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Citation for published version:

Digital Object Identifier (DOI):
10.1016/j.seppur.2024.127924

Link:
Link to publication record in Heriot-Watt Research Portal

Document Version:
Publisher's PDF, also known as Version of record

Published In:
Separation and Purification Technology

Publisher Rights Statement:
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Open access, thermodynamically consistent, electrolyte NRTL model for piperazine, AMP, water, CO₂ systems on Aspen Plus

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A R T I C L E I N F O

Editor: S. Yi

Keywords:
AMP
PZ
eNRTL thermodynamic modelling
Vapor liquid equilibrium
Volatile emissions
CESAR1

A B S T R A C T

This study developed a comprehensive, open-access, thermodynamically consistent, validated vapour-liquid equilibrium model for CO₂ absorption into aqueous solutions of piperazine (PZ) activated 2-amino-2-methyl-1-propanol (AMP) on Aspen Plus. This solves a two-decade-old problem of inconsistent specification of PZ, and lacking AMP/PZ, thermodynamic models on Aspen Plus, supporting robust process modelling of AMP/PZ-based CO₂ capture systems, considered the contemporary benchmark. The model coverage is wide: total amine concentrations from 30 wt% to 50 wt%, AMP/PZ mole ratios from 0.46 to 23.1, CO₂ loadings from 0.04 to 1.07 mol CO₂/mol amine, and temperatures from 20 °C to 160 °C. The significance lies in the model’s innovative treatment of the zwitterion PZH⁺CO₂, leading to accurate VLE predictions and closed charge balances. Absolute average relative deviations (AARD) are 16.6 % to 22.3 % for CO₂ partial pressure predictions and 6.3 % to 7.7 % for absorption heats. Gibbs-Helmholz and flash calculated absorption heats consistently compare within 1.5 % to 7.0 %, signalling the model’s thermodynamic consistency.

1. Introduction

Carbon capture, utilisation, and storage (CCUS) remains central to the IPCC’s greenhouse gas emissions (GHG) mitigation pathways, offering a pivotal means to substantially diminish CO₂ emissions from both power plants and major industrial processes [1]. CO₂ absorption in aqueous amine solutions is the most widely employed process for large-scale point-source emitters [2,3], offering the advantage of retrofitting to existing processes with modest modifications, while it has been demonstrated at industrial scale. Noteworthy examples include operational CO₂ capture plants in SaskPower’s Boundary Dam power plant (Canada) and NRG’s Petra Nova facility (USA) [4]. Extensive efforts have been directed towards the development of optimised solvent systems that exhibit high CO₂ loading capacity, rapid absorption kinetics, low regeneration duties and minimal environmental impact.

Monoethanolamine (MEA) has traditionally served as a benchmark absorbent. Rochelle et al. [5] proposed a new standard process that uses 40 wt% piperazine (PZ) with regeneration at 150°C by a two-stage flash, aiming to reduce energy requirement to 220 kWh/tonnes CO₂ removed. Meanwhile, a recent study by Feron et al. and the IEAGHG [6] suggests updating the reference to CESAR1, an aqueous blend of 27 wt% 2-amino-2-methyl propanol (AMP) and 13 wt% PZ. This non-proprietary sorbent has properties representative of advanced sorbent systems, making it more relevant a benchmark. CESAR1 was developed in the frame of the European Union project CESAR [7]. Since its development, CESAR1 has undergone extensive testing [8,9], including at the Technology Centre Mongstad, the SINTEF pilot plant at Tiller, Trondheim, RWE’s Coal Innovation Centre at Niederaussem, and the PACT facilities at Sheffield. This solvent has shown lower degradation and corrosion rates and lower energy requirements for solvent regeneration than MEA [10–12].

Given the significance of Piperazine and CESAR1 to the post-combustion CO₂ capture field, the development of high quality, open-access thermodynamic models is crucial. These models would enable both academia and industry to rigorously assess the performance of these solvents using process models. Thermodynamics play a crucial role in predicting properties including chemical equilibrium, enthalpy of absorption, and amine volatility [13].

So far, open access, validated, and thermodynamically consistent PZ and CESAR1 thermodynamic models are lacking on the most widely used process modelling platform, Aspen Plus. Such models are only available in specialist (proprietary) acid gas treating software like Pro-
treat \([14]\), \(\text{CO}_2\text{Sim}\) [15], and \(\text{PPS}\) [16]. Additionally, Hartono et al. developed consistent open access PZ-AMP thermodynamic models in Matlab \([17–20]\). While separate models for PZ and AMP systems are available in Aspen Plus, the PZ model suffers from thermodynamically inconsistent treatment of the PZ zwitterion \([13]\) leading to charge balance issues and model regression problems. Although several studies have endeavoured to address these challenges, they consistently utilised the Aspen Plus representation of piperazine as a basis and did not tackle the zwitterion issue \((e.g., [13,21,22])\). Finally, Frailie et al. \([23]\) proposed a workaround for the Aspen Plus piperazine zwitterion problem by treating the \(\text{PZH}^+\text{CO}_2^-\) (as well as the PZ molecule) as a Henry component, hence adopting an infinite dilution reference state with a volatility of zero. While allowing them to neatly represent measured thermodynamic data, and the further development of an AMP/PZ model by Li et al \([24]\), this treatment is inconsistent with the nature of the species: the zwitterion does not exist in the gas phase and piperazine is a main component of the system, thus its concentration expands well beyond the Henry regime.

In response to this caveat, we here developed an open access, thermodynamically consistent, and widely validated eNRTL thermodynamic model for \(\text{CO}_2\) absorption into aqueous solutions of piperazine, AMP, and their blends on the Aspen Plus platform. Given the model implementation in Aspen Plus, this allows easy use as the basis for process modelling of AMP, PZ, and CESAR1-based \(\text{CO}_2\) capture processes on that software, plus further refining it where bespoke needs. The model is available on GitHub (https://github.com/mijndertvanderspek/PZ-...
CESAR1-thermo-model), providing scientists and industries a robust basis for CO₂ capture process modelling.

2. Methods

2.1. Thermodynamic modeling

The PZ-AMP-CO₂-H₂O system is characterized as a highly non-ideal electrolyte solution. An often-used model to describe such systems is the electrolyte Non-Random Two-Liquid (eNRTL) activity coefficient model [25]. This model was chosen here for its widespread adoption in the thermodynamic investigation of CO₂ capture solvents [24,26–28].

The phase equilibrium between vapor and liquid phase for non-Henry (such as PZ, AMP, H₂O) and Henry components (such as CO₂) can be represented by Eqs. (1)-(2).

\[
y_i^{\phi_v} P = x_i^{\gamma} \Omega
\]

\[
\hat{I}_0 = \begin{cases} 
\omega_i^{S_p} \omega_i^{S_p} & \text{pure component reference state} \\
H^\infty & \text{infinite dilution reference state}
\end{cases}
\]

Where \(x_i\) and \(y_i\) are the component \(i\) mole fraction in the liquid phase and the gas phase respectively; \(\phi_v^S\) is the gas phase fugacity coefficient of component \(i\) at the system temperature and pressure (\(\cdot\)); \(P\) is the system pressure (Pa); \(\gamma_i\) is the activity coefficient of component \(i\) in the mixture; \(p_i^S\) is the saturation vapor pressure of pure component \(i\); \(\phi_v^L\) is the liquid phase fugacity coefficient of component \(i\) at the system temperature and pressure; \(H^\infty\) is the Henry’s constant of component \(i\) at infinite dilute reference state

2.1.1. General assumptions

In this model, the liquid phase non-idealities are modeled by the eNRTL (named ELECNRTL in Aspen Plus) method in terms of the activity coefficients, \(\gamma_i\). Vapor phase non-idealities are modeled by the Redlich-Kwong-Soave (SRK) equation of state. PZ, AMP and H₂O are set as non-Henry components, their liquid fugacity is calculated from Extended Antoine Equation [29]. CO₂, O₂, and N₂ are treated as Henry components as the system temperature is higher than their critical temperature.

2.1.2. Chemical reaction system

The ten equilibrium reactions describing the AMP-PZ-CO₂-H₂O system are given below. Altogether fifteen species are present in the system, yet the generation of PZH₂²⁺ and AMPCO₂⁻ ions was here neglected to simplify the model: the dissociation constant of PZH₂⁺ is very high [30–32] and the AMP is a sterically hindered amine, therefore both will hardly be formed.

\[
2H_2O \rightleftharpoons H_3O^+ + OH^- \tag{R1}
\]

\[
CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^- \tag{R2}
\]

\[
H_2O + HCO_3^- \rightleftharpoons H_3O^+ + CO_3^{2-} \tag{R3}
\]

\[
H_2O + PZH^- \rightleftharpoons PZ + H_3O^+ \tag{R4}
\]

\[
H_2O + PZH^2+ \rightleftharpoons PZH^+ + H_3O^+ \tag{R5}
\]

\[
H_2O + CO_3 + PZ \rightleftharpoons PZCO_2 + H_3O^+ \tag{R6}
\]

\[
H_2O + PZH^+ + CO_2 \rightleftharpoons PZCO_2 + H_3O^+ \tag{R7}
\]
H_2O + CO_2 + PZ\textsubscript{2} \rightleftharpoons K_{\text{PZCO}_2} \text{PZ(CO}_2\textsubscript{2}) + H_2O^+ \tag{R8}

H_2O + AMPH \rightleftharpoons AMP + H_2O^+ \tag{R9}

H_2O + CO_2 + AMP \rightleftharpoons AMPCO_2 + H_2O^+ \tag{R10}

To ensure thermodynamic consistency between speciation and Gibbs free energy, the equilibrium constants are calculated based on Gibbs free energy difference between products and reactants, as suggested by Hilliard. [13].

Key parameters for this model were regressed by a sequential regression method using experimental VLE and calorimetry data [13,20,33]. A sequential regression method consists of consecutively regressing the binary interaction parameters of the ions and molecules that are present first in the secondary amine-H_2O systems, then of those present in the ternary amine-CO_2-H_2O systems and finally for the quaternary AMP-PZ-CO_2-H_2O system.

2.1.3. Treatment of the PZ zwitterion

CO_2 reacts with PZ via a zwitterion mechanism to form carbamates (CO_2 + PZ \rightleftharpoons K_{\text{PZCO}_2} \text{PZ(HCO}_2\textsubscript{2}) \text{CO}_2 \text{H}_2O). The PZ\textsuperscript{2}CO\textsubscript{2} is thus a common zwitterion in the PZ-AMP-CO\textsubscript{2}-H\textsubscript{2}O system, and its molar concentration increases at high CO\textsubscript{2} loadings in the sorbent [13]. However, the Aspen Plus ELECNRTL model does not allow defining PZ\textsuperscript{2}CO\textsubscript{2} as a zwitterion. Hilliard et al. [13] and the Aspen Plus eNRTL default model for the PZ-CO\textsubscript{2} system [34] define PZ\textsuperscript{2}CO\textsubscript{2} as a normal ion with a very small charge of 10\textsuperscript{-5} e. However, if implemented in this manner, the eNRTL interaction parameters between PZ\textsuperscript{2}CO\textsubscript{2} and other species cannot be regressed in Aspen Plus, since this thermodynamic model only considers interactions between molecular species and pairs of electrolytes/ions with no charge. Frailie et al. [35] used a different approach to overcome this issue by defining the zwitterion PZ\textsuperscript{2}CO\textsubscript{2} as a Henry component with an infinite dilution reference state. They also defined PZ as a Henry component, necessitating to fit PZ volatility by adjusting the Henry constant (parameter HENRY in Aspen Plus) instead of using the extended Antoine equation (parameter PLXANT in Aspen Plus). In this way, the PZ volatility calculation bypasses pure PZ data and is calculated by extrapolating PZ-H_2O regression VLE data.

The zwitterion problem was approached here in a different way from the two options described above, and one that is thermodynamically consistent, by treating the zwitterion as a zwitterion instead of a molecule with infinite dilution reference state, or as a normal ion with a very small charge. To this end, the ENRTL-RK (Redlich-Kwong) was added to the Aspen thermodynamic models list, which does allow the zwitterion functionality, while still only using the ELECNRTL model for the interaction parameters regression. This approach was successful because the ENRTL-RK method allows using the unsymmetric zwitterion calorimetric parameters in the mixture thermodynamic calculation. Therefore, there will be no energy imbalance in the process simulation, which proved important to obtain fulfilling results. Table 1 shows the calculation reference state of the mixture Gibbs free energy, Enthalpy and activity coefficient when using different property methods in Aspen Plus.

The activity coefficient of PZ\textsuperscript{2}CO\textsubscript{2} is calculated as a solute. The binary interactions between the zwitterion PZ\textsuperscript{2}CO\textsubscript{2} and other molecules are treated as molecule-molecule interactions, described using binary NRTL interaction parameters [29]. To optimise the thermodynamic model predictions, the binary interactions between the zwitterion PZ\textsuperscript{2}CO\textsubscript{2} and electrolyte pairs were included by regressing molecule-electrolyte pair parameters.
Table 4
Regression data included and rejected and absolute average relative deviation (AARD) for the ternary AMP-CO$_2$-H$_2$O system.

<table>
<thead>
<tr>
<th>Data Type</th>
<th>Author</th>
<th>Year</th>
<th>Points</th>
<th>Data screening</th>
<th>AARDtype</th>
<th>AARDvalue</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ VLE</td>
<td>Chen [50]</td>
<td>2011</td>
<td>13</td>
<td>Accept</td>
<td>CO$_2$ partial pressure</td>
<td>8.9 %</td>
</tr>
<tr>
<td></td>
<td>Hartono [19]</td>
<td>2020</td>
<td>109</td>
<td>Accept</td>
<td></td>
<td>23.7 %</td>
</tr>
<tr>
<td></td>
<td>Li &amp; Chang [51]</td>
<td>1994</td>
<td>27</td>
<td>Accept</td>
<td></td>
<td>25.4 %</td>
</tr>
<tr>
<td></td>
<td>Seo &amp; Hong [52]</td>
<td>1996</td>
<td>17</td>
<td>Accept</td>
<td></td>
<td>19.8 %</td>
</tr>
<tr>
<td></td>
<td>Jane [53]</td>
<td>1997</td>
<td>8</td>
<td>Reject</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dash [26]</td>
<td>2011</td>
<td>166</td>
<td>Accept</td>
<td></td>
<td>20.4 %</td>
</tr>
<tr>
<td></td>
<td>Kundu [54]</td>
<td>2003</td>
<td>51</td>
<td>Accept</td>
<td></td>
<td>15.4 %</td>
</tr>
<tr>
<td>Total pressure VLE</td>
<td>Hartono [19]</td>
<td>2020</td>
<td>53</td>
<td>Accept</td>
<td>Total pressure</td>
<td>16.1 %</td>
</tr>
<tr>
<td></td>
<td>Silkenba [55]</td>
<td>1998</td>
<td>66</td>
<td>Reject</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tong [56]</td>
<td>2012</td>
<td>45</td>
<td>Accept</td>
<td></td>
<td>8.0 %</td>
</tr>
</tbody>
</table>

Average CO$_2$ VLE Error: 18.9 %
Average Total Pressure Error: 12.1 %

Fig. 4. Regressed CO$_2$ solubility data and model prediction for 0.1 m AMP (a) and 4.8 AMP (b).
2.1.4. Reduction principle of NRTL parameters to be regressed

NRTL interaction parameters are key parameters in the regression process. They determine the local interactions of excess Gibbs free energy, from which the activity coefficient $\gamma^*_i$ is calculated (Eq. (1)). There are three types of these binary parameters: molecule–molecule, molecule–electrolyte, and electrolyte–electrolyte. Each parameter consists of both the non-randomness factor ($\alpha$) and energy parameter ($\tau$) (Eqs. (3)–(8)).

Molecule-molecule:

$$\gamma^*_i = \frac{A_{m,m}}{T} + B_{m,m} + F_{m,m} \ln T + G_{m,m} T$$

Molecule-electrolyte:

$$\gamma^*_i = \frac{A_{m,c}}{T} + B_{m,c} \left(\frac{T^{\alpha}}{T} + \ln \frac{T}{T^*}\right)$$

Electrolyte-electrolyte:

$$\gamma^*_i = \frac{A_{c,c}}{T} + B_{c,c} \left(\frac{T^{\alpha}}{T} + \ln \frac{T}{T^*}\right)$$

Where, $\alpha$ is the non-randomness parameter; $\tau$ is the binary energy interaction parameter; the subindices m, c, a represent molecule, cation, and anion respectively; A, B, C, D, E, F, G, are parameters to be regressed.

In theory, interaction energy parameters for all pairs, including molecule–molecule, molecule–electrolyte, and electrolyte–electrolyte need to be regressed. The electrolyte–electrolyte pair parameters can however be set to default values to simplify the regression [29] (Table 2). Of the many molecule–electrolyte parameters, some only have a small effect on the mixture Gibbs free energy and enthalpy because the corresponding component concentrations are very low. Such species can be removed from the regression, leading to a more robust model and reducing the risk of overfitting. For example, the pair parameters for the $AMP – H_2O$ $PZCO_2$ pair have a very small effect since the $H_2O^+$ mole fraction is expected to be smaller than $10^{-6}$.

To avoid over-fitting and simplify the regression, only the NRTL parameters that have a significant effect on the solution thermodynamics were regressed instead of all NRTL parameters. This means that all the parameters of the minor components (mole fraction always $<10^{-4}$) were dismissed and default values were used for these (Table 2).

2.1.5. Heat of CO$_2$ absorption verification

The heat of CO$_2$ absorption constitutes a significant portion of energy consumption in the CO$_2$ regeneration process. Additionally, it serves as a key element for validating the thermodynamic model [36]. The heat of absorption predicted by the eNRTL model can be obtained from the Aspen flash block, calculated by determining the enthalpy difference between products and reactants. The heat of CO$_2$ absorption can also be calculated using the estimated fugacity coefficients, using the Gibbs-Helmholtz equation Eq. (9). Here, the predicted values from these two distinct methods were compared with each other and with experimentally measured calorimetric data, to validate the thermodynamic consistency of the regressed models.

$$\frac{d\ln f_{\text{CO}_2}}{dT} = -\frac{\Delta H_{\text{ABS}}}{R}$$

In Eq. (9), $f_{\text{CO}_2}$ is the CO$_2$ fugacity, obtained from the model, and $\Delta H_{\text{ABS}}$ is the CO$_2$ absorption heat.
2.2. Input data screening process

A crucial step in the model regression process is the selection of the experimental VLE data sets, as their quality can vary significantly due to several factors, including the experiment procedure, the analytical method used, or the accuracy and precision of the measurement instrumentation. Including all available experimental VLE data sets without screening could introduce substantial errors. The systematic data screening process followed in the selection of the data sets consisted of three steps:

1) Create the initial model using trustworthy datasets (e.g., data from different groups demonstrating consistency with each other, and/or data from groups recognised for their strong track record in CO₂ dissolution measurements). Each data set was given the same total regression weight ($W_n$). The initial selection should cover a wide range of amine concentrations, CO₂ loadings, and temperatures whenever possible.

2) Introduce a new data set with the same total regression weight ($W_n$). Run the regression and assess the absolute average relative deviation (AARD) of each data set. If the AARD of the new data set surpasses 40 % (chosen to indicate substantial disagreement with trusted data sets) reject the new data set. Additionally, if the mean AARD of all previous data set increases more than 20 percent points after adding new data set, reject it. Otherwise, accept the new dataset.

3) Repeat step 2 until all available data sets have been scrutinized.

The objective of the data screening process was to identify a group of data sets that are reliable and of sufficient quality, aiming for consistency among them. At a minimum, our aim was to include all trusted data sets in the selection.

Table 5
Regression data included and rejected and absolute average relative deviation (AARD) for the quaternary AMP-PZ-CO₂-H₂O system.

<table>
<thead>
<tr>
<th>Data Type</th>
<th>Author</th>
<th>Year</th>
<th>Points</th>
<th>Data screening</th>
<th>AARD Type</th>
<th>AARD Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ VLE</td>
<td>Bruder</td>
<td>2011</td>
<td>49</td>
<td>Accept</td>
<td>CO₂ partial pressure</td>
<td>29.4 %</td>
</tr>
<tr>
<td></td>
<td>Li</td>
<td>2013</td>
<td>83</td>
<td>Accept</td>
<td></td>
<td>14.9 %</td>
</tr>
<tr>
<td></td>
<td>Dash</td>
<td>2012</td>
<td>136</td>
<td>Reject</td>
<td></td>
<td>61.7 %</td>
</tr>
<tr>
<td></td>
<td>Dash</td>
<td>2011</td>
<td>160</td>
<td>Accept</td>
<td></td>
<td>24.7 %</td>
</tr>
<tr>
<td></td>
<td>Hartono</td>
<td>2021</td>
<td>43</td>
<td>Accept</td>
<td></td>
<td>20.1 %</td>
</tr>
<tr>
<td></td>
<td>Yang</td>
<td>2010</td>
<td>145</td>
<td>Reject</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total pressure VLE</td>
<td>Tong</td>
<td>2013</td>
<td>99</td>
<td>Accept</td>
<td>Total pressure</td>
<td>23.7 %</td>
</tr>
<tr>
<td></td>
<td>Hartono</td>
<td>2021</td>
<td>276</td>
<td>Accept</td>
<td></td>
<td>20.4 %</td>
</tr>
</tbody>
</table>

Average CO₂ VLE Error | 22.3 %
Average Total Pressure Error | 22.0 %

Fig. 6. Regressed CO₂ solubility data and eNRTL model prediction of the (a) total pressure for 3 M AMP/1.5 M PZ, and partial CO₂ pressure for (b) 3 M AMP/1.5 M PZ CO₂ VLE, (c) 35 wt% AMP/5 wt% PZ CO₂ VLE, and (d) 2.3 m AMP/5 m PZ CO₂ VLE.
2.3. Model optimization

Once the first data screening and regression were completed, the model should present a good prediction of the CO\textsubscript{2} solubility and amine volatility but should also correctly predict speciation and heat of absorption as a function of varying temperature and solution composition. The latter two conditions were not always met and, therefore, further model optimization was needed. Note that the speciation prediction is a rigorous means to validate the Gibbs-calculated equilibrium constants of a system’s chemical reactions. The following approach was taken for model optimization (i.e., re-regressing the parameters).

1) The weight of each data set was adjusted by giving a lower weight to those data sets with larger AARD and by removing outliers.
2) Adjust the regression eNRTL parameters network (Fig. 1).
3) Add additional constraints (here, heat capacity data) to the regression to reduce the risk of overfitting.
4) Adjust the symmetric standard Gibbs free energy of formation (DGFORM) of PZH\textsuperscript{+} CO\textsubscript{2} and heat capacity (CPAQ) of protonated amines (i.e., AMPH\textsuperscript{+}, PZH\textsuperscript{+}).
5) Adjust regression initial values for parameters.

The models were optimized balancing the following output indicators.
1) The total system pressure and/or CO\textsubscript{2} partial pressure AARD of each VLE data set.
2) Uncertainty (expressed as standard deviation) of each regressed parameter.
3) The predicted heat of CO\textsubscript{2} absorption calculated by the Aspen Plus flash block and Gibbs-Helmholtz equation compared with experimental data.
4) Speciation prediction compared with NMR data or temperature dependent experimental polynomial [17].
5) The amine volatility AARD.

3. Results and discussion

The model setting of the physical property method, reactions and zwitterions are based on model assumptions and modelling principles in
Section 2.1. The $\text{PZH}^+\text{CO}_2$ was successfully implemented as a zwitterion as discussed in Section 2.1.3.

The different thermodynamic submodels (binary, ternary, and quaternary) were developed from scratch using a sequential approach [1415]. To ensure broad applicability of the model across a range of temperatures, pressures, and concentrations, extensive efforts were made to incorporate a diverse set of VLE data from the scientific literature. A rigorous systematic data screening and selection process was employed to evaluate the suitability of data sets. Some data sets were excluded for the regression due to uncertainties in their validity, as discussed in Section 2.2.

Following Section 2.3, in the model optimization, the heat of absorption calculated by model calorimetry and the Gibbs-Helmholtz equation were compared with experimental data to maintain thermodynamic consistency. Meanwhile, speciation data from reported Nuclear Magnetic Resonance (NMR) measurements were used as a means of validation for the model calculated Gibbs free energy. All regressed parameters and a link to the model repository are presented in the Supplementary Information.

3.1. Binary PZ-H$_2$O and ternary PZ-CO$_2$-H$_2$O systems

Before conducting the regression of the VLE binary interaction parameters for PZ-H$_2$O, the pK$_a$ experimental data of $\text{PZH}^+$ from 20°C to 80°C was used to determine the aqueous heat of formation and Gibbs free energy of $\text{PZH}^+$. This reduced two regression parameters, thus the uncertainty of other binary regression parameters.

For the PZ-H$_2$O binary regression, there are four VLE data sets available, two were included in the regression (Table S1). Two binary heat capacity data sets were also added to further constrain the regression. The resulting model predictions compare well with experimental data from Hartono and Wilson (Figure S1), less so with data from Nguyen and Hilliard (believed due to experimental error, measurements too close to the instrument’s detection limit [37]).

For the PZ-CO$_2$-H$_2$O ternary regression, twelve CO$_2$ VLE data sets and three total pressure VLE data sets were available. Once the data screening was completed, the eNRTL model of the PZ-CO$_2$-H$_2$O systems presented good prediction of CO$_2$ solubility with an AARD of 17.9%.

The data regression total weight of Dash et al. [21] and Derks et al.

![Fig. 8. NMR validation data (points) and model speciation prediction (lines) for 4 m AMP/2 m PZ (a) and 2.3 m AMP/5 m PZ (b) at 40°C.](image-url)
was reduced due to their relatively high AARD. Their data were still very helpful for obtaining correct speciation prediction and hence they were not fully excluded, plus they provide CO$_2$ VLE data at very low PZ concentration (0.2 m PZ), which is a region underrepresented in other data sets. The results after model optimization are shown in Table 3.

Fig. 2 shows that the model predictions align well with the experimental data inputs, signifying a sound regression result. The model is especially good at predicting experimental data with PZ concentration > 1 m, while there is slightly worse prediction of CO$_2$ dissolution for the data sets with a PZ concentration of 0.2 m. Concentrations higher than 1 m PZ are common in the absorber and regeneration sections of a CO$_2$ capture plant. Lower PZ concentration (e.g., 0.2 m) mainly exists under water wash conditions. Although we underestimated the data of 70 °C, this temperature is rarely observed during water washing operations. Importantly, the model accurately predicts the experimental absorption heat data and speciation (Fig. 3). The absorption heat decreases with the increase of CO$_2$ loading, which is due to the generation of more bicarbonate. Compared to Kim et al.’s [46] data, the model absolute average deviation of the heat of absorption was 7.2 % at 40 °C and 8.2 % at 80 °C. The heat of absorption calculated by the Aspen flash block based on calorimetry was consistent with those calculated by CO$_2$ fugacity through the Gibbs-Helmholtz equation. The differences between them were 2.0 % at 40 °C and 7.0 % at 80 °C. The speciation prediction of 11.1 wt% PZ is very close to Hartono’s [17] results. When the PZ concentration increases to 30 wt%, our model predicts a little higher $\text{PZ}^+$ and $\text{HCO}_3^-$. The trend of speciation varies with CO$_2$ loading is consistent with Hartono et al. [17].

Finally, limited public data was available to validate loaded PZ volatility, primarily sourced from Hilliard et al. [131] (Figure S17), while this dataset is acknowledged to exhibit significant errors, largely attributed due to the used FTIR detection limits. Nguyen et al. [44] employed an FTIR method that demonstrated improvement compared to Hilliard’s study, contributing to a more reliable data set for validating the accuracy of our model predictions (Figure S17, red markers) and more in line with our model predictions.

### 3.2 Binary AMP-$\text{H}_2\text{O}$ and ternary AMP-CO$_2$-$\text{H}_2\text{O}$ system

The regression procedure of the AMP system was the same as for PZ. The $pK_a$ experimental data of $\text{AMPH}^+$ were used to determine the
aqueous heat of formation and Gibbs free energy of AMPH. Then, three VLE data sets and two heat capacity data sets were evaluated for the AMP-H$_2$O binary regression. Table S2 and Figure S18 show that all available data sets passed the screening process and demonstrate good fit with the model predictions.

In the loaded AMP system, the absence of carbamates and zwiterions simplifies its ion system significantly, resulting in a notably simpler regression process. It is essential to highlight that the quality of certain older data sets [47–49] was constrained by the measurement equipment used at the time. However, the data range covered by these older data sets is included in more recent and improved data, allowing to exclude the older samples from the screening process (Table 4).

Among the data available, only Hartono reported data with low AMP concentration (0.1 M AMP). Therefore, it was given a double weight in the regression to assure this region of the solution space would be represented well by the model. Fig. 4 shows the resulting model accurately predicts the experimental input data across a wide range of AMP concentrations, amine loadings, and temperatures. More figures can be found in Supplementary Information (Figure S.20 – S.23).

Fig. 5 validates the model predictions for heat of absorption with experimental data by Kim et al.[46], and Arcis et al. [57]. The modelled heat of absorption shows an expected smooth decline from a starting point between 80–90 kJ/mol CO$_2$ towards a sharp drop around a loading of 1 mol CO$_2$/mol amine (resulting from the transition to physi-sorption). The reaction heat does not show significant change with AMP concentration in the range of 15 wt%-30 wt%. If the outliers are excluded, the model absolute average deviation was 5.1 % for 15 wt% AMP and 7.8 % for 30 wt% AMP, while the difference between the heat of absorption calculated by the flash block and via the CO$_2$AMP and 7.8 % for 30 wt% AMP, while the difference between the heat excluded, the model absolute average deviation was 5.1 % for 15 wt%

concentration in the range of 15 wt%-30 wt%. If the outliers are excluded due to inconsistencies with other data sets, particularly at low temperatures. In Fig. 7(a), experimental data from Xie et al. [65] at 80°C are much lower than modelling results. The reaction heat was measured by the Differential Reaction Calorimeter system, while the validation of the experimental system was only done at 40°C. At 80°C and high CO$_2$ loading, the pressure of the reaction cell could be very high. The difference in pressure state between the reaction cell and reference cell may cause significant errors. The experimental data from Hartono et al. [20] and Bruder et al. [62] are also higher than Xie’s data, which further suggests that Xie’s data at 80°C may not be accurate. The thermodynamic consistency in this work was ensured as the heat of absorption calculated by the Aspen Plus flash block and via CO$_2$ fugacity were similar at different AMP/PZ ratios (absolute average deviation of 5.0 %).

As an additional validation step, we compared the model-predicted speciation results to NMR analysis data by Li et al. [24]. They conducted NMR speciation measurements for various AMP/PZ blends, yet the mass balance of AMP and PZ showed a deviation exceeding 20 %–pt, a trend also observed by Hartono et al. [20] Comparative analysis with these data reveals that our model predicts higher concentrations of PZ$^+$ /CO$_2$/PZO$_2^-$ and lower concentrations of PZ/PZH$^+$ (Fig. 8a,b). This trend is consistent with Hartono’s MATLAB eNRTL model [20]. This discrepancy may be caused by the challenges in the assignments and quantifications of the NMR spectra.

The detailed speciation prediction results for 3 M AMP/1.5 M PZ are presented in Fig. 9. As the CO$_2$ loading increases, free AMP first accepts protons and converts to AMPH$^-$ . A considerable part of CO$_2$ exists in the solution in the form of CO$_2^-$ and PZ(CO$_2$)$_2^-$ around 0.5 mol CO$_2$/mol amine. When the CO$_2$ loading reaches 1 mol /mol amine, most of the PZ ultimately converts into PZH$^+$ /CO$_2$ zwiterions.

Finally, Fig. 9b compares our model predictions with amine volatility data from Li et al. [59], also obtained through FTIR analysis. The predicted amine vapour pressures for an unloaded AMP-PZ system closely align with the measured data (continuous lines in Fig. 9b). However, a discrepancy is observed for a loaded system at 0.3 mol CO$_2$/mol alk. (dashed lines in Fig. 9b), particularly for piperazine. This deviation may be attributed to experimental error, given that the piperazine partial pressure approaches the detection limit of the instrument used (i.e., 1 ppm), while calibration ranges often exceed 1 ppm. The model amine volatility accuracy is difficult to guarantee when the partial pressures of AMP and PZ are below 10 Pa, primarily due to a lack of reliable low pressure amine volatility data. This should be taken into consideration when utilizing the model.

4. Conclusions

This study developed a comprehensive, open-access, thermody-namically consistent, and validated vapour-liquid equilibrium (VLE) model for the absorption of CO$_2$ into aqueous solutions of piperazine (PZ) activated 2-amino-2-methyl-1-propanol (AMP), on the simulation platform Aspen Plus. It solved a two-decade old problem of inconsistent specification of PZ, and thus AMP/PZ, thermodynamic models on Aspen Plus and lays the foundation for robust process modelling of AMP/PZ-based CO$_2$ capture systems.

The significance of this model lies in its innovative approach to
handle the zwitterion $\text{PZH}^+\text{CO}_2$. Overcoming a major obstacle in achieving a thermodynamically consistent PZ model, the key challenge has been the inability to specify the $\text{PZH}^+\text{CO}_2$ dipolar ion as a zwitterion in the symmetric Aspen Plus ELECNRTL model. A workaround was implemented by incorporating the unsymmetric Electrolyte NRTL activity coefficient model to the methods list, enabling the specification of the $\text{PZH}^+\text{CO}_2$ as an actual zwitterion without charge, contrary to previous model formulations. This approach facilitates the regression of $\text{PZH}^+\text{CO}_2$/molecule and $\text{PZH}^+\text{CO}_2$/electrolyte interaction parameters, particularly crucial at higher CO$_2$ loadings as often found in real CO$_2$ capture processes.

The model utilised the gamma-phi formulation, integrating the electrolyte NRTL model to describe the activity coefficient in the electrolyte system and the Soave-Redlich-Kwong equation of state for gas fugacity. To ensure broad applicability, efforts were made to include a wide range of relevant data sets following a systematic data screening process. To ensure broad applicability, efforts were made to include a range of 0.46 to 23.1, and a CO$_2$ loading range of 0.04 to 1.07 mol CO$_2$/mol amine, representative of values expected in real capture processes.

The excellent agreement between the experimental and predicted VLE data demonstrates the viability of the proposed thermodynamic model to represent the equilibrium systems. The average absolute relative deviation (AARD) values in estimating CO$_2$ partial pressure are 16.6 % for PZ ternary system, 18.9 % for AMP ternary system and 22.3 % for AMP-PZ quaternary system. The AARD values in estimating heat of CO$_2$ absorption are 7.7 % for PZ ternary system, 6.5 % for AMP ternary system and 6.3 % for AMP-PZ quaternary system. The model ensures broad applicability covering a temperature range of 20°C to 160°C, an amine concentration range of 30 wt% to 50 wt%, an AMP/PZ mole ratio range of 0.46 to 23.1, and a CO$_2$ loading range of 0.04 to 1.07 mol CO$_2$/mol amine, representative of values expected in real capture processes.

CRediT authorship contribution statement

Ningtong Yi: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Laura Herraz: Writing – review & editing, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Mengxiang Fang: Supervision. Susana García: Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing. Mijdert van der Spek: Writing – review & editing, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

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

We have made the model available open access on GitHub and have added all data as supplementary files.

Acknowledgements

This research was part of the SCOPE Project, funded through the ACT programme (Accelerating CCS Technologies). ACT 3 Project No 327341 with financial contribution from the Research Council of Norway (NO), RVO (NL), BEIS (UK), FZJ/PTJ (DE), DoE (USA) and Department of Science and Technology (India); www.scope-act.org.). NY gratefully acknowledges financial support from the China Scholarship Council (202006320308) for his stay at the Research Centre for Carbon Solutions at Heriot-Watt University.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jseppur.2024.127924.

References

[7] CESAR, 2011. EU-Project, CO2 Enhanced Separation and Recovery (CESAR). Integrated research project partially funded by the European commission under the 7th frame work program, Grant agreement number 213569, (nd). http://www.cocesar.eu


