Solubility of Carbon Dioxide in Aqueous Blends of Piperazine and N-Methyldiethanolamine

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Abstract
In the present work, new experimental data are reported on the equilibrium solubility of carbon dioxide into aqueous mixtures of N-methyldiethanolamine (MDEA) and piperazine (PZ). The experimental results are generally well in line with existing experimental data. Also, the newly obtained and existing experimental VLE data on this system have been correlated with the use of an Electrolyte Equation of State. It was found that the thermodynamic model derived was able to describe the CO$_2$-H$_2$O-PZ-MDEA system reasonably well over a wide range of conditions.

Keywords: CO$_2$, solubility, equilibrium, piperazine, MDEA, equation of state

Introduction
The removal of carbon dioxide from process gas streams is frequently carried out with an absorption / desorption technology, using (aqueous) solutions of (alkanol)amines as reactive solvent. Nowadays, it is common to add (small amounts) of ‘promotors’ to aqueous solutions of (alkanol)amines, such as piperazine (PZ) in aqueous N-methyldiethanolamine (MDEA). The basic principle behind this development is to enhance the rate of absorption via the relatively high rate of reaction of PZ with CO$_2$, while maintaining the low heat of regeneration in the stripper section, stemming from the relatively low heat of reaction of MDEA with CO$_2$. Requirements for an optimal design and operation of both absorber and stripper are detailed information on the mass transfer characteristics, the kinetics of the reactant(s) with CO$_2$, and detailed knowledge on the thermodynamics of the solvents.
Therefore, the present paper presents experimental data on the solubility of carbon dioxide into aqueous solutions of MDEA blended with PZ, which are complementary to the data sets already available in literature [2,10,14,15,19]. Next, the total set of experimental data, originating from this work and literature, are used to develop a thermodynamic model based on the electrolyte equation of state (EoS), as originally introduced by Fürst & Renon [6]. The application of this EoS based model is a relatively new approach for describing acid gas solubilities in aqueous (alkanol)amine systems. One of the major advantages is the use of identical equations for describing both the liquid and the gas phase, as – among others – pointed out by Solbraa [16].

Experimental
The experimental setups and procedures are almost identical to the ones applied in the preceding work of Derks et al. [5] on the ternary system CO$_2$-PZ-H$_2$O, and will therefore not be explained in detail here. One modification has been made to the experimental setups: both a conductivity meter and a pH electrode have been included in the system by means of a sampling loop in the reactor part, in order to obtain additional information on the speciation of the liquid phase.
As in the previous study, experimental data have been obtained using two different setups/modes of operation, depending on the desired CO$_2$ equilibrium partial pressure. Solubility data with carbon dioxide partial pressures lower than ca. 10 kPa were obtained using the continuously operated setup, whereas a batchwise type of operation was applied for experiments targeted at CO$_2$ equilibrium partial pressures ranging from 10 to about 100 kPa.
Electrolyte Equation of State

General
As mentioned in the introduction, the Electrolyte EoS will be applied to describe the CO\(_2\) solubility into aqueous solutions of piperazine and MDEA. In this EoS approach, the system’s non-ideality is given as the sum of four different molecular and ionic contributions to the reduced Helmholtz free energy \(A^R\), as given in Equation 1:

\[
\frac{A - A^G}{RT} = \frac{A^R}{RT} = \frac{A^R}{RT} + \frac{A^R}{RT} + \frac{A^R}{RT} + \frac{A^R}{RT}
\]  
\text{Eq 1}

Governing equations for the molecular interactions, which include both repulsive forces (RF) and short range interactions (SR1), and the ionic (short range, SR2, and long range, LR) contributions, are listed in the previous work [5]. For the present study, the model from the previous work, which was used to successfully describe the CO\(_2\) solubility in aqueous piperazine solutions, was extended to include the tertiary alkanolamine MDEA. Basically, the EoS model for the quaternary MDEA-PZ-H\(_2\)O-CO\(_2\) system can be represented as a tree structure consisting of the subsystems involved, as illustrated in Figure 1.

![Diagram of the equilibrium model](image)

Figure 1. Schematic buildup of the equilibrium model.

As one can see from Figure 1, the final (quaternary) model requires (sets of) parameters which are to be determined from the various subsystems present in the tree structure. Furthermore, it is obvious that many parameters necessary for the final model fit, are also part of the ternary (reactive) system PZ-CO\(_2\)-H\(_2\)O which has been studied by Derks et al. previously [5]. For information on these sets of parameters (marked with § in Figure 1) and their respective values is therefore referred to [5].

\textit{MDEA-CO}_2\textit{-H}_2\textit{O}

The majority of the remaining, unknown, parameters (marked with # in Figure 1) are a part of the second ternary system, consisting of MDEA, carbon dioxide and water. As in the previous study, the molecular pure component and binary interaction parameters were determined by fitting them to experimental (VLE and/or freezing point depression) data, with the exception of the MDEA-CO\(_2\) interaction. Values and experimental data sources are listed in Table 1, along with the MDEA (molecular) and MDEAH\(^+\) (ionic) diameters. MDEA’s critical constants were taken from Chunxi et al. [4].

With respect to the implementation of the model describing the ternary MDEA-CO\(_2\)-H\(_2\)O system – and the subsequent regression of the required ionic interaction parameters – the following remarks should be made:
- The presence of both the H\(_3\)O\(^+\) and the CO\(_3\)\(^{2-}\) ion has not been taken into account, because their concentrations are negligibly low;

2
Interactions between ions of equal charge, as well as between anions and molecules, have been neglected;
- The reference state for all species in solution, with the exception of water, is infinite dilution in water, and the corresponding equilibrium constant for the MDEA protonation reaction has been (after conversion to the mole fraction scale) taken from Pérez-Salado Kamps & Maurer [13].
- The database used in the regression of the ionic interaction parameters on the MDEA-CO₂-H₂O system was identical to the one used by Huttenhuis et al. in their work [9].

Table 1. Parameters used in the modelling of the MDEA-CO₂-H₂O equilibrium.

<table>
<thead>
<tr>
<th>Single component parameters</th>
<th>Binary systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDEA</td>
<td>H₂O – MDEA</td>
</tr>
<tr>
<td>p₁</td>
<td>0.5244</td>
</tr>
<tr>
<td>p₂</td>
<td>-1.1529</td>
</tr>
<tr>
<td>p₃</td>
<td>0</td>
</tr>
<tr>
<td>source</td>
<td>[12]</td>
</tr>
<tr>
<td>Molecular diameter [-10⁻¹⁰ m]</td>
<td>4.50</td>
</tr>
<tr>
<td>Source</td>
<td>[4,5,16]</td>
</tr>
</tbody>
</table>

MDEAH⁺ – MDEA – CO₂

<table>
<thead>
<tr>
<th>Ionic diameter [-10⁻¹⁰ m]</th>
<th>Interaction parameter kₘᵢₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.50</td>
</tr>
<tr>
<td>Source</td>
<td>[4,16]</td>
</tr>
</tbody>
</table>

The EoS-model was able to correlate the experimental data used in the regression with an average absolute deviation of 26 %, which is comparable to other studies, which applied the Electrolyte EoS model to describe CO₂ solubilities in aqueous MDEA solutions. The obtained values for the ionic interaction parameters are listed in Table 2 and a graphical comparison between the experimental solubilities included in the database and model prediction is given in Figure 2.

Table 2. Ionic interaction parameters for the MDEA-CO₂-H₂O system.

<table>
<thead>
<tr>
<th>Wᵢⱼ</th>
<th>10⁻⁴ m³ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDEAH⁺ - H₂O</td>
<td>0.1189</td>
</tr>
<tr>
<td>MDEAH⁺ - MDEA</td>
<td>0.0756</td>
</tr>
<tr>
<td>MDEAH⁺ - CO₂</td>
<td>-0.0705</td>
</tr>
<tr>
<td>MDEAH⁺ - HCO₃⁻</td>
<td>-0.1473</td>
</tr>
</tbody>
</table>

The extension to the final model containing both piperazine and MDEA will be discussed in the ‘Results’ section, after the newly obtained experimental data have been presented.

Results

Experimental results

Before the equilibrium experiments into aqueous blends of piperazine and MDEA were carried out, the experimental setup was experimentally validated by measuring the CO₂ solubility in aqueous solutions of 2.0 kmol MDEA at 313 K. Results are shown graphically in Figure 3.
From Figure 3, it can be concluded that the data from the setup are in good agreement with literature data, and that the addition of the sampling loop has no influence on the outcome of the experiments. Next, CO₂ solubility experiments have been carried out with aqueous solutions containing 2.8 M MDEA and 0.7 M PZ, at temperatures of 30 and 50 °C. These conditions were chosen to compare and extend one of the equilibrium dataseries of Liu et al. [10], who report CO₂ partial pressures ranging from about 15 to 450 kPa at these conditions. The newly obtained experimental data are shown in Figures 4a&b. A comparison to the data reported by Liu et al. [10] is given in Figure 4b.

From Figures 4a&b, it can be concluded that the experimental data at 50 °C are well in line with those of Liu et al. [10]. However, there seems to be a discrepancy between the two data sets at 30 °C. Secondly, the log-log plot (Figure 4a) shows a linear relation between the partial pressure and the loading for the experimental data taken at low CO₂ partial pressures, which is expected at low loadings (see e.g. [4]) and thus proves that they are internally consistent.

**Modelling results**

Next, an attempt was made to regress the remaining (quaternary) ionic parameters to the available experimental CO₂ solubilities in aqueous blends of piperazine and MDEA. Also the binary interaction parameter $k_{\text{mix}}$ describing the PZ-MDEA interaction was adjusted, since the model turned out to be very sensitive to its value. The results of the regression are shown graphically in the parity plot given in Figure 5.
Figure 5. Parity plot for the PZ-MDEA-CO$_2$-H$_2$O system.

Now, the experimental speciation data of a partially loaded PZ-MDEA solution, obtained via NMR spectrometry, as reported by Bishnoi & Rochelle [2], are compared to the model prediction in Table 6.

Table 6. Comparison between experimental speciation data and model prediction, in a 1M PZ, 3 M MDEA solution with a 0.52 loading at 298K.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>PZ(COO$^-$)$_2$ / (MDEA + MDEAH$^+$)</td>
<td>0.12</td>
<td>0.21</td>
</tr>
<tr>
<td>PZ(COO$^-$)$_2$ / (PZCOO$^-$ + HPZCOO$^-$)</td>
<td>0.63</td>
<td>2.7</td>
</tr>
<tr>
<td>(PZCOO$^-$ + HPZCOO$^-$) / (PZ + PZH$^+$)</td>
<td>4.1</td>
<td>1.9</td>
</tr>
</tbody>
</table>

It can be concluded from Figure 5, that the present model is able to nicely correlate all experimental solubility data, with an average absolute deviation of less than 25%. However, the model was not able to predict the experimentally obtained speciation results of the single available speciation data point, as shown by Table 6.

**Conclusions**

The present study reports experimental data on the solubility of CO$_2$ in aqueous solutions of 2.8 M MDEA and 0.7 M piperazine at 30 and 50 ºC. After validating the experimental setup and procedure with the well known MDEA-CO$_2$ system, new experimental data were measured. The obtained experimental data were found to be internally consistent and well in line with the results of Liu et al. [10] at 50 ºC. However, VLE data taken at 30 ºC were found to deviate from the values reported by Liu et al.. The thermodynamic model used, based on the Electrolye Equation of State, was able to predict the experimental data over a wide range of conditions, despite various simplifications and assumptions made in the implementation of the model.

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Reference list


