$. Due to the strong bond energy between the absorbent and CO$_2$, the absorption process can be carried out at ambient temperature and pressure. The CO$_2$ rich solution is desorbed through a temperature swing absorption process [23]. The high temperature (373–393 K) breaks the bond between CO$_2$ and the absorbent, which desorbs CO$_2$ from the solution and releases high concentrations of CO$_2$. Alkanolamine solutions commonly used in industry include monoethanolamine (MEA) [24], diethanolamine (DEA) [25], N-methyl-diethanolamine (MDEA) [26]. Alkanolamine solutions used for CO$_2$ removal have some drawbacks, such as corrosivity and high regeneration energy consumption. The mixed solvent [27–29] based on alkanolamine solution can improve the performance. Very recently, Liu et al. [30,31] have made extensive studies on the physical...
properties and reaction kinetics of the CO$_2$-H$_2$O-1-dimethylamino-2-propanol solutions, and they have shown how to correlate the physical properties using artificial intelligence models and proposed a methodology to screen solvents effectively for CO$_2$ absorption. Recently, imidazoles have been proposed as potential alternatives for CO$_2$ capture because of their excellent performance. Imidazoles are often used as the precursors for imidazolium ionic liquids, and the organic ligand for Zeolitic Imidazolate Frameworks (ZIFs) [32]. The weak alkalinity of imidazole and the pore structure, ZIFs have also been widely studied in the separation and purification of CO$_2$ [33]. In addition, imidazoles are used as co-solvents to strengthen the performance of the separation media, such as increasing the solubility of CO$_2$ in traditional physical absorbents [34], and improving the mass-transfer rates of CO$_2$ in amines solutions [35]. Imidazoles aqueous solutions are also used for CO$_2$ capture applications [36]. They have high thermal stability and low volatility compared with amine solutions [37], because the reaction mechanism of imidazole and CO$_2$ in water is the same as that of tertiary amines [38] and will not generate carbamates [39]. 2-methylimidazole (2-Melm) is a methyl substituent on the imidazole ring, and its acid dissociation constant $pK_a$ is 7.87. The 2-Melm aqueous solutions have CO$_2$ absorption solubility comparable to MDEA solution, which is widely used in industry, as shown in Table 1. However, the solubility of CO$_2$ in 2-Melm aqueous solutions is more sensitive to temperature, and the greater CO$_2$ cyclic capacity can be achieved by changing temperature, then the CO$_2$ desorption gas of high pressure can be obtained, which reduces the cost of pressurization for transportation. Therefore, the 2-Melm aqueous solution is suitable for processing high-pressure CO$_2$ mixtures, like the integrated gasification combine cycle syngas, and the high-pressure CO$_2$ desorption is convenient for the subsequent transportation and storage [40,41].

Many experimental works of imidazole aqueous solutions to capture CO$_2$ have been reported in literature, including information about the basic properties of imidazole aqueous solutions [37,43], reaction mechanism of CO$_2$ [39], CO$_2$ solubility and enthalpy [42,44,45], kinetics of absorption rate [35,46]. On one hand, however, these are still not enough for designing the corresponding processes and explore optimal operating conditions. On the other hand, a thermodynamic model that can accurately describe physical properties and CO$_2$ solubility over wide ranges of temperature, pressure and solution composition, will make process design no longer limited by experimental data and also help to explore optimal operating conditions. The absorption of CO$_2$ in the alkaline solution not only has a physical effect but also introduces a chemical reaction. This means that new species are formed in the alkaline substances-water-CO$_2$ ternary system, so in principle both phase equilibria and chemical equilibria should be considered. There have been several thermodynamic models used to model the vapor–liquid equilibria (VLE) of CO$_2$ in alkaline aqueous solutions. Electrolyte thermodynamic models are commonly applied to describe the phase equilibria and chemical equilibria of CO$_2$ capture process with consideration of interactions among the molecular and ionic species in an aqueous electrolyte system. Mondal et al. [47] predicted the liquid phase speciation, solvent capacity, pH of the solution and absorption heat of CO$_2$ in aqueous hexamethylenediamine (HMDA) solutions with the electrolyte Non-Random Two Liquid (e-NRTL) model. Faramarzi et al. [48–50] applied the extended Universal Quasi-Chemical Correlation Activity Coefficient (extended-UNIQUAC) model to calculate the CO$_2$ solubility and various thermodynamic properties of alkylammonium solutions. Uyan et al. [51] predicted the CO$_2$ solubility in aqueous MDEA solutions with electrolyte Perturbed-Chain Statistical Associating Fluid Theory (ePC-SAFT) model. For the electrolyte thermodynamic models, there are 3 pure components and 5 ions in the CO$_2$-alkaline solution systems, and each species has 3–5 model parameters. In addition, ion pairs or ion–molecule pairs introduce more parameters, which require multiple and numerous experimental data and cause complicated calculations. It may be difficult to apply such electrolyte models to novel CO$_2$ capture media when there are not much data available. Another simplified approach to build a suitable thermodynamic model for such applications is to treat the chemical reaction as a strong cross-association, usually called pseudo chemical reaction approach. Rodriguez et al. [52] proposed this approach and successfully used it with the Statistical Associating Fluid Theory for potentials of variable attractive range (SAFT-VR model) to satisfactorily describe the solubility of CO$_2$ in amine solutions without the consideration of ionic species. Subsequently, Wang et al. [53] used a similar approach with the Peng-Robinson - Cubic-Plus-Association Equation of State (PR-CPA EoS) to model the solubility of H$_2$S and CO$_2$ in MEA and MDEA aqueous mixtures, and the model can also accurately predict the speciation of acid gas reacting with aqueous amine solutions. Leon-tiadis et al. [54] also used the pseudo chemical reaction approach with the CPA EoS to model the CO$_2$-MPA-H$_2$O and CO$_2$-MDEA-H$_2$O systems. In this work, new experimental data of CO$_2$ solubilities in 5–30 wt% 2-Melm aqueous solutions at 293.15–313.15 K are reported. The CPA EoS combined with the pseudo chemical reaction approach is developed to model the thermodynamic properties of the 2-Melm-H$_2$O-CO$_2$ system. For the first time, the physical and chemical effects of CO$_2$ solubility in a chemical absorbent are distinguished using thermodynamic model calculations. The thermodynamic model presented in this study has the potential of being used in process design/simulation for reducing the experimental costs.

2. Experimental section

The experimental equipment, procedures, and data processing have been explained in detail in the previous studies [55–57]. In brief, the gas-liquid phase equilibrium experiments were conducted in the sapphire cell, which receives a specific mole of feed gas from a blind cell. The experimental temperature is controlled by an air bath. The solubility of CO$_2$ is expressed in terms of the mole fraction of CO$_2$ in 2-Melm aqueous solution:

$$x_{CO_2} = \frac{n_{CO_2}}{n_{2-Melm} + n_{H_2O}}$$

where $n_{CO_2}$, $n_{2-Melm}$, and $n_{H_2O}$ represent the moles of CO$_2$, 2-Melm and H$_2$O in solution, respectively. The standard uncertainty in temperature $u(T) = 0.1$ K, in pressure $u(P_{blind\ cell}) = 10$ kPa and $u(P_{sapphire\ cell}) = 4$ kPa, in height $u(h) = 0.1$ cm, in weight $u(m) = 0.01$ g, and in CO$_2$ solubility $u(x_{CO2})$ are then calculated.

Table 1

<table>
<thead>
<tr>
<th>Amine</th>
<th>Amine concentration (mol/L)</th>
<th>pK$_a$</th>
<th>$x$ (mol/mol amine)</th>
<th>cyclic capacity (mol/mol amine)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDEA</td>
<td>3</td>
<td>8.51</td>
<td>1.023</td>
<td>0.823</td>
</tr>
<tr>
<td>2-Melm</td>
<td>3</td>
<td>7.87</td>
<td>0.956</td>
<td>0.859</td>
</tr>
</tbody>
</table>

$a$: at 313.15 K and 1.6 MPa.
$a$: absorption at 313.15 K and 1.6 MPa – desorption at 393.15 K and 0.4 MPa.
b: absorption at 313.15 K and 1.6 MPa – desorption at 393.15 K and 1.6 MPa.

Comparison of properties of MDEA solution and 2-MeIm aqueous solution [42].
3. Thermodynamic model

3.1. CPA EoS

The Cubic-Plus-Association EoS (CPA EoS) [58], in terms of pressure

\[
P = \frac{RT}{V_n - b} \left[ 1 + \frac{\alpha(T)}{2} \left( \frac{1 + \rho}{\rho} \right) \sum_i \sum_j x_i x_j (1 - X_{ij}) \right] \tag{2}
\]

where, \(V_n\) is the molar volume, \(b\) is the temperature independent co-volume parameter, and \(\alpha(T)\) is the temperature dependent energy parameter.

\[
b = \sum_i x_i b_i \tag{3}
\]

\[
\alpha(T) = \sum_i \sum_j x_i x_j \alpha_{ij}(T) \tag{4}
\]

\[
\alpha_{ij}(T) = \sqrt{\alpha_i(T) \alpha_j(T) \left( 1 - k_{ij} \right)} \tag{5}
\]

where \(k_{ij}\) is the binary interaction parameter, which could be temperature-dependent [59]. \(\alpha_i(T)\) reads:

\[
\alpha_i(T) = a_{ij} \left[ 1 + c_1 \left( 1 - \sqrt{\frac{T}{T_{ci}}} \right) \right]^2 \tag{6}
\]
The association strength (Eq. (9) without the radial distribution function) of H$_2$O and 2-Melm molecules at different temperatures.

![association strength](image)

**Table 5**

<table>
<thead>
<tr>
<th>Type of data</th>
<th>T, K</th>
<th>x$_i$, wt%</th>
<th>Number of points</th>
<th>AAD, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>298.15–353.15</td>
<td>10–30</td>
<td>32</td>
<td>0.45</td>
</tr>
<tr>
<td>$P_i$</td>
<td>313.15–373.15</td>
<td>15–30</td>
<td>20</td>
<td>1.14</td>
</tr>
<tr>
<td>2-Melm</td>
<td>313.15–373.15</td>
<td>15–30</td>
<td>20</td>
<td>14.1</td>
</tr>
</tbody>
</table>

where the parameter $a_{0,i}$ can also be expressed as:

$$\Gamma_i = a_{0,i} / (R_b i)$$

(7)

In Eq. (2), $\rho$ is the molar density, $g$ is the radial distribution function, and $X_{\alpha}$ is the fraction of sites A on molecule $i$ that do not form bonds with other hydrogen bonding sites. $X_{\alpha}$ is dependent on the association strength $\Delta^A_{\alpha}B$ between association sites belonging to the different molecules. For example, the association between the $A$ site of the $i$ molecule and the $B$ site of the $j$ molecule can be expressed as:

$$X_{\alpha} = \frac{1}{1 + \rho \sum_{\beta} \sum_{\gamma} X_{\beta} \Delta^A_{\gamma}}$$

(8)

where the association strength $\Delta^A_{\alpha}B$ can be expressed as:

$$\Delta^A_{\alpha}B = g(\rho) \left[ \exp\left(\frac{\epsilon^A_{\alpha}B}{RT}\right) - 1 \right] \beta^A_{\alpha}$$

(9)

where, $\epsilon^A_{\alpha}B$ and $\beta^A_{\alpha}$ are the association energy and the association volume, respectively.

CPA has, for pure components, 5 parameters, 3 ($\Gamma$, $b$, $c_1$) in the cubic term and 2 ($\epsilon^A_{\alpha}B$, $\beta^A_{\alpha}$) in the association term. These 5 parameters can be obtained by fitting the saturated vapor pressure and liquid density of the pure components. For non-associative components, such as CO$_2$, hydrocarbons, only the 3 parameters of the cubic term are required, and they can also be calculated from the critical properties and the acentric factor (although they too are typically fitted to vapor pressure and liquid densities together with the other parameters).

For self-associating components, the cross associative energy and cross associative volume using the CR-1 combining rule are expressed as:

$$\epsilon^{A,B}_i = \epsilon^{cross} = \frac{\epsilon^{A,\beta}_i + \epsilon^{A,\alpha}_i}{2}$$

(10)

and

$$\beta^{A,\beta}_i = \beta^{cross} = \sqrt{\beta^{A,\alpha}_i \beta^{A,\beta}_i}$$

(11)

A modified CR-1 combining rule can be used to account for the association (solvation effect or chemical reaction) between an associative component and a non-associative component:

$$\epsilon^{A,\beta}_i = \epsilon^{cross} = \text{adjustable parameter}$$

and

$$\beta^{A,\beta}_i = \beta^{cross} = \text{adjustable parameter}$$

### 3.2. Pseudo chemical reaction approach

In this work, the CPA EoS and a pseudo chemical reaction approach are applied to the 2-Melm-H$_2$O-CO$_2$ system, using pseudo chemical association sites to describe the chemical reaction between 2-Melm and CO$_2$. Combined with the characteristics of 2-Melm and the reaction mechanism with CO$_2$, molecular models and association schemes suitable for 2-Melm-H$_2$O-CO$_2$ system are proposed, as shown in Fig. 1.

The pure component CO$_2$ is treated as a non-self-associating molecule. In order to represent its interaction with an associating component and the chemical reaction with 2-Melm, solvation (a) site and active chemical reaction (ch) site are added, and both of them are negative association sites. The a site can associate with the d site of H$_2$O and 2-Melm molecules, indicating solvation effect, while the ch site only associates with d site of 2-Melm molecule, simulating thus a chemical reaction.

For the H$_2$O molecule, the 4C scheme used in previous work [59] is adopted. There are two proton donor (d) and two proton acceptor (a) sites. There is no difference in association behavior between d and a sites. There is a cross association between the a and d sites of the H$_2$O and 2-Melm molecules.

For the 2-Melm molecule, a typical secondary amine molecular mode [60], the 2B scheme, is used according to its molecular structure. A 2-Melm molecule has 2 sites, a proton donor (d) site and a proton acceptor (a) site. The d site of 2-Melm molecule can associate with the a site of CO$_2$ and the ch site of CO$_2$, respectively, indicating the physical absorption and chemical absorption of CO$_2$ in the 2-Melm aqueous solution. Because CO$_2$ has only one ch site and 2-Melm also has only d site, one CO$_2$ molecule can interact with one 2-Melm molecule, and simultaneously associate with one H$_2$O molecule, which conforms to the stoichiometry: 2-Melm:CO$_2$:H$_2$O = 1:1:1 [42]. The chemical reaction of the 2-Melm-H$_2$O-CO$_2$ ternary system is:

$$\text{2-Melm} + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{2-Melm} + \text{HCO}_3^-$$

(14)

### 3.3. Parameters of the model

Critical properties and acentric factors of pure components are listed in Table 2. The parameters of pure compounds of H$_2$O and CO$_2$ are taken from literature [59]. Since 2-Melm is a solid at room temperature and pressure, there are no saturated vapor pressure and liquid density data. Therefore, the pure compound parameters of 2-Melm are obtained by fitting the saturated vapor pressure, liquid density and VLE data of the 2-Melm aqueous solution [43].
\[ f = \frac{1}{N_P} \sum_{i=1}^{N_P} \left( \frac{P_{i}^{cal} - P_{i}^{exp}}{P_{i}^{exp}} \right)^2 + \frac{1}{N_Y} \sum_{i=1}^{N_Y} \left( \frac{y_{i}^{cal} - y_{i}^{exp}}{y_{i}^{exp}} \right)^2 + \frac{1}{N_\rho} \sum_{i=1}^{N_\rho} \left( \frac{\rho_{i}^{cal} - \rho_{i}^{exp}}{\rho_{i}^{exp}} \right)^2 \] (15)

where \( P_{i}^{exp}, y_{i}^{exp}, \) and \( \rho_{i}^{exp} \) are the experimental values of saturated vapor pressure, 2-MeIm concentration in the gas phase and liquid density, respectively. \( P_{i}^{cal}, y_{i}^{cal}, \) and \( \rho_{i}^{cal} \) are the calculated values by CPA model.

The average absolute deviation (AAD) is used to evaluate the performance of the model. For the 2-MeIm-H\( _2 \)O binary system, the following AADs are used:

\[ AAD_P = \frac{100}{N_P} \sum_{i=1}^{N_P} \left| \frac{P_{i}^{cal} - P_{i}^{exp}}{P_{i}^{exp}} \right| \] (16)

\[ AAD_y = \frac{100}{N_Y} \sum_{i=1}^{N_Y} \left| \frac{y_{i}^{cal} - y_{i}^{exp}}{y_{i}^{exp}} \right| \] (17)

**Fig. 3.** Comparison of experimental data and calculated values of (a) density, (b) saturated vapor pressure and (c) VLE data of 2-MeIm aqueous solution. Symbols: experimental data, lines: CPA EoS.

**Table 6**

Experimental data for CO\(_2\) solubility in 2-MeIm aqueous solutions.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>( T, ) K</th>
<th>( P, ) MPa</th>
<th>Number of points</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>5–30 wt%</td>
<td>293.15–313.15</td>
<td>0–1.2</td>
<td>70</td>
<td>This work</td>
</tr>
<tr>
<td>30 wt%</td>
<td>313.15, 353.15</td>
<td>0–0.5</td>
<td>18</td>
<td>Evjen et al. 2018 [36]</td>
</tr>
<tr>
<td>24.5 wt% (3 mol/L)</td>
<td>313.15–393.15</td>
<td>0.4–1.6</td>
<td>12</td>
<td>Tomizaki et al. 2010 [42]</td>
</tr>
<tr>
<td>24.5 wt% (3 mol/L)</td>
<td>313.15</td>
<td>0.5–4.2</td>
<td>5</td>
<td>Tomizaki et al. 2010 [39]</td>
</tr>
</tbody>
</table>
AAD
\[ \rho \sum_{i=1}^{N \rho} \frac{P_{\text{cal}} - P_{\text{exp}}}{P_{\text{exp}}} \] (18)
\[ \text{AADP} = \frac{100}{N_{P}} \sum_{i=1}^{N_{P}} \left( \frac{P_{i}^{\text{cal}} - P_{i}^{\text{exp}}}{P_{i}^{\text{exp}}} \right)^2 \] (19)

where \( P_{i}^{\text{exp}} \) is the experimental value of the equilibrium pressure, \( P_{i}^{\text{cal}} \) is the calculated values using CPA model, and \( N_{P} \) is the number of experimental data points.

AADP is defined as:

The binary systems considered in this work are CO\(_2\)-H\(_2\)O, 2-MeIm-H\(_2\)O and 2-MeIm-CO\(_2\). Each binary system has the interaction parameter \( k_{ij} \) and the interaction association parameters \( \varepsilon_{A_{i}B_{j}} \) and \( \beta_{A_{i}B_{j}} \). The binary parameters of CO\(_2\)-H\(_2\)O are taken from literature [59]. The interaction association parameters of 2-MeIm-H\(_2\)O are based on CR-1 combining rule Eqs. (10) and (11). Due to the lack of experimental data for the 2-MeIm-CO\(_2\) binary system, the parameters of 2-MeIm-CO\(_2\), which are based on modified CR-1 combining rule Eqs. (12) and (13), were fitted to the VLE data of 2-MeIm-H\(_2\)O-CO\(_2\) ternary system.

The objective function of the 2-MeIm-H\(_2\)O-CO\(_2\) ternary system is:

\[ f = \frac{1}{N_{P}} \sum_{i=1}^{N_{P}} \left( \frac{P_{i}^{\text{cal}} - P_{i}^{\text{exp}}}{P_{i}^{\text{exp}}} \right)^2 \] (19)

4. Results and discussion

4.1. The 2-MeIm-H\(_2\)O binary system

The pure compound parameters are listed in Table 3 and the binary parameters of 2-MeIm-H\(_2\)O are presented in Table 4. Compared with the association parameters of pure water which indicates the strength of hydrogen bonds between water molecules, the association volume of 2-MeIm is smaller and the association energy is larger. The self-association strength calculated by Eq. (9), with \( g_{\rho} \) ignored, is plotted in Fig. 2. It can be seen that the association strength gradually decreases with increasing temperature, and that of 2-MeIm molecules is always greater than that of water molecules. In fact, 2-MeIm molecule has two N atoms, one as imine N atom and the other as amine NH group, as shown in Fig. 1 (d), to accept or donate of proton, so 2-MeIm can both undergo protonated and deprotonation reactions [62]. Therefore, the interaction between 2-MeIm molecules is a strong chemical interaction. The cross associative parameters are calculated by CR-1 combining rule (Eqs. (10)
and (11)), that is, no extra new parameters are introduced.

The density and vapor pressure of the separation medium are both important parameters for simulating and designing the absorption–desorption process, where the former affects energy consumption and the latter determines its loss during the absorption–desorption cycle process. The ranges of experimental data of the liquid density ($\rho$), saturated vapor pressure ($P_s$) and vapor phase composition of the 2-MeIm aqueous solution in the literature and the AADs are presented in Table 5. The comparison between the calculated results of the CPA model and the experimental data is shown in Fig. 3. The AADs of liquid density and saturated vapor pressure are 0.45% and 1.14%, respectively, which indicates that the model results are in excellent agreement with the experimental data. Because 2-MeIm is a non-volatile compound, the mole fraction of 2-MeIm ($y_{2\text{-MeIm}}$) in the gas phase is at the magnitude of $10^{-4}$, and the slight difference between experimental and calculated results will lead to a large relative deviation. The calculated results are of the same order of magnitude as the experimental values, and the AAD is 14.1%, which can be considered satisfactory.

4.2. The 2-MeIm-H$_2$O-CO$_2$ ternary system

The solubility data of CO$_2$ in the 2-MeIm aqueous solution from the literature are summarized in Table 6. There are 105 data points in total, with a solution concentration range 5–30 wt%, temperature range 293.15–393.15 K, and pressure range 0–4.2 MPa. These data will be used to fit the model parameters and verify the accuracy of the model.

The binary parameters are shown in Table 6. Using the CO$_2$ solubility data in 24.5 wt% and 30 wt% 2-MeIm aqueous solution at 293.15 ~ 393.15 K (Figs. 4 and 5), two sets of 2-MeIm-CO$_2$ binary parameters are fitted: one set is the temperature independent $k_{ij}$, and the other set is temperature dependent $k_{ij}(T)$, with 4 cross-association parameters, 2 for the physical effect, and 2 for the chemical reaction. It is found out that it is reasonable to fix the chemical association volume of 2-MeIm-CO$_2$ to be the same as for 2-MeIm molecules, possibly because they represent a strong chemical interaction. This simplification reduces the number of parameters while ensuring the accuracy of the model. The chemical reaction between 2-MeIm and CO$_2$ is stronger than the solvent effect, so the association energy of the chemical reaction is larger ($\varepsilon_{ch} > \varepsilon_{cross}$), and the association volume is smaller ($\beta_{ch} < \beta_{cross}$), similar to the discussion with regard to Fig. 2. The AAD with temperature independent $k_{ij}$ is 29%, while with temperature dependent $k_{ij}(T)$ it drops to 11%, greatly improving the model accuracy. Different forms of $k_{ij}(T)$ have been investigated. The simple linear relationship shows the best correlation capability, so the results using this set of parameters are shown in this paper.
Table 7
CO₂ solubility in 30 wt% 2-MeIm aqueous solution at 293.15, 303.15, 313.15 K.

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>x_{CO₂} ± u (x_{CO₂})</th>
<th>P (MPa)</th>
<th>x_{CO₂} ± u (x_{CO₂})</th>
<th>P (MPa)</th>
<th>x_{CO₂} ± u (x_{CO₂})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>293.15 K</td>
<td>303.15 K</td>
<td>313.15 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.004</td>
<td>0.01147 ± 0.00013</td>
<td>0.006</td>
<td>0.009934 ± 0.00012</td>
<td>0.010</td>
<td>0.00998 ± 0.00012</td>
</tr>
<tr>
<td>0.013</td>
<td>0.02192 ± 0.00013</td>
<td>0.018</td>
<td>0.01905 ± 0.00013</td>
<td>0.030</td>
<td>0.01941 ± 0.00013</td>
</tr>
<tr>
<td>0.028</td>
<td>0.03248 ± 0.00014</td>
<td>0.036</td>
<td>0.02797 ± 0.00013</td>
<td>0.059</td>
<td>0.02729 ± 0.00013</td>
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<td>0.04138 ± 0.00015</td>
<td>0.063</td>
<td>0.03669 ± 0.00014</td>
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<td>0.06367 ± 0.00017</td>
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</tr>
<tr>
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<td>1.147</td>
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</tr>
<tr>
<td>0.894</td>
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<td>0.767</td>
<td>0.06953 ± 0.00018</td>
<td>0.914</td>
<td>0.06953 ± 0.00018</td>
</tr>
<tr>
<td>1.194</td>
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<td>0.981</td>
<td>0.07231 ± 0.00018</td>
<td>1.222</td>
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The physical solubility of CO₂ in alkaline solution is one of the useful parameters for calculating properties such as diffusion coefficient, reaction rate, and mass transfer coefficient [63]. Previously, the N₂O analogy method [64,65] was used to measure the physical solubility of CO₂ in solution, and it was fitted by empirical equations [66], semi-empirical equations [67,68], and the Redlich-Kister equations [69]. Defining physical absorption helps to analyze enthalpy from a thermodynamic viewpoint, thereby optimizing the operating conditions in the process. Tomizaki et al. [39] studied the dissolution mechanism of CO₂ in alkanolamine and imidazole solution by ¹³C NMR, and provided the contribution ratio of physical and chemical effects. The experimental results showed that when the equilibrium pressure is 1 MPa, the physical absorption of CO₂ in 2-MeIm aqueous solution accounts for 12% of total absorption, while that in MDEA solution is about 5%.

4.3. Physical and chemical absorption

The physical solubility of CO₂ in 2-MeIm aqueous solutions with different concentrations at 303.15 K. Symbols: experimental data, solid lines: CPA EoS with kij(T).

The experimental data of CO₂ solubility in 5–30 wt% 2-MeIm aqueous solutions at 293.15–313.15 K are presented in Tables 7 and 8. Fig. 4 compares the experimental data with the published data, and the good consistency verifies the reliability of the new measurements. The temperature dependent kij is valid in the range of 293.15–313.15 K, while the model deviation increases rapidly with increasing temperature. In contrast, temperature dependent kij(T) provides good accuracy in the temperature range 293.15–393.15 K, which covers the operating temperature range of the CO₂ absorption–desorption process, so the CPA model can be used for the design and optimization of process for CO₂ capture in 2-MeIm aqueous solution. The performance of the model at high temperature has not been fully validated due to the limited experimental data. More accurate model parameters could be possibly obtained when more experimental data become available.

Fig. 6 shows the comparison of CO₂ solubilities in the 5–30 wt% 2-MeIm aqueous solution at 303.15 K. For different concentration solutions, the CPA model can describe the overall trend of CO₂ solubility, but the model’s performance becomes worse with decreasing concentration. This is probably because the CO₂ solubility in pure water is underestimated using the CO₂–H₂O parameters from the literature [59], in low concentration 2-MeIm aqueous solution we also see an underestimation. The CPA model is more suitable for high concentration (>20 wt%) 2-MeIm solution absorbing CO₂ at 293.15–313.15 K with the currently available CO₂–H₂O parameters.
proposed and validated without physical solubility experimental data and adding any parameters. To the best of our knowledge, this is the first time the calculation of physical solubility is obtained through an equation of state. For 2-MeIm-H$_2$O-CO$_2$ ternary system, the calculation of physical absorption only considers the association between the d site of 2-MeIm and the a site of CO$_2$, without the association between the d site of 2-MeIm and the ch site of CO$_2$, i.e. keep the $\lambda_{\text{cross}}$ and $\beta_{\text{cross}}$ of 2-MeIm-CO$_2$ and set the $\lambda_{\text{ch}}$ and $\beta_{\text{ch}}$ to zero, while preserving the rest of the parameter values. For the MDEA-H$_2$O-CO$_2$ ternary system, the physical solubility and total solubility of CO$_2$ in the MDEA solution have been calculated using the CPA model with the parameters from literature [54]. The calculation method of physical solubility is to retain the interaction parameters $k_{ij}$ of MDEA-CO$_2$, and the association parameters of MDEA-CO$_2$ adopt the CR-1 rule instead of values from the literature, while other parameters and association rules remain unchanged. Correspondingly, the chemical solubility can be calculated by subtracting the physical solubility from the total solubility.

Using this calculation approach, the physical and total solubility of CO$_2$ in 24.5 wt% for the 2-MeIm aqueous solution and 35 wt% for the MDEA aqueous solution at 313.15 K were calculated and these are presented and compared with experimental data in Fig. 7. It can be seen that the total absorption first increases rapidly with pressure, then increases slowly until saturation is reached, while the physical absorption increases almost linearly with pressure. The CPA model describes the total solubility and physical solubility very reasonable for both the 2-MeIm and MDEA solutions, indicating that the CPA model can distinguish physical and chemical absorption with corresponding calculation approaches for different CO$_2$-chemical absorbent systems. It is interesting to note that the predicted physical solubility increases almost linearly as the pressure increases, which implies that the Henry’s law may be able to successfully correlate the physical solubility, especially when the pressure is below 2.5 MPa.

### 4.4. Enthalpy

In the CO$_2$ capture process, another important characteristic is the absorption enthalpy, which determines the energy consumption of the separation process. Evjen et al. [36] measured the CO$_2$ absorption enthalpy in 30 wt% 2-MeIm and MDEA aqueous solution using heat-flow reaction calorimeter. We have used the CPA model to calculate the absorption enthalpy under the same conditions with the Clausius-Clapeyron equation (21).

$$Q = - R \frac{d(\ln P)}{d(1/T)}$$  \hspace{1cm} (21)

where $d(\ln P)/d(1/T)$ can be obtained by differentiating the absorption isotherms at different temperatures, so the absorption enthalpy corresponding to CO$_2$ solubility can be calculated.

A comparison between the CPA model results and experimental data is shown in Fig. 8. The estimated results are rather close with the experimental data at low temperatures, but not at high temperatures. Overall, the CPA model estimates the trend and range of enthalpy at a typical operating temperature of 313.15 K for the CO$_2$ absorption column, while the model underestimates the absorption enthalpy at high CO$_2$ solubility. At a typical desorption temperature of 353.15 K, the CO$_2$ enthalpy in 2-MeIm aqueous solution is smaller than that of MDEA solution, which indicates that the separation process using 2-MeIm aqueous solution has low energy consumption. However, the enthalpy estimated by the CPA model and the experimental data show a different trend with increasing CO$_2$ solubility at this temperature. It can also be seen in Fig. 8, there is a larger deviation between the experimental data and calculation results of the CO$_2$ absorption enthalpy in MDEA aqueous solution.
solution at 353.15 K were measured, and a thermodynamic model for the 2-Melm-CO₂-H₂O system was developed by combining CPA EoS and a pseudo chemical reaction approach. The properties of the 2-Melm aqueous solution such as density, vapor pressure and gas composition can be accurately represented by CPA with average deviations of 0.45%, 1.1%, and 14%, respectively. The absorption of CO₂ in 2-Melm aqueous solution is greatly influenced by temperature, and thus using a temperature dependent κ₀(T) of 2-Melm-CO₂ represents better the VLE data of 2-Melm-H₂O-CO₂ system. A method to distinguish the physical and chemical solubility of CO₂ in chemical absorbents has been proposed, and the calculated physical solubilities of CO₂ in 2-Melm and MDEA aqueous solutions show an excellent agreement with the experimental data. However, it is surprising to see that the predicted CO₂ capture enthalpy does not match the experimental values satisfactorily, not even at qualitative level, especially since the vapor pressure can be correlated satisfactorily. More detailed experimental and molecular simulation studies will be useful in classifying the problems and resolving the modeling challenges. In general, the proposed modeling approach shows promising results, especially for relatively high concentration of 2-Melm aqueous solutions at temperatures of 293.15–393.15 K, which covers the operating conditions of CO₂ capture process design and simulations.

CRediT authorship contribution statement

Wan Chen: Conceptualization, Methodology, Software, Writing – original draft, Data curation. Zixuan Huang: Data curation, Writing – review & editing. Xiaodong Liang: Conceptualization, Methodology, Software, Writing – review & editing, Supervision. Georgios M. Kon- toergis: Conceptualization, Methodology, Supervision. Bei Liu: Conceptualization, Methodology, Writing – original draft, Supervision. Guangjin Chen: Conceptualization, Methodology, Writing – original draft, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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