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The acid gas solubility in Aqueous N-Methyldiethanolamine
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Appendix A

Solubility of \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) in Aqueous Solutions of N-methyldiethanolamine

Abstract

Alkanolamines are used in the industry to remove acid gases such as \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) from natural and industrial gas streams. The acid components react with the basic alkanolamine via an exothermic, reversible reaction in a gas/liquid absorber. The composition of these amine solutions is continuously changed to optimise the (selective) removal of the several acid components. For the design of gas treating equipment mass transfer, reaction kinetics and solubility data of acid gases in aqueous alkanolamine solutions are required. In this appendix new solubility data of \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) in aqueous MDEA at different conditions encountered in modern gas treating facilities are presented. The experimental pressures are varied from 6.9 to 69 bar (methane is used as make-up gas) and temperatures from 283 to 298 K. The measured values are evaluated and correlated with an electrolyte equation of state (E-EOS) as originally proposed by Fürst and Renon [Fürst, W., Renon, H., 1993. Representation of Excess Properties of Electrolyte Solutions Using a New Equation of State. AIChE J., 39 (2), pp. 335.]. The application of an equation of state for the
prediction of solubilities for reactive, ionic systems is a new development in this field.

A.1 Introduction

Acid gases such as CO₂, H₂S and other sulphuric components are often present in natural and industrial gases. They may have to be removed (selectively) from these gas streams for operational, economical or environmental reasons. A commonly used process is absorption in aqueous alkanolamine solvents. Here the acidic components react with the alkanolamine in a gas/liquid contactor. The acidic components are then removed from the solvent in a regenerator, usually at a low pressure and/or high temperature. For the design of such processes reliable solubility data are indispensable. In this appendix newly obtained solubility data of CO₂ and H₂S in aqueous MDEA solutions will be presented.

The ability of an alkanolamine solution to remove acidic gases is determined by the acid gas solubility, the reaction rate and the mass transfer properties. This study considers the solubility of CO₂ and H₂S in aqueous MDEA at temperatures of 283 and 298 K, acid gas partial pressures 0.05-1000 kPa and a total system pressure of 6.9-69 bar with methane as make-up gas. In literature usually only the partial pressure acid gas is specified and not the total system pressure, because experiments are carried out at low pressure. In this thesis the influence of the total system pressure (with methane as make-up gas) on the acid gas solubility is also studied. This system pressure is an important parameter, because there usually is a substantial difference in system pressure between an industrial absorber (70-100 bar) and a regenerator (2-3 bar). So if the system pressure influences the acid gas solubility, the low pressure experimental solubility data cannot be used in the high pressure absorber. Also measurements of the acid gas solubilities at low temperatures of 283 and 298 K are scarce. The new solubility data are used to
develop an electrolyte equation of state (E-EOS) that can be used to predict the equilibria for these treating processes.

### A.2 Experimental

For all experiments demineralised water was used. N-methyldiethanolamine (purity > 99%) was supplied by Acros; hydrogen sulfide (purity > 99.6%), carbon dioxide (purity > 99.7%) and methane (purity > 99.5%) were supplied by Hoekloos.

For the determination of the gas solubility data a stirred, 1 litre, Büchi reactor was used. The reactor system is shown in Figure 1. From this reactor both gas and liquid samples are withdrawn and analysed.

![Figure 1 Reactor of the experimental set-up](image-url)
The experimental set-up consists of three parts:

- A gas supply system: From this section the gases are supplied to the reactor batchwise or continuously;
- A reactor section: this section contains a heating bath, a high intensity stirrer (stirrer speed > 1000 rpm) and a liquid sampling system;
- Gas outlet system: this system contains a gas analyser, off-gas treatment and a vacuum pump.

With this set-up it is possible to measure the total $\text{H}_2\text{S}$ and $\text{CO}_2$ concentration in both the gas and the liquid independently. As it is also possible to determine the total amount of added $\text{H}_2\text{S}$ or $\text{CO}_2$ added to the reactor, a mass balance check can be made to determine the accuracy of the experiments.

During an experiment the reactor is filled with approximately 0.5 litre of aqueous amine solution and evacuated until the vapor pressure of the solution is reached. A predefined amount of acid gas is sent to the reactor. The partial pressure of methane is increased to the required total system pressure. Under intensive stirring of the reactor, a small sweep stream of methane (approximately 200 Nml min$^{-1}$) is passed through the reactor and the outlet is analysed using a gas chromatograph. When equilibrium is reached the reactor is blocked, a small liquid sample is taken, and the amount of acid gas is analysed with a suitable liquid titration technique. The $\text{CO}_2$ content is measured with an automated organic acid-base titration and the $\text{H}_2\text{S}$ content is measured with an automated iodometric back titration with thiosulfate.

The liquid sample containing $\text{CO}_2$ is added to a vessel containing boiling sulfuric acid. The high acidity and high temperature and addition of a small nitrogen purge flow cause that the $\text{CO}_2$ to be completely stripped from the sample. A reflux cooler is used to prevent contamination of $\text{CO}_2$ with sulfuric acid and water. The $\text{CO}_2$ is sent to a second vessel containing MEA and an organic solvent (DMF). In this vessel the $\text{CO}_2$ is captured by the MEA and subsequently the pH falls. The total amount of $\text{CO}_2$ is determined by keeping the MEA solution at its original pH with a
Appendix A

strong base (TBAH). For the determination of the amount H$_2$S in the liquid sample, an excess amount of iodine is added. The excess iodine is determined by a sodium thiosulphate titration. Both titration methods are calibrated extensively with samples containing a known amounts of Na$_2$CO$_3$ and Na$_2$S.

When the acid gas partial pressure and liquid loading are determined a consecutive experiment at a higher liquid loading is started. The reactor is depressurized and additional amount of acid gas from the gas supply vessel is added. For each experiment it is verified that the amount of acid gas removed during the depressurizing phase is negligible compared to the total amount of acid gas absorbed by the alkanolamine solution.

A.3 Results

A.3.1 Experiments with CO$_2$

To establish the accuracy of the experimental technique, set-up and procedures, some validation experiments have been carried out and the results are compared with CO$_2$ solubility data available in the literature. The validation experiments have been carried out with a 20 wt.% aqueous diethanolamine (DEA) solution at 323 K, because at these conditions a large amount of experimental data are available. The experimental results are compared to data of Haji-Sulaiman [7], [8], Bullin [4] and Lee [16]. The comparison is presented in Figure 2.
Figure 2  Validation experiments for the solubility of CO₂ in 20 wt.% DEA at 323 K

Figure 2 shows some scatter in literature data of the different authors. The newly obtained values are in good agreement with the other data. At high liquid loadings (> 0.4 mole/mole) the measured CO₂ partial pressure is lower than measured by Haji-Sulaiman [8] and Lee [16]. However, most of the experiments presented in the present study were carried out at lower liquid loadings. The data of Lee [16] show substantial deviations in the low loading range. From Figure 2, it can be concluded that our experimental set-up is able to reproduce existing results of the CO₂-DEA-H₂O system.

New solubility data of CO₂ were obtained for two different amine solutions (35 and 50 wt.% MDEA) at two temperatures (283 and 298 K) and three system pressures (6.9, 34.5 and 69 bar) with methane as make-up gas. The data are given in Table 1 (35 wt.% MDEA) and Table 2 (50 wt. % MDEA).
<table>
<thead>
<tr>
<th>P [bar]</th>
<th>α [mole/mole]</th>
<th>P$_{CO_2}$ [kPa]</th>
<th>P [bar]</th>
<th>α [mole/mole]</th>
<th>P$_{CO_2}$ [kPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.9</td>
<td>0.048</td>
<td>0.054</td>
<td>6.9</td>
<td>0.048</td>
<td>0.170</td>
</tr>
<tr>
<td></td>
<td>0.143</td>
<td>0.314</td>
<td></td>
<td>0.048</td>
<td>0.168</td>
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<tr>
<td></td>
<td>0.276</td>
<td>1.000</td>
<td></td>
<td>0.143</td>
<td>1.001</td>
</tr>
<tr>
<td></td>
<td>0.325</td>
<td>1.324</td>
<td></td>
<td>0.270</td>
<td>3.037</td>
</tr>
<tr>
<td>34.5</td>
<td>0.143</td>
<td>0.385</td>
<td>34.5</td>
<td>0.048</td>
<td>0.198</td>
</tr>
<tr>
<td></td>
<td>0.275</td>
<td>1.237</td>
<td></td>
<td>0.048</td>
<td>0.195</td>
</tr>
<tr>
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<td>0.319</td>
<td>1.658</td>
<td></td>
<td>0.143</td>
<td>1.204</td>
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<tr>
<td>69.0</td>
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<td>69.0</td>
<td>0.047</td>
<td>0.245</td>
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<td></td>
<td>0.047</td>
<td>0.235</td>
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<tr>
<td></td>
<td>0.320</td>
<td>2.141</td>
<td></td>
<td>0.143</td>
<td>1.340</td>
</tr>
</tbody>
</table>

Table 1 Experimental solubility data of CO$_2$ in an aqueous solution of 35 wt.% MDEA
### Table 2  
**Experimental solubility data of CO$_2$ in an aqueous solution of 50 wt.% MDEA**

<table>
<thead>
<tr>
<th>$T = 283$ K</th>
<th>$P$ [bar]</th>
<th>$\alpha$ [mole/mole]</th>
<th>$P_{CO2}$ [kPa]</th>
<th>$T = 298$ K</th>
<th>$P$ [bar]</th>
<th>$\alpha$ [mole/mole]</th>
<th>$P_{CO2}$ [kPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.9</td>
<td>0.144</td>
<td>0.671</td>
<td></td>
<td>6.9</td>
<td>0.047</td>
<td>0.441</td>
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<tr>
<td></td>
<td>0.270</td>
<td>1.754</td>
<td></td>
<td></td>
<td>0.111</td>
<td>2.379</td>
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<tr>
<td></td>
<td>0.428</td>
<td>3.848</td>
<td></td>
<td></td>
<td>0.139</td>
<td>2.143</td>
<td></td>
</tr>
<tr>
<td>34.5</td>
<td>0.150</td>
<td>0.781</td>
<td></td>
<td></td>
<td>0.238</td>
<td>7.206</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.273</td>
<td>2.103</td>
<td></td>
<td></td>
<td>0.265</td>
<td>5.492</td>
<td></td>
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<tr>
<td></td>
<td>0.428</td>
<td>5.036</td>
<td></td>
<td></td>
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<td>7.773</td>
<td></td>
</tr>
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<td></td>
<td></td>
<td>0.424</td>
<td>37.07</td>
<td></td>
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<td></td>
<td></td>
<td>0.551</td>
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<td></td>
<td>0.409</td>
<td>5.887</td>
<td></td>
<td></td>
<td>0.700</td>
<td>212.6</td>
<td></td>
</tr>
<tr>
<td>34.5</td>
<td>0.048</td>
<td>0.487</td>
<td></td>
<td></td>
<td>0.141</td>
<td>2.698</td>
<td></td>
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<tr>
<td></td>
<td>0.272</td>
<td>7.315</td>
<td></td>
<td></td>
<td>0.887</td>
<td>180.7</td>
<td></td>
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<tr>
<td></td>
<td>1.105</td>
<td>351.4</td>
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<td></td>
<td>0.936</td>
<td>986.8</td>
<td></td>
</tr>
<tr>
<td>69.0</td>
<td>0.047</td>
<td>0.570</td>
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<td></td>
<td>0.128</td>
<td>3.092</td>
<td></td>
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<tr>
<td></td>
<td>0.272</td>
<td>8.720</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

**A.3.2 Experiments with H$_2$S**

The first validation runs were carried out with 50 wt.% MDEA at 313 K and 3.5 bar (with nitrogen as make-up gas). The results of these experiments are compared with literature data from Huang [9], Rogers [23] and Jou [11] in Figure 3.
Figure 3  Validation experiments for the solubility of $\text{H}_2\text{S}$ in 50 wt.% MDEA at 313 K

The literature data from Jou [11] differ significantly from the other sources and our new data. They also show a different trend in the low loading range. For this reason, the accuracy of these data is questionable. A possible explanation of the differences is the influence of contaminations (primary and/or secondary amines) on the solubility of aqueous MDEA. However, if this is the reason, the effect should be vanished at higher liquid loadings and this is not the case.

New solubility of $\text{H}_2\text{S}$ were obtained for two different blends (35 and 50 wt.% MDEA) at two temperatures (283 and 298 K) and three pressure (6.9, 34.5 and 69 bar). The experimental data are given in Table 3 (35 wt.% MDEA) and Table 4 (50 wt. % MDEA).
Table 3  Experimental solubility data of H₂S in an aqueous solution of 35 wt.% MDEA

Table 4  Experimental solubility data of H₂S in an aqueous solution of 50 wt.% MDEA

A.3.3 Discussion

From the CO₂ and H₂S data the following observations can be made. The acid gas partial pressure increases (solubility decreases) with:

- increasing liquid loading (and constant temperature, pressure and amine concentration);
- increasing temperature (and constant liquid loading, pressure and amine concentration);
- increasing amine concentration (and constant temperature, pressure and liquid loading).
These observations agree with data presented by other authors in this field.

It can also be concluded that the solubility of H₂S and/or CO₂ is substantially affected by the methane partial pressure. Increasing the methane partial pressure results in a pronounced decrease of the solubility of the acidic component. This is line with the results of the experiments carried out by Addicks [1]. He measured the solubility of CO₂ and CH₄ in aqueous MDEA at pressures up to 200 bar. At this time it is not known whether the changing acid gas solubility is caused by the increased system pressure or by the presence of methane in the system.

A.4 Validation of the model

A.4.1 Model description

The experimental results are compared with an electrolyte equation of state (E-EOS), originally proposed by Fürst and Renon [6]. In this model the same equations are used for both the liquid and vapor. The model can be extrapolated and the speciation of the components in the liquid can be calculated. Moreover the solubility of physically dissolved hydrocarbons (such as methane) can be calculated. This is important for the design of high pressure gas treating equipment and for mass transfer calculations.

The model used in the present study was originally developed by Solbraa [26]. Details of the model can be found in his work. His electrolyte equation of state is derived from an expression of the Helmholtz energy (Equation 1) with non-electrolyte parts (RF and SR1) and an electrolyte parts (SR2, LR and BORN).

\[
\frac{A}{RT} = \frac{A}{RT}_{RF} + \frac{A}{RT}_{SR1} + \frac{A}{RT}_{SR2} + \frac{A}{RT}_{LR} + \frac{A}{RT}_{BORN}
\]

Equation 1
The first two terms describe repulsive forces (RF) and attractive short range interactions (SR1) in the molecular part of the equation of state. This model was based on a cubic equation of state (Schwarzentuber’s [25] modification of the Redlich-Kwong EOS with a Huron-Vidal mixing rule). The important parameters of this part of the model are the critical properties, Schwarzentuber parameters and molecular (Huron-Vidal) interaction parameters. These molecular interaction parameters are determined by fitting experimental molecular binary data to the EOS model.

To account for ions, three ionic terms are included: a short-range ionic term (SR2), a long range ionic term (LR) and a Born term. The most important parameters in SR2 are the molecular and ionic diameter and the ionic binary interaction parameters. These ionic interaction parameters are determined by fitting the E-EOS with experimental solubility data for the system CO₂-MDEA-H₂O. In this thesis only the cation-molecules and cation-anion interactions are taken into account. The most important parameter of the LR term is the dielectric constant of the solvent.

A Born term has been added to correct the standard states of ions. This term gives the solvation energy of an ion in a dielectric medium, relative to vacuum. The Born term is important for modelling both liquid and vapor with an E-EOS, because this parameter causes the ions to stay mainly in the liquid. Fürst and Renon [6] did not use the Born term in their original publication, but it was added in a later paper on LLE in electrolyte systems (Zuo [30]). Solbraa [26] developed his E-EOS for a CO₂-MDEA-water system. The model was also validated by Solbraa for a high pressure system (100-200 bar) of CO₂-MDEA-water-methane. In this E-EOS the following parameters have to be obtained:

- Molecular and ionic pure component parameters, such as critical data and polar parameters. These data are independent of the model and can be found in literature;
- Binary and ionic interactions parameters. These parameters are part of the model and have to be determined via fitting procedures or from estimations.
The following chemical reactions occur in an aqueous MDEA solution when CO$_2$ and H$_2$S are present:

\[
\begin{align*}
CO_2 + H_2O & \rightleftharpoons HCO_3^- + H^+ \\
HCO_3^- & \rightleftharpoons CO_3^{2-} + H^+ \\
H_2O & \rightleftharpoons OH^- + H^+ \\
RR_2'NH^+ & \rightleftharpoons RR_2'N + H^+ \\
H_2S & \rightleftharpoons HS^- + H^+ \\
HS^- & \rightleftharpoons S^{2-} + H^+
\end{align*}
\]

Here $R$ corresponds to a methyl group and $R'$ to an ethanol group.

**A.4.2 Validation of the Solbraa model**

The results of the CO$_2$ experiments in this appendix have been compared with the E-EOS of Solbraa [26]. A large systematic deviation is observed between the experimental results and the predictions of the E-EOS. The E-EOS always underestimates the CO$_2$ partial pressure. The AAD and BIAS deviations of these experiments are both 40%.

\[
\begin{align*}
AAD &= \frac{1}{n} \sum_{i=1}^{n} \left| \frac{y_{i,exp} - y_{i,calc}}{y_{i,exp}} \right| \times 100\% \\
BIAS &= \frac{1}{n} \sum_{i=1}^{n} \frac{y_{i,exp} - y_{i,calc}}{y_{i,exp}} \times 100\%
\end{align*}
\]

In the following sections, the reason for this difference is discussed. In Figure 4 the influence of the methane partial pressure can be seen for both the experiments and the E-EOS.
From Figure 4 it can be concluded that the slopes of both graphs (influence of methane partial pressure) are almost similar, a proportional relation exists between total system pressure and the CO$_2$ partial pressure. However, the intercept with the y-axis is much higher for the experiments than calculated by the model. The results at a system pressure of zero bar can be compared with results at zero partial pressure of methane. It appears that the large deviations between model and experiments are not caused by the input parameters and properties of methane in the model, but by the parameters used for the ternary system CO$_2$-MDEA-water. For this reason the determination of the ionic parameters of the CO$_2$-MDEA-water system as carried out by Solbraa [26] was critically reviewed. The relevant ionic parameters in this system were fitted against experimental data available in literature.
A.4.3 Influence of experimental database

Figure 5 shows an overview of available CO\(_2\) solubility data in 50 wt.% MDEA at 313 K.

![Figure 5: Literature data of the CO\(_2\)-MDEA-H\(_2\)O system at 313 K and 50 wt.% MDEA](image)

The figure shows that a lot of scatter exists in the literature data. The results of the present experiments are in line with a large group of literature sources. However, the data of Jou [10], [11] give CO\(_2\) partial pressures, which are substantially lower than the other sources. This observation has also been seen at other conditions; data by Jou show a lower CO\(_2\) partial pressure (higher CO\(_2\) solubility), which is also seen in Figure 3. An explanation of this under-prediction of the acid gas partial pressure might be that the MDEA used by Jou contained some impurities, such as primary and secondary amines. These can have a large influence on the measured...
acid gas solubility. However, the influence of amine impurities on the solubility should vanish at higher liquid loadings and that is not seen in Figure 5, so the real reason is not understood at this stage. The database used by Solbraa [26] for the determination of the ionic interaction parameters of the CO₂-MDEA-water system was largely (approximately 35%) based on data by Jou; so a critical review of available data has been carried out and new data have been included in the database. The following modifications to the original database of Solbraa [26] were incorporated:

- All data of Jou [10], [11] have been omitted. As mentioned before these data showed a systematically under-prediction of the acid gas partial pressure;
- All data of Bhairi [3] have been omitted. These data showed a strange behaviour at low loadings (no straight line of log-log graph of partial pressure versus liquid loading);
- All data of Chakma [5] have been omitted, because of assumptions made in the experimental procedure. The experiments of Chakma were carried out at high temperatures (373-473 K) and no corrections for change in liquid density and water evaporation were made. Also possible degradation of MDEA at these high temperatures was not taken into account;
- Data of Rho [22] measured with 5 wt.% and 75 wt.% MDEA have been omitted. These results cannot be validated and model simplifications, such as neglecting CO₃²⁻ and OH⁻ concentrations are not valid under these conditions;
- Recent data of Kamps [13], Rogers [23] and Huang [9] were included. Low loading data of Rogers [23] at 50 wt.% MDEA and 313 K were not used, because these data were measured at very low loadings (< 0.004 mole CO₂ / mole amine) and at these conditions the model assumption that concentration of OH⁻-ions may be neglected is not correct.

An analysis of the quality of the solubility data of CO₂ and H₂S in MDEA available in open literature is presented by Weiland [28]. In this work the experimental solubility
data (up to 1992) are compared with the Deshmukh-Mather thermodynamic model. When experimental data deviate more than a factor 3 from the model result, the data are qualified as not good. Compared with the database used in our work Weiland concluded that 25% of the data of Jou [10] did not fulfill the criterium. In contrast with this work, the data of Chakma [5] and Bhairi [3] were qualified as good.

Incorporation of the above described modifications has resulted in the experimental database in Table 5.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>$C_{MDEA}$ [wt.%]</th>
<th>Temperature [K]</th>
<th>Liquid loading [mole CO$_2$/mole amine]</th>
<th>Data points [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lemoine [17]</td>
<td>23.6</td>
<td>298</td>
<td>0.02-0.26</td>
<td>13</td>
</tr>
<tr>
<td>Austgen [2]</td>
<td>23.4</td>
<td>313</td>
<td>0.006-0.65</td>
<td>14</td>
</tr>
<tr>
<td>Kuranov [15]</td>
<td>19.2, 18.8, 32.1</td>
<td>313, 313, 313,333,373,413</td>
<td>1.56-2.46, 0.36-2.62, 0.41-4.46</td>
<td>9, 32, 40</td>
</tr>
<tr>
<td>Rho [22]</td>
<td>20.5, 50</td>
<td>323,348,373,323,348,373</td>
<td>0.026-0.848, 0.0087-0.385</td>
<td>32, 26</td>
</tr>
<tr>
<td>Kamps [13]</td>
<td>32.0, 48.8</td>
<td>313, 313,353,393</td>
<td>0.85-1.24, 0.12-1.15</td>
<td>5, 23</td>
</tr>
<tr>
<td>Huang [9]</td>
<td>23, 50</td>
<td>313,343,373,393,313,343,373</td>
<td>0.00334-1.34, 0.00119-1.16</td>
<td>29, 37</td>
</tr>
<tr>
<td>Rogers [23]</td>
<td>23, 23</td>
<td>313, 323</td>
<td>0.000591-.1177, 0.001-0.07</td>
<td>14, 6</td>
</tr>
</tbody>
</table>

Table 5  Literature references used for the fitting of the ionic parameters of the CO$_2$ MDEA-H$_2$O system

When the predictions of the original model of Solbraa [26] are compared with the experimental data in Table 5, the BIAS and AAD are found to be 19.8 % and 26.7
%. For this reason a new fit with the data base of Table 5 has been carried out to get values for the ionic interaction parameters of MDEA\(^+\)-MDEA, MDEA\(^+\)-H\(_2\)O, MDEA\(^+\)-CO\(_2\), and MDEA\(^+\)-HCO\(_3\)^-. 

### A.4.4 Influence of the MDEA dissociation constant (K\(_a\))

In an aqueous MDEA solution with CO\(_2\) the following chemical reactions will occur:

\[
\begin{align*}
2H_2O & \rightleftharpoons K_1 H_3O^+ + OH^- \\
2H_2O + CO_2 & \rightleftharpoons K_2 HCO_3^- + H_3O^+ \\
H_2O + HCO_3^- & \rightleftharpoons K_3 CO_3^{2-} + H_3O^+ \\
H_2O + MDEA^+ & \rightleftharpoons K_4 H_3O^+ + MDEA
\end{align*}
\]

The equilibrium constants (based on mole fractions) of these reactions can be correlated by the following equation:

\[
\ln K_4 = A + \frac{B}{T} + C\ln T \tag{Equation 2}
\]

The parameters for the equilibrium constants used by Solbraa [26] are given in Table 6.

<table>
<thead>
<tr>
<th>$K_\alpha$</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
<th>$T$ [K]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$</td>
<td>132.899</td>
<td>-13445.9</td>
<td>-22.4773</td>
<td>273-498</td>
<td>Posey [26]</td>
</tr>
<tr>
<td>$K_2$</td>
<td>231.465</td>
<td>-12092.1</td>
<td>-36.7816</td>
<td>273-498</td>
<td>Posey [26]</td>
</tr>
<tr>
<td>$K_3$</td>
<td>216.049</td>
<td>-12431.7</td>
<td>-35.4819</td>
<td>273-498</td>
<td>Posey [26]</td>
</tr>
<tr>
<td>$K_4$</td>
<td>-56.2</td>
<td>-4044.8</td>
<td>7.848</td>
<td>298-419</td>
<td>Posey [26]</td>
</tr>
</tbody>
</table>

Table 6  Parameters for calculation of the chemical equilibrium constants of the system CO\(_2\)-MDEA-H\(_2\)O

The formation of carbonate-ions is usually limited, so reaction $K_3$ is neglected. Also the formation of OH\(^-\) ions is neglected (reaction $K_1$); this assumption may not be
correct at very low liquid loadings. So, only reaction \( K_2 \) and \( K_4 \) are incorporated in the E-EOS. The most important reaction is the protonation of MDEA to MDEAH⁺. The fit of Posey [21] which was used by Solbraa [26] was based on experiments carried out by Schwabe [24], Kim [14] and Oscarson [19]. In Figure 6 the \( pK_a \) measured by different authors is given as function of temperature and compared with the fit of Posey [21]. For the fit of Posey a unit conversion from mole fraction to molality has been incorporated.

![Figure 6 pKa of MDEA as function of temperature](image)

The data measured by Schwabe [24], Kim [14], Oscarson [19], Littel [18] and Kamps [12] presented in Figure 6 are at a reference state of infinite dilution for MDEA. However, the data used in the work of Posey are based on a different reference state: that of pure MDEA. The following relation is applicable between the equilibrium constants at the two reference states of infinite dilution (\( K_{a1} \)) and pure MDEA (\( K_{a2} \)):

\[
\gamma_{MDEA}^{\infty} = \frac{K_{a2}}{K_{a1}}
\]

Equation 3
Here $\gamma^{*}_{\text{MDEA}}$ is called the normalized activity coefficient. A new fit was prepared using the literature data given in Figure 6, because in our model a reference state at infinite dilution is used for all components except water. Only the data of Littel [18], were not used, because these results were not in line with the other results. The fitted equation was of the same type as the equations given by Posey [21] (refer to Equation 2). The new fit results in the following fit parameters:

<table>
<thead>
<tr>
<th>$K_x$</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
<th>$T,[\text{K}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_d$</td>
<td>-77.262</td>
<td>-1116.5</td>
<td>10.06</td>
<td>278-423</td>
</tr>
</tbody>
</table>

*Table 7  New fit parameters for the calculation of the MDEA dissociation constant*

This equation is based on a reference state of infinite dilution. A conversion from the molality scale (experiments) to the mole fraction scale (fit equation) has been incorporated. Now the normalized activity coefficient as used by Posey can be calculated and compared with the activity coefficient as calculated by the E-EOS. It appears that these two activity coefficients do not match. At 313 K the two values match very well, but at higher and lower temperatures, the deviations increase to above 50 %. For this reason it was decided to use the new fit relation for the dissociation of MDEA as described in Table 7. This new relation is then used in the model with the reference state of infinite dilution. The new fit is shown in Figure 6. With this new relation for the dissociation of MDEA, new ionic interaction parameters of the system (CO$_2$-MDEA-H$_2$O) have been determined with the modified database of Table 5.

**A.4.5 Influence of the binary interaction parameters**

With the new ionic interaction parameters a comparison between the changed model results and the experimental data from Table 5 was carried out. The overall BIAS and AAD deviations were 1.2 % and 23.8 %. When the model results were compared it appeared that the fit with the higher concentration MDEA (50 wt.%) with literature data was not good at lower liquid loadings.
Appendix A

There was a significant under-prediction of the partial pressure CO$_2$ of the model. At lower MDEA concentrations the fit of the model gave satisfactory results. A comparison between model results and experimental data is presented for 50 wt.% MDEA (Figure 7) and 23 wt.% MDEA (Figure 8).

---

Figure 7  Model results compared with experimental data for 50 wt.% MDEA at 313 K
When the physical solubility (solubility without reaction) of CO₂ in the aqueous MDEA solution calculated by the model is compared with experimental results (using the CO₂ - N₂O analogy) the following graph was obtained.

*Figure 8  Model results compared with experimental data for 23 wt.% MDEA at 313 K*
Because CO₂ reacts with MDEA, its physical solubility cannot be measured directly and hence the CO₂ - N₂O analogy was used. This analogy is widely used in literature and proven to be reliable for MDEA concentrations up to approximately 30wt.%. In view of the similarities of the configuration, molecular volume and electronic structure N₂O is often used as a non reacting gas to estimate the physical properties of CO₂ (Versteeg [27]). With this analogy the physical solubility (the Henry constant $H$) for CO₂ in aq. MDEA has been calculated in the following way:

$$H_{CO_2,aq,MDEA} = \frac{H_{CO_2,water}}{H_{N_2O,water}} \cdot H_{N_2O,aq,MDEA}$$

* experiments of Pawlak [20] have been converted from N₂O to CO₂ solubility using N₂O-CO₂ analogy

Figure 9  Physical solubility of CO₂ in aqueous MDEA
From Figure 9 it can be seen that the estimation of the physical solubility in the E-EOS contradicts to the experimental results. The model predicts a maximum in solubility (minimum in $H$) as function of the MDEA concentration and the experiments show a minimum solubility. The maximum error is seen at approximately 50 wt.% MDEA. The physical solubility of CO$_2$ in MDEA is mainly determined by binary interaction parameters. Because no binary data are available for the system CO$_2$-MDEA, the interaction parameters were used as a fit parameter in the ternary system (CO$_2$-H$_2$O-MDEA). So the calculated fit parameter from this fit is probably in line with the data for the ternary ionic system, but does not agree with the data from the binary system. A new approach to obtain a better value for this interaction parameter has been proposed. The interaction parameters of the CO$_2$-MDEA system will be determined by fitting this value with the experimental data available of the N$_2$O solubility in aqueous MDEA and applying the N$_2$O-CO$_2$ analogy to these data. This new approach has been included in Chapter 3 of this thesis.

A.5 Conclusions and recommendations

In the present Appendix new solubility data of CO$_2$ and H$_2$S in aqueous MDEA are presented. Experiments have been carried out in a stirred reactor at elevated pressures up to 69 bar (with methane as make-up gas). From these experiments it is concluded that an increasing methane partial pressure results in a higher acid gas partial pressure.

The results of the CO$_2$ experiments are used to validate an electrolyte equation of state (E-EOS). The E-EOS developed by Solbraa [26] has been improved in the following aspects:

- The database used for the determination of ionic parameters for the CO$_2$-MDEA-H$_2$O has been reviewed and modified;
- The equation for calculation of the dissociation of MDEA has been modified. Instead of using the equation of Posey [21], which is based on a reference
state pure MDEA a new fit equation was developed based on a reference state of infinite dilution.

The modified model is not able to estimate the CO₂ partial pressure satisfactorily. When the physical solubility of CO₂ in aqueous MDEA is compared with experimental data, a large deviation is observed. Most likely the binary interaction parameter of CO₂-MDEA, which is fitted using the reactive system of CO₂-MDEA-water is not correct. A new method is proposed to fit this parameter with the experimental data of the N₂O solubility in aqueous MDEA.

The results of the E-EOS look promising and the development will be continued. However, as for every other model the input parameters are not known with sufficient accuracy. The model is sensitive to the binary interaction parameters and if they can not be determined accurately from data available in literature, additional experiments will have to be carried out.

The following improvements to the electrolyte equation of state will be incorporated:

- Formation of carbonate will be included in the model. This reaction will become important for high MDEA concentrations and/or high acid gas liquid loadings;
- Formation of OH⁻-ions will be included in the model. This reaction will become important for low acid gas liquid loadings;
- A critical review of binary interaction coefficients will be carried out and additional experiments done if not enough literature data are available;
- The model will be extended to predict the system H₂S-MDEA-H₂O-CH₄;
- The model will be extended to predict the system H₂S-CO₂-MDEA-H₂O-CH₄.
List of symbols

\[ A^R \quad \text{Residual Helmholtz Energy} \quad [\text{J}] \]
\[ \text{DEA} \quad \text{Diethanolamine} \quad [-] \]
\[ \text{MDEA} \quad \text{N-methyldiethanolamine} \quad [-] \]
\[ \text{MEA} \quad \text{Monoethanolamine} \quad [-] \]
\[ \text{DMF} \quad \text{Dimethylformamide} \quad [-] \]
\[ \text{TBAH} \quad \text{TetrabutylammoniumHydroxide} \quad [-] \]
\[ P \quad \text{(partial) Pressure} \quad [\text{kPa}] \]
\[ \text{AAD} \quad \text{Absolute Average Deviation} \quad [%] \]
\[ \text{BIAS} \quad \text{Mean BIAS Deviation} \quad [%] \]
\[ K \quad \text{Chemical equilibrium constant} \quad [-] \]
\[ H \quad \text{Henry’s coefficient} \quad [\text{kPa.m}^3.\text{kmole}^{-1}] \]

Greek symbols

\[ A \quad \text{Acid gas liquid loading} \quad \text{[mole acid gas / mole amine]} \]
\[ \Gamma \quad \text{Activity coefficient} \quad [-] \]

Sub/super-scripts

\[ i,j,l,n,x \quad \text{Index} \]
\[ \text{exp} \quad \text{Experiments} \]
\[ \text{calc} \quad \text{Calculated by model} \]
\[ \infty \quad \text{Infinite dilution in water} \]
\[ \text{Aq} \quad \text{Aqueous} \]
References


