Chapter 4

Solubility of Hydrogen Sulfide in Aqueous N-methyldiethanolamine

Abstract

In this chapter the electrolyte equation of state as developed previously for the system MDEA-H$_2$O-CO$_2$-CH$_4$ (P.J.G. Huttenhuis, N.J. Agrawal, E. Solbraa, G.F. Versteeg, Fluid Phase Eq., 264 (2008) 99-112) is further developed for the system MDEA-H$_2$O-H$_2$S-CH$_4$. With this thermodynamic model the solubility of hydrogen sulfide and the speciation in aqueous solutions of N-methyldiethanolamine can be described quantitatively. The model results are compared with experimental H$_2$S solubility data in aqueous MDEA in absence and in presence of methane. The application of an equation of state to these acid gas – amine systems is a new development in the literature. These systems are difficult to describe because both molecular and ionic species are present in the liquid. Schwarzentruber’s modification of the Redlich-Kwong-Soave EOS with a Huron-Vidal mixing rule is used as molecular part of the equation of state and ionic interactions terms are
added to account for non-idealities caused by ionic interactions. The newly developed model is compared with experimental data.

4.1 Introduction

Gases like CO$_2$ and H$_2$S are often removed to a certain extent from natural and industrial gas streams, for environmental or operational reasons. An absorption – regeneration process with an aqueous amine solution is commonly used. The acid gas stream enters at the bottom in the absorber where it is contacted counter-currently with an aqueous amine solution. In the absorber the acid components are absorbed in the liquid and converted to non volatile ionic species. The gas stream leaving the top of the absorber has a low acid gas concentration. The loaded solvent from the absorber is heated and/or depressurized and sent to a stripper where the solvent is regenerated and returned to the absorber. Thermodynamic data, mass transfer properties and the rate of the chemical reactions need to be known for a robust process design. Reliable thermodynamic data are necessary to prevent costly over-design of equipment. In this thesis a rigorous thermodynamic model (an electrolyte equation of state) is used to predict the solubility of H$_2$S in an aqueous MDEA solution at elevated methane pressure. In general the acid gas solubility is determined in absence of high partial pressures of inert components like nitrogen or hydrocarbons. However, in absorbers in the gas industry often high methane pressures are encountered, so it is important to study the influence of hydrocarbons on the acid gas solubility. The thermodynamic model developed in this study has been validated with experimental data for the MDEA-H$_2$O-H$_2$S-CH$_4$ system as presented by Huttenhuis et al. [5].
4.2 The electrolyte equation of state

An equation of state uses the same equations for both the vapor and liquid. This also applies to the electrolyte equation of state (E-EOS). In the present study Schwarzentruber’s [1] modification of the Redlich-Kwong-Soave EOS with a Huron-Vidal [2] mixing rule is used. Additional interactions are added to this equation of state to allow for ions in the liquid as originally proposed by Fürst and Renon [3]. A major advantage of this approach is that complex multi-component systems can be described quantitatively by studying less complex systems containing a smaller number of components. The system CO\textsubscript{2}-MDEA-H\textsubscript{2}O-CH\textsubscript{4} is described with an E-EOS by Huttenhuis et al. [6]: in this chapter the system H\textsubscript{2}S-MDEA-H\textsubscript{2}O-CH\textsubscript{4} is dealt with. The parameters of the system MDEA-H\textsubscript{2}O-CH\textsubscript{4} are already known from the system CO\textsubscript{2}-MDEA-H\textsubscript{2}O-CH\textsubscript{4} and these are used in the new model. Only additional pure component data and interaction parameters due to the presence of H\textsubscript{2}S and its related ionic species are required.

The electrolyte equation of state used in this study contains the following terms:

\[
\frac{A^R}{RT} = \left( \frac{A^R}{RT} \right)_R + \left( \frac{A^R}{RT} \right)_{SR1} + \left( \frac{A^R}{RT} \right)_{SR2} + \left( \frac{A^R}{RT} \right)_{LR} + \left( \frac{A^R}{RT} \right)_{BOm} \tag{Equation 1}
\]

The first two terms describe the molecular equation of state – here the Redlich-Kwong-Soave EOS as modified by Schwarzentruber (ScRK-EOS) [1]. To account for interactions between molecules the Huron-Vidal mixing rule is used, because this mixing rule can also be used for highly non-ideal (polar) molecular systems, such as MDEA-H\textsubscript{2}O. In this mixing rule 5 interaction parameters are required for each binary molecular system. Another advantage of this Huron-Vidal mixing rule is that it can easily be converted to the van der Waals mixing rule using only one interaction parameter per binary pair. The other terms in the Helmholtz expression are to allow for interactions with the ions in the system. For a detailed description of the E-EOS used in this thesis reference is made to Huttenhuis et al [6].
Chapter 4

4.3 Model development

4.3.1 Former work

As described above the system MDEA-H$_2$O-CH$_4$ which is part of the H$_2$S-MDEA-H$_2$O-CH$_4$ system was already described quantitatively in Chapter 3. Only additional pure component and interaction parameters for H$_2$S and the related ionic species are required.

The following additional information is required to account for the presence of H$_2$S in the system:

- Pure component parameters of H$_2$S, HS$^-$ and S$^{2-}$;
- Molecular interactions of the binary systems: H$_2$S-MDEA, H$_2$S-H$_2$O and H$_2$S-CH$_4$;
- Ionic interaction parameters for: H$_2$S-MDEAH$^+$, HS$^-$-MDEAH$^+$, S$^{2-}$-MDEAH$^+$. 

In the scheme shown in Figure 1 an overview of the involved pure and binary parameters is presented for the H$_2$S-MDEA-H$_2$O-CH$_4$ system.
4.3.2 Chemical reactions

When hydrogen sulfide absorbs in the liquid several acid-base reactions take place and ionic species are formed. For the \( \text{H}_2\text{S-MDEA-H}_2\text{O-CH}_4 \) system the following reactions take place:

water dissociation: \[ 2\text{H}_2\text{O} \rightleftharpoons K_1 \rightarrow \text{H}_3\text{O}^+ + \text{OH}^- \]  

bisulfide formation: \[ \text{H}_2\text{O} + \text{H}_2\text{S} \rightleftharpoons K_2 \rightarrow \text{HS}^- + \text{H}_3\text{O}^+ \]  

Sulfide formation: \[ \text{H}_2\text{O} + \text{HS}^- \rightleftharpoons K_3 \rightarrow \text{S}^{2-} + \text{H}_3\text{O}^+ \]  

MDEA protonation: \[ \text{H}_2\text{O} + \text{MDEAH}^+ \rightleftharpoons K_4 \rightarrow \text{MDEA} + \text{H}_3\text{O}^+ \]
The relation between the equilibrium constant $K_x$ and temperature is:

$$\ln K_x = A + \frac{B}{T} + C \ln T$$

Equation 2

The parameters for the equilibrium constants are given in Table 1.

<table>
<thead>
<tr>
<th>$K_x$</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>Austgen [8]</td>
</tr>
<tr>
<td>$K_2$</td>
<td>214.582</td>
<td>-12995.4</td>
<td>-33.5471</td>
<td>273-423</td>
<td>Austgen [8]</td>
</tr>
<tr>
<td>$K_3$</td>
<td>-32.0</td>
<td>-3338.0</td>
<td>0.0</td>
<td>287-343</td>
<td>Austgen [8]</td>
</tr>
<tr>
<td>$K_4$</td>
<td>-77.262</td>
<td>-1116.5</td>
<td>10.06</td>
<td>278-423</td>
<td>Huttenhuis et al. [5]</td>
</tr>
</tbody>
</table>

Table 1 Parameters to calculate the equilibrium constants of system $H_2S$-MDEA-$H_2O$

The $K_1$ and $K_4$ relations are the same as used by Huttenhuis et al. [6] for the system MDEA-$H_2O$-$CO_2$. In this thesis all chemical equilibrium constants are defined in the mole fraction scale with infinite dilution in water as reference state for all species. The concentration of $H_3O^+$-ions is neglected, because the mole fraction of this component is very low. The thermodynamic model is able to calculate the mole fraction in both the gas and liquid of the following species: $H_2O$, $OH^-$, $H_2S$, $HS^-$, $S^{2-}$, MDEA, MDEAH$^+$ and $CH_4$.

### 4.3.3 Pure component model

In the MDEA-$H_2O$-$H_2S$-$CH_4$ system the following species are present: MDEA, MDEAH$^+$, $H_2O$, $H_2O^+$, $OH^-$, $H_2S$ $HS^-$, $S^{2-}$ and $CH_4$. The pure component parameters of these components are the same as used by Huttenhuis et al. [6] except the following values, which are taken from Vallée et al. [4]:


4.3.4 Binary molecular interaction parameters

4.3.4.1 Overview

For the determination of the binary molecular interaction parameters, the same approach as presented by Huttenhuis et al. [6] is followed. Before simulating the quaternary system H$_2$S-MDEA-H$_2$O-CH$_4$, the following binary systems have to be studied and optimized:

- **H$_2$S-H$_2$O**: For this system the binary interaction data were determined from the three following sources: Selleck et al. [9], Lee and Mather [10] and Clarke and Glew [11];
- **H$_2$S-MDEA**: For this molecular binary system no experimental data are available, because it is difficult to measure the physical solubility of H$_2$S in
pure MDEA. This is because trace amounts of water which are always present in the MDEA increase the solubility significantly. Therefore the N$_2$O analogy was used as frequently applied for CO$_2$;

- **CH$_4$-H$_2$S:** The van der Waals equation was used with an interaction parameter $k_{ij} = 0.08$ [19];
- **CH$_4$-MDEA, H$_2$O-MDEA, CH$_4$-H$_2$O:** For these binary molecular systems the same interaction parameters as used by Huttenhuis et al. [6] were incorporated in the model.

### 4.3.4.2 H$_2$S-H$_2$O

From an evaluation it was concluded that the experimental data of the following sources were consistent: Selleck et al. [9], Lee and Mather [10] and Clarke and Glew [11]. Lee and Mather [10] measured the total system pressure at a specified temperature and H$_2$S liquid concentration. Selleck et al. [9] and Clarke and Glew [11] measured both the system pressure and the H$_2$S vapor concentration. In the paper of Selleck et al. [9] also extrapolated data and experimental data with two liquid phases are presented, however these are not used in this chapter, because our E-EOS cannot deal with two liquid phases at this stage. The experimental data (both system pressure and vapor concentration) are used to determine the binary Huron-Vidal parameters of the H$_2$S-H$_2$O system. The experimental conditions of these literature sources and the comparison with the EOS are presented in Table 3.
H₂S solubility in aqueous MDEA

Table 3 Experimental conditions and model results for the H₂S-H₂O system

<table>
<thead>
<tr>
<th>Data</th>
<th>P [bar]</th>
<th>T [K]</th>
<th>P [bar]</th>
<th>y_{H₂S} [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clarke and Glew [11]</td>
<td>0.5-0.95</td>
<td>273-323</td>
<td>36</td>
<td>-4.0</td>
</tr>
<tr>
<td>Lee and Mather [10]</td>
<td>1.5-66.7</td>
<td>283-453</td>
<td>325</td>
<td>0.64</td>
</tr>
<tr>
<td>Selleck et al. [9]</td>
<td>6.9-121</td>
<td>311-444</td>
<td>26</td>
<td>3.2</td>
</tr>
<tr>
<td>Total</td>
<td>0.5-121</td>
<td>273-453</td>
<td>387</td>
<td>0.36</td>
</tr>
</tbody>
</table>

The AAD and BIAS are defined as:

\[
AAD = \frac{1}{n} \sum_{i=1}^{n} \frac{P_{\text{acidgas,exp}} - P_{\text{acidgas,calc}}}{P_{\text{acidgas,exp}}} \cdot 100\%
\]

\[
BIAS = \frac{1}{n} \sum_{i=1}^{n} \frac{P_{\text{acidgas,exp}} - P_{\text{acidgas,calc}}}{P_{\text{acidgas,exp}}} \cdot 100\%
\]

From Table 3 it can be concluded that the model results are well in line with the three literature sources. In Figure 2 the experimental data of Lee and Mather [10] are compared with the model results. Figure 3 compares the experimental data of Selleck et al. [9] and Clarke and Glew [11] with the model. The data of Clarke and Glew are measured over small temperature intervals (of 5 K), so not all data are shown in the graph. However, for the model regression all experimental data have been used.
Figure 2  Total pressure against the H$_2$S liquid concentration for the H$_2$S-H$_2$O system; model results compared with experimental data of Lee and Mather [10]
Figure 3 Total pressure against the H₂S liquid concentration for the H₂S-H₂O system; model results compared with experimental data of Selleck et al. [9] and Clarke and Glew [11]

4.3.4.3 H₂S-MDEA

For this molecular binary system no direct experimental data are available, because it is difficult to measure the physical solubility of H₂S in MDEA. This is because trace amounts of water present in MDEA will cause chemical reactions and the formation of ionic species. Therefore the same approach as used by Huttenhuis et al. [6]. The physical solubility of H₂S in aqueous MDEA is determined from the N₂O analogy as is frequently used to determine the physical solubility of CO₂ in reactive solvents. According to this H₂S-N₂O analogy the physical solubility of H₂S in aqueous MDEA can be calculated in the following manner:
The experimental data for the solubility of N$_2$O in water and N$_2$O in aqueous MDEA are taken from Huttenhuis et al. [6] and the solubility of H$_2$S in water is taken from the data of Clarke and Glew [11], Lee and Mather [10] and Selleck et al. [9] for the H$_2$S-H$_2$O system (refer to Section 4.3.4.2)

The physical solubility of H$_2$S in aqueous MDEA can be calculated, when the interaction parameters of the following binary molecular systems are known: MDEA-H$_2$O, H$_2$S-H$_2$O and H$_2$S-MDEA. So in the present case the unknown binary interaction parameters of the H$_2$S-MDEA system can be calculated when the binary molecular interactions of H$_2$S-H$_2$O (refer to Section 4.3.4.2) and MDEA-H$_2$O (Huttenhuis et al. [6]) and the physical solubility of H$_2$S in aqueous MDEA (see above) are known. The physical solubility of N$_2$O in water is based on the relation developed by Jamal [12]. The physical solubility of N$_2$O in aqueous MDEA is based on experimental data produced by the following authors:

- Versteeg and van Swaaij [13];
- Haimour and Sandall [14];
- Jou et al. [15];
- Li and Mather [16];
- Pawlak and Zarzycki [17].

In the work carried out by Rinker and Sandall [18] the physical solubility of H$_2$S was determined by neutralizing the aqueous MDEA solvent with HCl. In Figure 4 the calculated physical solubility of H$_2$S using the N$_2$O analogy (based on experimental data of Versteeg and van Swaaij, Haimour and Sandall and Jou et al.) is compared with the experimental data in neutralized aqueous MDEA as reported by Rinker and Sandall [18].
$H_2S$ solubility in aqueous MDEA

From Figure 4 it can be concluded that the physical solubility of $H_2S$ in aqueous MDEA using the $N_2O$ analogy ([13], [14] and [15]) is very well in line with the physical solubility determined in neutralised aqueous MDEA [18].

After the new binary interaction parameters for the $H_2S$-MDEA system were calculated from the experimental data, the calculated physical solubility of $H_2S$ in aqueous MDEA was compared with the physical solubility calculated by the updated EOS; the results were good (BIAS of 0.61 % and AAD of 8.8%).
4.3.4.4 H₂S-CH₄

During the model simulations it was found that the calculated H₂S solubility was not sensitive to the value of the molecular interaction parameter of the H₂S-CH₄ binary system. Therefore it was decided to use a value of 0.08 for the binary interaction parameter \( k_{ij} \) of the van der Waal mixing rule, based on a binary interaction parameter \( k_{ij} \) for the binary system H₂S-propane [19].

4.3.4.5 Summary

In this chapter all molecular interaction parameters for describing the system H₂S-MDEA-H₂O-CH₄ have been determined. These parameters are shown in Table 4:

<table>
<thead>
<tr>
<th>comp.( i )</th>
<th>H₂S</th>
<th>H₂S</th>
<th>H₂S</th>
<th>MDEA</th>
<th>MDEA</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>comp.( j )</td>
<td>MDEA</td>
<td>H₂O</td>
<td>CH₄</td>
<td>H₂O</td>
<td>CH₄</td>
<td>CH₄</td>
</tr>
<tr>
<td>( k_{ij} ) [-]</td>
<td>-</td>
<td>-</td>
<td>0.08</td>
<td>-</td>
<td>0.600</td>
<td>-</td>
</tr>
<tr>
<td>( a_{ij} ) [-]</td>
<td>-0.907</td>
<td>0.104</td>
<td>-</td>
<td>0.208</td>
<td>-</td>
<td>0.150</td>
</tr>
<tr>
<td>( \Delta g_{ij} ) [Jmol⁻¹]</td>
<td>5567</td>
<td>26082</td>
<td>-</td>
<td>-9148</td>
<td>-</td>
<td>1028</td>
</tr>
<tr>
<td>( \Delta g''_{ij} ) [Jmol⁻¹]</td>
<td>2928</td>
<td>-2148</td>
<td>-</td>
<td>6095</td>
<td>-</td>
<td>40532</td>
</tr>
<tr>
<td>( \Delta g'''_ij ) [Jmol⁻¹ K⁻¹]</td>
<td>-2.44</td>
<td>-18.45</td>
<td>-</td>
<td>42.35</td>
<td>-</td>
<td>17.40</td>
</tr>
<tr>
<td>( \Delta g''''_{ij} ) [Jmol⁻¹ K⁻¹]</td>
<td>15.11</td>
<td>5.76</td>
<td>-</td>
<td>-49.93</td>
<td>-</td>
<td>-54.45</td>
</tr>
</tbody>
</table>

| reference | This work | This work | This work | Huttenhuis et al. [6] | Huttenhuis et al. [6] | Huttenhuis et al. [6] |

Table 4 Binary molecular interaction parameters

The binary molecular interaction parameters MDEA-H₂O, MDEA-CH₄ and H₂O-CH₄ were derived from systems containing no acid gas (CO₂ or H₂S), so the same values as used by Huttenhuis et al. [6] were used for these interaction parameters.
4.3.5 Binary ionic interaction parameters

4.3.5.1 Ionic interaction parameters in MDEA-H$_2$S-H$_2$O system

Following the work of Fürst and Renon [3], only the cation-anion and cation-molecular ionic interaction parameters are regressed in the model. The cation-cation, anion-anion and anion-molecular interactions are neglected. To describe the ternary system H$_2$S-MDEA-H$_2$O, the following ionic interaction parameters need to be determined:

- MDEAH$^+$ - MDEA;
- MDEAH$^+$ - H$_2$O;
- MDEAH$^+$ - H$_2$S;
- MDEAH$^+$ - HS$^-$;
- MDEAH$^+$ - S$^{2-}$.

The first two interaction parameters (MDEAH$^+$-MDEA and MDEAH$^+$-H$_2$O) are independent of the acid gas type. These interaction parameters have already been regressed by Huttenhuis et al. [6] for the CO$_2$-MDEA-H$_2$O system. However, the other ionic interaction parameters, which are H$_2$S specific, have to be derived from experimentally H$_2$S solubility data presented in literature. Before using the published experimental data of various research groups, a consistency check was carried out on the applicability of the data. The MDEA-H$_2$S-H$_2$O solubility data of the following authors were reviewed with mutual and internal consistency tests: Maddox et al. [20], Lemoine et al. [21], Huang and Ng [22], Kamps et al. [23], Kuranov et al. [24], MacGregor and Mather [25], Rogers and Bullin [26], Sidi-Boumedine et al. [27], Jou et al. [28] and [29], Li and Shen [30].

An overview of the experimental data used for model regression is presented in Table 5.
<table>
<thead>
<tr>
<th>Ref.</th>
<th>$C_{\text{MDEA}}$ [wt.%]</th>
<th>Temperature [K]</th>
<th>loading [mole H$_2$S/mole amine]</th>
<th>Data points [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lemoine at al. [21]</td>
<td>11.8</td>
<td>298</td>
<td>0.01-0.26</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>23.6</td>
<td>313</td>
<td>0.015-0.15</td>
<td>13</td>
</tr>
<tr>
<td>Maddox et al. [20]</td>
<td>11.8</td>
<td>298</td>
<td>0.64-2.17</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>311, 339, 389</td>
<td>0.18-1.59</td>
<td>30</td>
</tr>
<tr>
<td>Huang and Ng [22]</td>
<td>23.1</td>
<td>313, 373, 393</td>
<td>0.003-0.20</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>313, 343, 373, 393</td>
<td>0.003-1.74</td>
<td>33</td>
</tr>
<tr>
<td>Kamps et al. [23]</td>
<td>48.8</td>
<td>313, 353, 393</td>
<td>0.15-1.43</td>
<td>26</td>
</tr>
<tr>
<td>Kuranov et al. [24]</td>
<td>18.7</td>
<td>313, 333, 373, 393, 413</td>
<td>0.50-1.93</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>32.2</td>
<td>313, 333, 373, 393, 413</td>
<td>0.48-1.63</td>
<td>36</td>
</tr>
<tr>
<td>MacGregor and Mather [25]</td>
<td>20.9</td>
<td>313</td>
<td>0.13-1.73</td>
<td>27</td>
</tr>
<tr>
<td>Rogers and Bullin [26]</td>
<td>23</td>
<td>313</td>
<td>0.013-0.31</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>313</td>
<td>0.0022-0.093</td>
<td>10</td>
</tr>
<tr>
<td>Sidi-Boumedine et al. [27]</td>
<td>46.8</td>
<td>313, 373</td>
<td>0.039-1.12</td>
<td>26</td>
</tr>
</tbody>
</table>

Table 5  Literature references used for the fitting of the ionic parameters of the $H_2S$-MDEA-$H_2O$ system; total 291 data points

The data of Jou et al. [28] and [29] and Li et al. [30] were not included in the database which was used to determine the ionic interaction parameters for the following reasons:

- When the presented experimental data of Jou et al. [28] at 313 K were compared for self-consistency, it was concluded that there was almost no difference in $H_2S$ solubility between 35 wt.% and 49 wt.% aqueous MDEA. This seems questionable, because at fixed loading and temperature, the
acid gas partial pressure increases with the MDEA concentration (refer to Chunxi and Fürst [31]);

• Data of Jou et al. [29] in 50 wt.% MDEA were not consistent at loadings below 0.05. The trend of a log-log graph of the liquid loading versus H$_2$S partial pressure at low loadings should be almost linear and this was not the case. There was also a mutual inconsistency when Jou’s data were compared with data of Lemoine et al. [21], Huang and Ng [22] and Rogers and Bullin [26]. For more details reference is made to Huttenhuis et al. [5];

• Data of Li et al. [30] at higher temperature are highly non-linear at elevated temperatures as can be seen in Figure 5. At low loadings (< 0.3), a linear relation between the logarithm of the partial pressure and the gas loading exists for acid gas – aqueous alkanolamine systems (refer to Chunxi and Fürst [31]).

![Figure 5 Solubility of H$_2$S in 2.57 M aqueous MDEA at different temperatures (Li et al. [30])]
With the experimental solubility data in Table 5 all binary ionic interaction parameters have been determined except the MDEAH$^+$ - S$^{2-}$ interaction parameter. Because the concentration of S$^{2-}$ will be low (due to the low dissociation constant of the bisulfide ion) the influence of the MDEAH$^+$ - S$^{2-}$ ionic interaction parameter is negligible and therefore this parameter is not regressed with the experimental solubility data of H$_2$S in aqueous MDEA. This ionic interaction parameter was calculated with the correlation proposed by Chunxi and Fürst [31]. The other ionic binary interaction parameters $W_{ij}$ have been determined by regressing the electrolyte equation of state with the experimental database given in Table 5. The values of all derived binary ionic interaction parameters are presented in Table 6.

<table>
<thead>
<tr>
<th>comp. $i$</th>
<th>MDEAH$^+$</th>
<th>MDEAH$^+$</th>
<th>MDEAH$^+$</th>
<th>MDEAH$^+$</th>
<th>MDEAH$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>comp. $j$</td>
<td>MDEA</td>
<td>H$_2$O</td>
<td>H$_2$S</td>
<td>HS</td>
<td>S$^{2-}$</td>
</tr>
<tr>
<td>$W_{ij}$ [m$^3$/mol$^{-1}$]</td>
<td>-1.16E-04</td>
<td>6.17E-05</td>
<td>2.58E-05</td>
<td>-1.46E-04</td>
<td>2.52E-05</td>
</tr>
</tbody>
</table>

Table 6 Ionic interaction parameters regressed with solubility data of H$_2$S in aqueous MDEA

The AAD and BIAS deviations for the H$_2$S experiments derived from these regressions are 19% and 3.6%. The binary interaction parameters which are not acid gas specific (MDEAH$^+$-MDEA and MDEAH$^+$-H$_2$O) were compared with the values of these parameters regressed by Huttenhuis et al. [6]. In that work these interaction parameters were derived from experimental solubility data of CO$_2$ in aqueous MDEA; in Table 7 these regressed ionic interaction parameters are shown.
From Table 6 and Table 7 it can be concluded that the common interaction parameters of the single H$_2$S and single CO$_2$ solubility experiments do not coincide at all. The MDEAH$^+$-H$_2$O interaction parameter is an order of magnitude higher for CO$_2$ compared to that for H$_2$S. The difference for the MDEAH$^+$-MDEA parameter is even higher; here the H$_2$S parameter has a negative sign, while the CO$_2$ parameter has a positive value!

One of the aims of using the E-EOS is to obtain a unique set of model parameters. So the differences in regressed ionic interaction parameters are unacceptable and have to be eliminated. Therefore a different approach was used to determine the ionic binary interaction parameters $W_{ij}$. All seven interaction parameters reported in Table 6 and Table 7 were regressed simultaneously with both the experimental solubility data of H$_2$S-only in aqueous MDEA and CO$_2$-only in aqueous MDEA. So the experimental databases of this chapter (H$_2$S solubility) and of Chapter 3 (CO$_2$ solubility) are used simultaneously for model regression. The same approach was used by Chunxi and Fürst [31]. From the simultaneous regression with CO$_2$-only and H$_2$S–only solubility data, the following values for the ionic binary interaction parameters were derived (Table 8).

<table>
<thead>
<tr>
<th>comp. $i$</th>
<th>MDEAH$^+$</th>
<th>MDEAH$^{2+}$</th>
<th>MDEAH$^-$</th>
<th>MDEA $H^+$</th>
<th>MDEAH$^{+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>comp. $j$</td>
<td>MDEA</td>
<td>H$_2$O</td>
<td>CO$_2$</td>
<td>HCO$_3^-$</td>
<td>CO$_3^{2-}$</td>
</tr>
<tr>
<td>$W_{ij}$ [m$^3$mol$^{-1}$]</td>
<td>1.95E-03</td>
<td>4.09E-04</td>
<td>2.48E-04</td>
<td>-1.29E-04</td>
<td>-3.58E-04</td>
</tr>
</tbody>
</table>

*Table 7  Ionic interaction parameters regressed with solubility data of CO$_2$ in aqueous MDEA (refer to Huttenhuis et al. [6])*
When the values of the ionic interaction parameters as presented in Table 8 are compared with the values presented in Table 6 and Table 7 it can be concluded that:

- The values of the new common (H₂S and CO₂) interaction parameters (MDEAH⁺-MDEA and MDEAH⁺-H₂O) have changed substantially compared to the values derived from the single gas H₂S experiments specified in Table 6. However, differences compared with the values derived from the CO₂-only experiments presented in Table 7 are significantly lower. The value of the MDEAH⁺-MDEA interaction parameter has increased 18% while the MDEAH⁺-H₂O interaction parameters has increased by only 2%.

The values of the CO₂ specific interaction parameters (MDEAH⁺-CO₂, MDEAH⁺-HCO₃⁻, MDEAH⁺-CO₃²⁻) have not changed significantly due to the addition of the H₂S-only data in the regression procedure. The maximum change was seen for the MDEAH⁺-CO₃²⁻ interaction parameter which showed an increase of 23% owing to the change in the MDEAH⁺-MDEA interaction parameter. However, because of the low concentrations of CO₃²⁻ in loaded amine solutions, the value of this parameter will have only a minor influence on the overall results of the E-EOS. The prediction of the E-EOS with the new ionic interaction parameters $W_{ij}$ specified in Table 8 were compared with the experimental CO₂-only solubility data from Huttenhuis et al. [6].
Similar results are obtained with the new interaction parameters. The calculated AAD and BIAS of the experiments changed from 24 % [6] to 25 % and from 8.3 % [6] to 8.4 % respectively.

However, the H₂S specific ionic interaction parameter (MDEAH⁺-H₂S) and the ionic interaction parameters MDEAH⁺-MDEA and MDEAH⁺-H₂O, which are independent of acid gas type, changed significant when the parameter regression was carried out with solubility data of CO₂ and H₂S simultaneously, compared with regression of these parameters with H₂S-only solubility data. For the H₂S solubility experiments, the BIAS deviation improved from 3.6% (H₂S-only) to 2.1 % (H₂S and CO₂ simultaneously), while the AAD deviation increased from 19% to 26%.

In Table 9 the AAD and BIAS deviations of the E-EOS calculations with the different sets of ionic interaction parameters are given.

<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th>H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Table 7</td>
<td>Table 8</td>
</tr>
<tr>
<td>AAD [%]</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>BIAS [%]</td>
<td>8.3</td>
<td>8.4</td>
</tr>
</tbody>
</table>

*Table 9  AAD and BIAS deviations for H₂S-only and CO₂-only experiments; ionic interaction parameters based on Table 6, Table 7 and Table 8 respectively*

**4.3.5.2 Ionic interaction parameters in H₂S-MDEA-H₂O-CH₄ system**

Only one additional ionic interaction parameter is required when methane is added to the H₂S-MDEA-H₂O system, i.e. that of MDEAH⁺-CH₄. This parameter has been determined in a previous study [6]. The value of this parameter has been determined by regressing this interaction parameter with experimental solubility data of Addicks et al. [7], who measured the solubility of CO₂ in aqueous MDEA at elevated methane partial pressure. However due to the new ionic interaction parameters determined in this chapter as described in 4.3.5.1 the regression of this
parameter with Addick’s experimental solubility data has been repeated. This MDEAH$^\text{+}$-CH$_4$ ion interaction parameter changed marginally from 4.93E-04 to 5.77E-04.

### 4.3.5.3 Summary

All relevant ionic interaction parameters have been determined to characterize the H$_2$S-MDEA-H$_2$O-CH$_4$ system. It must be noted that the ionic interaction parameters which were used to describe the system CO$_2$-MDEA-H$_2$O-CH$_4$ as determined by Huttenhuis et al. [6] were changed marginally.

### 4.4 Modeling results

#### 4.4.1 Ternary system H$_2$S-MDEA-H$_2$O

With the derived parameters of the electrolyte equation of state, new calculations have been carried out to compare the model with the experimental database of Table 5. The calculated AAD and BIAS deviations between model and experimental data are 26% and 2 %. Figure 6 shows a parity plot of the H$_2$S solubilities for different H$_2$S liquid loadings.
At low loadings (< 0.1 mole H$_2$S / mole amine) the predicted H$_2$S partial pressures are consistently lower than the experimental data. The same conclusion was made by Huttenhuis et al. [6], where the CO$_2$-MDEA-H$_2$O system was studied. Both the AAD and BIAS deviations decreased significantly for an H$_2$S liquid loading above 0.1 mole H$_2$S / mole amine. For intermediate loadings (0.1 < loading < 1) a negative BIAS is found for low partial pressures and a positive BIAS for higher partial pressures. The best model results were obtained for very high H$_2$S liquid loadings (loading > 1). In this region the calculated BIAS was zero for the 96 experimental data points. The influence of temperature and MDEA concentration on the model performance was also analysed, however no clear conclusion could be drawn. At intermediate temperature (311-313 K) and intermediate MDEA concentrations (20-24 wt.%) a negative BIAS ($P_{\text{exp}} < P_{\text{model}}$) is found, while for all other conditions BIAS
deviations are positive (Table 10). In Figure 7 the E-EOS predictions are compared with the experimental data of the different research groups.

![Figure 7 Parity plot for data of different research groups](image)

It is clear that the model under-predicts all H$_2$S partial pressure data at partial pressures lower than 1 kPa (low H$_2$S liquid loadings). Also a lot of scatter is seen in this range (AAD > 25%). A probable explanation for this is that the MDEA used was contaminated with small amounts of primary and/or secondary amines. These contaminants usually have a higher pK$_a$ and therefore reduce the observed equilibrium partial pressures, especially at low loadings.

In the intermediate region (1 < P$_{H2S}$ < 1000 kPa) the experimental data of MacGregor and Mather [25] are remarkable. The BIAS and AAD for this data set are -60% and +60%; the H$_2$S partial pressures are always lower than the model
estimations. This is not in line with the data of the other authors, which agree well with model predictions for intermediate \( \text{H}_2\text{S} \) partial pressures and show positive BIAS deviations for low and high partial pressures. The same conclusion was presented by Huttenhuis et al. [6] with respect to the work of Jou et al. ([28] and [29]) who measured the solubility of \( \text{CO}_2 \) in aqueous MDEA. It was concluded in Appendix A that the solubility data of Jou et al. show \( \text{CO}_2 \) partial pressures which are significantly lower compared to the results of other authors at similar process conditions. MacGregor and Mather [25] measured the solubility of \( \text{H}_2\text{S} \) in 20.9 wt.% MDEA at 313 K; so the influence of their data on the model predictions is the reason that negative BIAS deviations are seen in the intermediate temperature range of 311-313 K and intermediate MDEA concentrations (20-24 wt.%). When the data of MacGregor and Mather [25] are excluded from the AAD and BIAS calculations for Table 8, the BIAS deviations for the temperature range of (311-313 K) and MDEA concentration range of (20-24 wt.%) change from respectively -11% to +4 % and -16% to -4% (respectively BIAS and AAD)! Comparing these results with those calculated by Huttenhuis et al. [6] for the \( \text{CO}_2\)-MDEA-\( \text{H}_2\text{O} \) system shows that the accuracy of the model for \( \text{H}_2\text{S} \) is similar to that for \( \text{CO}_2 \). For the different data sources, the best matching is obtained for the experimental data of Maddox et al. [20] and Kuranov et al. [24]. However, it should be noted that for these two sources experiments were carried out at relatively high acid gas partial pressures. These experiments are less difficult, than experiments at low acid gas partial pressures.
Table 10  BIAS (left column) and AAD deviation (right column) (%) for the experimental data points as function of liquid loading, temperature, MDEA concentration and author; number of experimental data points is given between brackets

<table>
<thead>
<tr>
<th>Liquid loading</th>
<th>&lt;0.01 (14)</th>
<th>0.01-0.1 (45)</th>
<th>0.1-1 (136)</th>
<th>&gt;1 (96)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>31</td>
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<table>
<thead>
<tr>
<th>Temperature [K]</th>
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<th>311-313 (121)</th>
<th>333-353 (41)</th>
<th>373-413 (94)</th>
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<td>19</td>
<td>11</td>
</tr>
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<table>
<thead>
<tr>
<th>Concentration MDEA [wt.%]</th>
<th>12 (35)</th>
<th>20-24 (125)</th>
<th>32 (36)</th>
<th>47-50 (95)</th>
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<td>11</td>
<td>17</td>
<td>20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Author</th>
<th>Lemoine et al. [21] (29)</th>
<th>Maddox et al. [20] (49)</th>
<th>Huang and Ng. [22] (41)</th>
<th>Kamps et al. [23] (26)</th>
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<td>29</td>
<td>17</td>
<td>20</td>
</tr>
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<td></td>
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<td>31</td>
<td>29</td>
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</table>

<table>
<thead>
<tr>
<th>Author</th>
<th>Kuranov et al. [24] (71)</th>
<th>MacGregor and Mather [25] (27)</th>
<th>Rogers and Bullin [26] (22)</th>
<th>Sidi-Boumedine et al. [27] (26)</th>
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<td>60</td>
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<tr>
<td></td>
<td>4</td>
<td>8</td>
<td>8</td>
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</tr>
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</table>

One of the advantages of the E-EOS model compared with less rigorous models is that the activity coefficient and speciation of each component in the liquid can be calculated. This speciation is important when rate based absorption models are required to predict the mass transfer rates in gas treating equipment. Figure 8 (MDEA and MDEAH⁺) and Figure 9 (H₂S and HS⁻) show the speciation of the species in a 35 wt.% aqueous MDEA solution at 313 K as calculated with the E-EOS.
Figure 8  Speciation of MDEA species in 35 wt.% MDEA at 313 K calculated by the E-EOS
The calculated mole fractions of the $S^{2-}$-ion in the liquid phase are lower than $10^{-9}$ for all liquid loadings, so this species has been omitted in Figure 9. Because of the low concentration of $S^{2-}$ the fraction of the MDEAH$^+$-ion is almost identical to that of the HS$^-$-ion. In Figure 10 and Figure 11 the calculated activity coefficients are presented for all species present in the H$_2$S-MDEA-H$_2$O system.
Figure 10 Activity coefficient of MDEA species in 35 wt.% MDEA at 313 K calculated by the E-EOS
From Figure 10 and Figure 11 it can be concluded that the MDEAH* activity coefficient decreases and the HS− activity coefficient increases as the H2S liquid loading increases. For the other species in the liquid, the influence of the H2S liquid loading on the activity coefficient is less pronounced. The activities of H2O and H2S are close to unity over a wide range of liquid loadings. However, the MDEA activity is lower than unity at low loadings but, remarkably, it increases with the loading and at 0.9 it even becomes larger than 1. The same behavior for the activity and speciation was seen in the system CO2-H2O-MDEA (Huttenhuis et al. [6]). The main difference is that the concentration of S2− in the liquid can be neglected over the entire range of H2S liquid loadings, but for CO2, the CO32− concentration is significant. This is due to the difference in dissociation constants of HS− and HCO3−.
The dissociation constant $K_a$ of HS$^-$ is more than two orders of magnitude higher than that of HCO$_3$.$^-$. 

In Figure 12 the H$_2$S partial pressure as calculated with the E-EOS model is shown for a 35 wt.% aqueous MDEA solution with a liquid loading of 0.5 as a function of temperature. The same calculations have been carried out for the solubility of CO$_2$ in aqueous MDEA with the model previously developed [6].

*Figure 12 Calculated partial pressure CO$_2$ and H$_2$S in 35 wt.% MDEA at a acid gas liquid loading of 0.5 mole acid gas / mole amine*
From Figure 12 it can be concluded that at 313 K, H$_2$S and CO$_2$ solubilities are comparable in 35 wt.% MDEA. With increasing temperature the acid gas solubility for H$_2$S becomes higher than for CO$_2$. This effect can be explained by the influence of the temperature on the acid gas dissociation constants and physical solubilities of both acid gases in the liquid. In Figure 13 the dissociation constants (pKa’s) and the Henry constants in water are presented as function of temperature for both H$_2$S and CO$_2$.

![Figure 13](image)

*Figure 13 Acid gas dissociation constant (based on mole fractions) for CO$_2$ [32] and H$_2$S [8] and acid gas Henry constant in water [24] as function of temperature*

In Figure 13 it can be seen that over the temperature range 283-363 K, the pKa of CO$_2$ is lower than for H$_2$S (i.e. CO$_2$ is a stronger acid), meaning that more molecular CO$_2$ will dissociate as ionic species in water. On the other hand, the Henry constant of CO$_2$ in water is higher than that of H$_2$S, i.e. the solubility of CO$_2$ in water is lower
than that of H$_2$S in water. According to the N$_2$O analogy as mentioned in 4.3.4.3, the acid gas solubility in water can be correlated with the physical solubility in aqueous MDEA when the N$_2$O solubilities in water and aqueous MDEA are known. So from the Henry constant presented in Figure 13 it can be concluded that the physical solubility in H$_2$S in aqueous MDEA is substantially higher than the physical solubility of CO$_2$. So due to the lower acidity of H$_2$S and the higher physical solubility in aqueous MDEA compared to CO$_2$, it is possible that the total solubility (both physical and chemical) of CO$_2$ and H$_2$S become equal as is seen in Figure 12 at 313 K. From Figure 13 it can also be seen that with increasing temperatures the difference in dissociation constants of CO$_2$ and H$_2$S becomes less. However, the difference in physical solubility between CO$_2$ and H$_2$S increases with temperature. As a result the total solubility of H$_2$S in aqueous MDEA will be higher than in CO$_2$ at elevated temperature. This is in line with the equilibrium – loading simulations of the E-EOS as can be seen in Figure 12.

4.4.2 Quaternary system H$_2$S-MDEA-H$_2$O-CH$_4$

To study the influence of methane on the solubility of H$_2$S in aqueous MDEA additional parameters are required:

- Pure component parameters of methane ([6]);
- Molecular binary interaction parameters CH$_4$-MDEA and CH$_4$-H$_2$O. Values for these parameters were taken from Huttenhuis et al. [6];
- Molecular binary interaction parameter CH$_4$-H$_2$S. A value of 0.08 is taken as stated in Section 4.3.4.4. The H$_2$S solubility is not very sensitive to the value of this parameter;
- Ionic binary interaction parameter CH$_4$-MDEAH$^+$. The value for this parameter was taken from Huttenhuis et al. [6] and slightly modified in this chapter (refer to Section 4.3.5.2).
The electrolyte equation of state is compared with the experimental solubility data of \( \text{H}_2\text{S} \) in aqueous MDEA at different partial pressures methane as presented in Appendix A of this thesis [5]. In this appendix experimental \( \text{H}_2\text{S} \) solubility data are presented in aqueous 35 – 50 wt.% MDEA at 283 and 298 K with methane as make-up gas up to a methane partial pressure of 69 bar. In Appendix A it is concluded from the experimental data, that the \( \text{H}_2\text{S} \) solubility decreases with increasing methane partial pressure. The experimental data in Appendix A, a total of 30 experiments with varying temperatures, MDEA concentrations, \( \text{H}_2\text{S} \) loadings and \( \text{CH}_4 \) partial pressures, are compared to the outcome of the E-EOS simulations. The results are shown in Table 11.

<table>
<thead>
<tr>
<th>Data Type</th>
<th>BIAS [%]</th>
<th>AAD [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>35 wt.% MDEA</td>
<td>12</td>
<td>17</td>
</tr>
<tr>
<td>50 wt.% MDEA</td>
<td>18</td>
<td>55</td>
</tr>
<tr>
<td>283 K</td>
<td>12</td>
<td>45</td>
</tr>
<tr>
<td>298 K</td>
<td>18</td>
<td>37</td>
</tr>
<tr>
<td>6.9 bar CH(_4)</td>
<td>10</td>
<td>55</td>
</tr>
<tr>
<td>34.5 bar CH(_4)</td>
<td>10</td>
<td>33</td>
</tr>
<tr>
<td>69 bar CH(_4)</td>
<td>10</td>
<td>31</td>
</tr>
</tbody>
</table>

*Table 11 Numbers of experimental data (Huttenhuis et al. [5]), BIAS and AAD for the \( \text{H}_2\text{S} \) solubility in aqueous MDEA and a methane partial pressure up to 69 bar*

Table 11 shows that the model calculates significantly lower \( \text{H}_2\text{S} \) partial equilibrium pressures for all process conditions. The overall BIAS and AAD deviations for all 30 experimental data points are 40% and 44% respectively. Best results are found at low temperature (283 K), low MDEA concentration (35 wt.%) and high methane partial pressure (69 bar). When the results of these \( \text{H}_2\text{S} \)-only experiments are compared with the \( \text{CO}_2 \)-only work reported by Huttenhuis et al. [6], the same trends
are seen. Also in the CO₂ work the model calculates lower acid gas partial pressures. The model predictions at 35 wt.% MDEA are significantly better than the predictions at 50 wt.% MDEA. This is also seen in the predictions for the system H₂S-MDEA-H₂O reported in Section 4.4.1. However, model results of the CO₂ work with methane (overall BIAS 16%) are better than the H₂S model calculations in this chapter. It is concluded that the CO₂-N₂O analogy used by Huttenhuis et al. [6] to regress the CO₂-MDEA molecular binary interaction parameter may be less applicable for higher MDEA concentrations. The same can be concluded for the H₂S-N₂O analogy used in this chapter to regress the H₂S-MDEA molecular binary interaction parameter.

In Figure 14 the experimental H₂S solubility as presented in Appendix A [5] is compared with the calculations of the E-EOS model.

Figure 14 Solubility of H₂S in 50 wt.% MDEA at 298 K and different partial pressure of methane
This figure shows that the E-EOS predicts too low H$_2$S solubilities over the entire range. However, the influence of methane on the solubility is predicted correctly by the model. If the partial pressure of methane increases the H$_2$S solubility in aqueous MDEA decreases.

In Figure 15 the partial pressure, fugacity and fugacity coefficient of H$_2$S are presented for a 35 wt.% MDEA solvent and a liquid loading of 0.1 as function of methane partial pressure. From this figure it can be seen that the H$_2$S partial pressure is a strong function of the methane partial pressure. However, from Figure 15 it can also be seen that the H$_2$S fugacity is more or less independent of the methane partial pressure. So the reason for the decreasing H$_2$S solubility at increasing methane partial pressure is mainly the decreasing fugacity coefficient of H$_2$S. So it is expected that the model predictions will be improved by incorporating additional experimental data from different research groups for the determination of the interaction parameters. Especially experimental solubility data with methane are lacking in literature. The ionic interaction parameter MDEAH$^+$-CH$_4$ has been based on experimental data of Addicks [7] and the molecular interaction parameter MDEA-CH$_4$ was based on data of Jou et al. [33].
Figure 15 Partial pressure, fugacity and fugacity coefficient of H₂S in 35 wt.% MDEA at 298 K at a liquid loading of 0.1 mole H₂S / mole amine

4.5 Conclusions

In the present study an electrolyte equation of state model as developed in Chapter 3 [6] for the system CO₂-MDEA-H₂O-CH₄ is further developed for the system H₂S-MDEA-H₂O-CH₄. The model has been validated with experimental solubility data of H₂S in aqueous MDEA in absence and presence of methane as a make-up gas. For both the system H₂S-MDEA-H₂O and H₂S-MDEA-H₂O-CH₄ the model underpredicts the acid gas partial pressure (and over-predicts the acid gas solubility). However, model predictions for the system in absence of methane are better. Both experimental data and model calculations show that an increase in partial pressure of methane results in a decrease of H₂S solubility. It is concluded that this
decreasing solubility is caused by a decreasing $H_2S$ fugacity coefficient at increasing methane partial pressure. More experimental data are required to improve the accuracy of the E-EOS. Especially additional acid gas solubility data with high methane partial pressures are required, because in this study only one single source could be used for model validations.

**List of symbols**

\begin{itemize}
  \item $A$ Helmholtz energy \hspace{1cm} [J]
  \item $AAD$ Absolute Average Deviation \hspace{1cm} [%]
  \item $BIAS$ Mean BIAS Deviation \hspace{1cm} [%]
  \item $d$ Coefficients for dielectric constant
  \item $g$ Interaction parameter in Huron-Vidal mixing rule \hspace{1cm} [J.m$^{-3}$]
  \item $H$ Henry coefficient \hspace{1cm} [kPa.m$^3$.kmole$^{-1}$]
  \item $K$ Chemical equilibrium constant \hspace{1cm} [-]
  \item $k$ Binary (molecular) interaction parameter
  \item $MDEA$ N-methyldiethanolamine \hspace{1cm} [-]
  \item $M$ Molar mass \hspace{1cm} [gram.mol$^{-1}$]
  \item $n$ Mole number \hspace{1cm} [mole]
  \item $P$ (partial) Pressure \hspace{1cm} [Pa]
  \item $p_1, p_2, p_3$ Polarity parameters \hspace{1cm} [-]
  \item $R$ Gas constant \hspace{1cm} [J.mole$^{-1}$.K$^{-1}$]
  \item $T$ Temperature \hspace{1cm} [K]
  \item $W$ Binary ionic interaction parameter \hspace{1cm} [m$^3$.mol$^{-1}$]
  \item $x$ Liquid mole fraction \hspace{1cm} [-]
  \item $y$ Vapor mole fraction \hspace{1cm} [-]
\end{itemize}
Greek symbols

$\alpha$ Binary nonrandomness parameter in Huron-Vidal mixing rule

$\sigma$ Ionic/molecular diameter [m]

$\omega$ Accentric factor [-]

Sub/super-scripts

$\infty$ Infinite dilution

$a$ Anion

$aq.$ Aqueous

$c$ Cation

$C$ Critical

$calc$ Calculated by model

$exp$ Experiments

$i,j$ Index

$L$ Liquid

$m$ Molecular

$mix$ Mixture

$R$ Reduced / residual

$S$ Solvent

$V$ Vapor
References


