The solubility of carbon dioxide in aqueous N-methyl diethanolamine solutions

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Abstract

In this study the electrolyte equation of state as proposed by Solbraa [E. Solbraa, Equilibrium and non-equilibrium thermodynamics of natural gas processing, Ph.D. thesis Norwegian University of Science and Technology, 2002] was systematically studied and improved to describe the solubility of carbon dioxide in aqueous solutions of N-methyl diethanolamine quantitatively. In this electrolyte equation of state approach both the vapour phase and the liquid phase are described with an equation of state. The molecular part of the equation is based on Schwarzentruber’s [J. Scharzentruber, H. Renon, S. Watanasiri, Fluid Phase Equilib. 52 (1989) 127–134] modification of the Redlich-Kwong equation of state with the Huron–Vidal mixing rule [M.J. Huron, J. Vidal, Fluid Phase Equilib. 3 (1979) 255–271]. Three ionic terms are added to this equation—a short-range ionic term, a long-range ionic term (MSA) and a Born term. The thermodynamic model has the advantage that it reduces to a standard cubic equation of state if no ions are present in the solution, and that publicly available interaction parameters used in the Huron–Vidal mixing rule can be utilized. In this work binary molecular- and ionic interaction parameters were studied and optimized. With the updated model it was possible to describe both low- and high pressure vapour–liquid-equilibrium for the MDEA–H\textsubscript{2}O–CO\textsubscript{2}–CH\textsubscript{4} system satisfactorily.

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1. Introduction

Acid components like CO\textsubscript{2} and H\textsubscript{2}S are normally (selectively) removed to a certain extent in natural and industrial gas streams. The most commonly used systems for this process are the alkanolamine solvents, where the acid components are removed with a reactive absorption liquid, i.e. an aqueous alkanolamine solution. The acid gas will partly be converted to non-volatile ionic species by the basic amine and partly be dissolved physically in the liquid solution. For a robust design of such process systems the acid gas solubility (VLE data), the reaction rate and the mass transfer properties should be known accurately. MDEA is a relatively cheap chemical, it is stable and the loaded solvent has a relatively low heat of regeneration. In this work experimental solubility data available in the literature are interpreted with an electrolyte equation of state (E-EOS) model for the system MDEA–H\textsubscript{2}O–CO\textsubscript{2}–CH\textsubscript{4}. MDEA is a commonly used alkanolamine in the gas treating industry. With the E-EOS thermodynamic model all molecular and ionic concentrations for the MDEA–H\textsubscript{2}O–CO\textsubscript{2}–CH\textsubscript{4} can be calculated at chemical equilibrium conditions. In the literature many models are presented to predict the acid gas solubility in alkanolamine systems. These models can be divided into three categories:

- Empirical models like Kent–Eisenberg [2]. The Kent–Eisenberg model is based on chemical reaction equilibrium in the liquid phase. All activity and fugacity coefficients are assumed to be equal to unity and both the equilibrium constant of the amine protonation reaction and the carbamate formation reaction are, respectively, used as fitting parameters in the model, to match the model with the experimental data. Extrapolation applicability outside the validity range is very limited. This model is commonly
used by process engineers because complexity and required computational effort are relatively low.

- Excess Gibbs energy models. In these models, a term for electrostatic forces caused by the presence of ions in the liquid phase is added to the molecular Gibbs free energy models like NRTL. This additional term is normally based on the Debye and Hückel expression. Approaches based on excess Gibbs energy are presented by: Desmukh–Mather [3], Clegg–Pitzer [4] and Austgen et al. [5]. The vapour phase is predicted with a suitable equation of state.

- Equation of state models (EOS). In this approach both the liquid and the vapour phase are represented with an equation of state. Additional electrolyte terms for the forces resulting from the presence of ions are added to the molecular equation of state. These kinds of models are rather new for the prediction of acid gas solubility in alkanolamine solutions (Fürst and Planche [6], Solbraa [7], Derks et al. [8]).

A more detailed comparison of these thermodynamic models used in the gas treating industry is presented by Huttenhuis and Versteeg [10].

In this work the experimental data will be interpreted with an electrolyte equation of state. This model selection is based on the following motivation:

- EOS models apply the same description for liquid and gas phase.
- The model should be able to model gas, condensate and amine equilibrium (VLE) in a consistent way.
- Extrapolation capabilities of the model seem feasible.
- Prediction at high pressures, typically found in the natural gas industry, is expected to be more reliable compared to other thermodynamic models.
- The model can be extended to systems where different kind of inert components like hydrocarbons are present.
- The model reduces to a standard cubic equation of state if no ions are present in the solution, and by that enables consistent overall natural gas process simulation.

2. Description of electrolyte equation of state model

2.1. General

The experimental results are interpreted with an electrolyte equation of state model (E-EOS), originally proposed by Fürst and Renon [9]. In this model the same equations, based on an equation of state, are used for both the liquid and vapour phase. It is expected that these EOS models will be superior in representing the thermodynamic properties outside the experimentally tested region. Moreover it is expected that the speciation of the components occurring in the liquid phase can be calculated more reliable. An accurate prediction of the speciation is important for the mass transfer calculations. Moreover, the solubility of physically dissolved hydrocarbons (i.e. methane) can be calculated in a thermodynamic consistent way. This hydrocarbon solubility is an important parameter for the correct design of high pressure gas treating equipment.

The basic equation of the model is based on an Helmholtz free energy expression. The Helmholtz energy is given by the equation below and is defined as the sum of five contributions:

\[
\frac{A_R}{RT} = \left( \frac{A^R_1}{RT} \right)_{RF} + \left( \frac{A^R_2}{RT} \right)_{SR1} + \left( \frac{A^R_3}{RT} \right)_{SR2} + \left( \frac{A^R_4}{RT} \right)_{LR} + \left( \frac{A^R_5}{RT} \right)_{BORN}
\]

The first two (molecular) terms are the terms obtained from the used (molecular) equation of state and the other terms are added due to the presence of electrolytes in the system.

In Fig. 1 an overview is given of which types of interaction parameters in the E-EOS model for the system MDEA–CO₂–H₂O–CH₄ are used and how these parameters are determined from the corresponding subsystems. At the bottom level the system independent pure component molecular and ionic parameters are presented. The binary molecular interaction parameters were determined from the binary systems. The binary ionic interaction parameters were determined by fitting them to the experimental VLE-database derived from open literature publications for the systems CO₂–MDEA–H₂O and CO₂–MDEA–H₂O–CH₄. More details about the model and the relevant parameters are described in the following sections.

2.2. Pure component model

The first term of the Helmholtz contributions accounts for the molecular repulsive forces (RF) and the second term for the short-range (attractive) interactions (SR1). The molecular part of the model was based on a cubic equation of state (Schwarzentruber’s [1] modification of the Redlich-Kwong-Soave EOS (ScRK-EOS) with a Huron–Vidal [11] mixing rule).

This ScRK-EOS is described by the following formulae:

\[
P = \frac{RT}{v-b} - \frac{a}{v(v+b)}
\]

\[
a = \frac{1}{9(21/3 - 1) \frac{(RT_c)^2}{P_c}} \alpha(T_R), \quad b = \frac{(21/3 - 1) RT_c}{3 P_c}
\]

\[
\alpha(T_R) = \left( 1 + m(\omega) (1 - \sqrt{T_R}) - p_1 (1 - T_R) (1 + p_2 T_R + p_3 T_R^2) \right)^2
\]

for \( T_R < 1 \), \( \alpha(T_R) = \left( \exp[c(1 - T_R^{d})] \right)^2 \) for \( T_R > 1 \)

\[
m(\omega) = 0.48508 + 1.55191 \omega - 0.15613 \omega^2, \quad c = 1 - \frac{1}{d}
\]

\[
d = \frac{1 + m(\omega)}{2 - p_1 (1 + p_2 + p_3)}
\]

Via the application of this Schwarzentruber modification of the RKS equation, it is also possible to calculate the vapour-pressure curve as function of temperature for polar (non-ideal) components. Parameters \( p_1, p_2 \) and \( p_3 \) are fitting parameters and are determined by regressing the model to the experimental vapour-pressure data.
2.3. Mixing rules

The equation of state can also be used to predict physical and thermodynamic properties for mixtures of components. The parameters applicable for pure components like ‘a’ and ‘b’ are then determined via a mixing rule. The most simple mixing rule is the linear mixing rule; however, for more accurate model predictions, the mixing rule developed by van der Waals is used:

\[ a = \sum_i \sum_j x_i x_j a_{ij}, \quad a_{ij} = \sqrt{a_i a_j (1 - k_{ij})}, \]
\[ b = \sum_i \sum_j x_i x_j b_{ij}, \quad b_{ij} = \frac{b_i + b_j}{2} \]

(4)

where \( k_{ij} \) is a fitting parameter.

In case where components with substantially different structures have to be described the van der Waals mixing rule is not reliable anymore. Huron and Vidal [11] proposed a mixing rule based on excess Gibbs energy models. In this mixing rule the attraction parameter of the mixture (\( a_{\text{mix}} \)) is calculated in a different way than in the van der Waals method. With this mixing rule better predictions can be obtained for polar, highly non-ideal mixtures:

\[ a_{\text{mix}} = b_{\text{mix}} \left( \sum_{i=1}^{n} \left( x_i \frac{a_i}{b_i} \right) - \frac{G_{\infty}^E}{\ln 2} \right) \]

(5)

\( G_{\infty}^E \) is the excess Gibbs energy at infinite pressure and can be calculated with a modified NRTL mixing rule:

\[ \frac{G_{\infty}^E}{RT} = \sum_{i=1}^{n} x_i \sum_{j=1}^{n} \frac{\tau_{ji} b_{ij} x_j \exp(-\alpha_{ji} \tau_{ji})}{\sum_{k=1}^{n} b_{ik} x_k \exp(-\alpha_{ki} \tau_{ki})} \]

(6)

\( \alpha_{ji} \) is a non-randomness parameter, which takes into account that the mole fraction of molecule \( i \) around molecule \( j \) may deviate from the total mole fraction of molecule \( i \) in the system.

\[ \tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \]

(7)

\( g_{ji} \) is an energy parameter caused by the interaction forces between molecule \( i \) and \( j \). In the present approach it is assumed that the \( g \)-parameters are temperature dependent according to:

\[ g_{ij} - g_{ji} = (g'_{ij} - g'_{ji}) + T(g''_{ij} - g''_{ji}), \]

\[ g_{ji} - g_{ii} = (g'_{ji} - g'_{ii}) + T(g''_{ji} - g''_{ii}) \]

(8)

An additional advantage of this Huron–Vidal mixing rule is that it can easily be converted for non-polar binary systems (i.e. hydrocarbons) to the van der Waals mixing rule by proper choice of parameters. In this work the non-polar binary mixtures are modelled with the van der Waals mixing rule and the polar, non-ideal binary mixtures with the Huron–Vidal mixing rule. In this model the linear mixing rule is used for the co-volume parameter \( b_{\text{mix}} \), while the presence of ions is included:

\[ b_{\text{mix}} = \sum_m x_m b_m + \sum_{\text{ion}} x_{\text{ion}} b_{\text{ion}} \]

The molecular co-volume (\( b_m \)) is calculated from the critical properties and the ionic co-volume (\( b_{\text{ion}} \)) is calculated from the ionic diameter.

The pure component parameters of the E-EOS model used in this work are presented in Table 1.

2.4. Electrolyte interactions

To describe the interactions caused by the presence of ions in the system the following terms were added to the (molecular) equation of state:

- SR2—a short-range ion–ion interaction term.
- LR—a long-range ion–ion interaction term.
- Born term, a correction term for the standard state of ions.
The short-range ionic interaction term is calculated by the following relation:

\[
\left( \frac{A_R}{RT} \right)_{SR2} = -\sum \sum \frac{x_i x_j W_{ij}}{v(1 - \varepsilon_3)}
\]  

(9)

where at least one \( i \) or \( j \) is an ion and \( W_{ij} \) is an ion–ion or ion–molecule interaction parameter. The packing factor \( \varepsilon_3 \) is calculated by the following formula:

\[
\varepsilon_3 = \frac{N \pi}{6} \sum_{i} \frac{x_i \sigma_i^3}{v}
\]  

(10)

with a summation over all species present, while \( \sigma_i \) is the molecular or ionic diameter, respectively.

The long-range ion–ion interaction term is given by:

\[
\left( \frac{A_R}{RT} \right)_{LR} = -\frac{\alpha_{LR}^2}{4 \pi} \sum \frac{x_i Z_{ion}^2 \Gamma}{1 + \Gamma \sigma_{ion}} + \frac{\Gamma^3 v}{3 \pi N}
\]  

(11)

The shielding parameter \( \Gamma \) is given implicitly by:

\[
4 \Gamma^2 = \frac{\alpha_{LR}^2}{4 \pi} \sum \frac{x_i Z_{ion}^2}{1 + \Gamma \sigma_{ion}}
\]  

(12)

\[
\alpha_{LR}^2 = \frac{\varepsilon_0^2 N}{\varepsilon_0 D \rho RT}
\]  

(13)

where \( \varepsilon_0 \) is the dielectric permittivity of free space. The dielectric constant \( D \) is calculated according to:

\[
D = 1 + \left( D_s - 1 \right) \left( 1 - \varepsilon_3'/\varepsilon_3' \right)/2
\]  

(14)

In this equation \( \varepsilon_3' \) is equal to \( \varepsilon_3 \) as defined in Eq. (10) above; however, the summation is only one for the ions present in the system!

The solvent dielectric constant is given by:

\[
D_s = \frac{\sum x_{mol} D_{mol}}{\sum x_{mol}}
\]  

(15)

The summation is only carried out for the molecular pure components present. The pure component dielectric constant is assumed to be temperature dependent (Eq. (16)). No interaction parameters are necessary for the calculation of the dielectric constant.

\[
D_i = d^{(0)} + \frac{d^{(1)}}{T} + \frac{d^{(2)}}{T^2} + \frac{d^{(3)}}{T^3} + \frac{d^{(4)}}{T^4}
\]  

(16)

In the above-described model the standard state of the long-range (LR) term is not equal to the standard state of the other terms (RF, SR1 and SR2) of the equation of state. The following standard states are used in the model:

- Ionic standard state in the solvent mixture at unit mole fraction and system temperature and pressure (for LR term)
- Ideal gas state at unit mole fraction and system temperature and 1 bar (for RF, SR1 and SR2 term)

To prevent this model discrepancy an additional term is added to the equation of state (Born term). This Born term is given by the equation below:

\[
\left( \frac{A_R}{RT} \right)_{BORN} = \frac{N e^2}{4 \pi \varepsilon_0 RT} \left( \frac{1}{D_s - 1} \right) \sum \frac{x_i Z_{ion}^2}{\sigma_i^3}
\]  

(17)

In this work (as in previous work by Fürst and Renon [9]) only the interactions between cations and molecules (\( W_{cm} \)) and cations and anions (\( W_{ca} \)) were taken into account. Other interactions were not incorporated due to the repulsive forces of anion–anion (\( W_{aa} \)) and cation–cation (\( W_{cc} \)) interactions and due to lower solvation of anions (\( W_{am} \)) as compared to cations (\( W_{cm} \)).

In this model it is assumed that the ionic binary interaction parameter (\( W_{ij} \)) is not temperature dependent.

### 2.5. Chemical reactions

An alkanolamine-acid gas system is a reactive absorption system, so chemical reactions have to be incorporated in the model. For the CO₂–MDEA–H₂O–CH₄ system, the following
chemical reactions will take place:

Water dissociation: \( 2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \)

Bicarbonate formation: \( 2\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+ \)

Carbonate formation: \( \text{H}_2\text{O} + \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}_3\text{O}^+ \)

MDEA protonation: \( \text{H}_2\text{O} + \text{MDEAH}^+ \rightleftharpoons \text{MDEA} + \text{H}_3\text{O}^+ \)

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

\[
\ln K_A = A + \frac{B}{T} + C \ln T
\]  

(18)

The relevant parameters for the equilibrium constants as used in the model are given in Table 2.

For a quantitative comparison of the model with the experimental data the average absolute deviation (AAD) and BIAS-deviation are used and they are given below:

\[
\text{AAD} = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{y_{i,\text{exp}} - y_{i,\text{calc}}}{y_{i,\text{exp}}} \right| \times 100\% ,
\]

\[
\text{BIAS} = \frac{1}{n} \sum_{i=1}^{n} \left( \frac{y_{i,\text{exp}} - y_{i,\text{calc}}}{y_{i,\text{exp}}} \right) \times 100\%.
\]

### 3. Model development

#### 3.1. Former work

As described in our previous paper (Huttenhuis et al. [15]) the agreement between the original model of Solbraa [7] and newly determined experimental data was not satisfactory. Therefore modifications to the original EOS model of Solbraa [7] were carried out:

- The experimental database used for the determination of the ionic interaction parameter of MDEAH\(^+\) with the other species in the system was critically reviewed and updated.
- The dissociation constant of MDEA of the model was changed, because the constant used previously appeared to be not correct compared with the experimental determined equilibrium constants in the literature.

Moreover, it was also concluded (Huttenhuis et al. [15]) that the physical solubility of the CO\(_2\) in the liquid phase, as calculated by the model, was not inline with the experimental data.

For a quantitative comparison of the model with the experimental data the average absolute deviation (AAD) and BIAS-deviation are used and they are given below:

\[
\text{AAD} = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{y_{i,\text{exp}} - y_{i,\text{calc}}}{y_{i,\text{exp}}} \right| \times 100\% ,
\]

\[
\text{BIAS} = \frac{1}{n} \sum_{i=1}^{n} \left( \frac{y_{i,\text{exp}} - y_{i,\text{calc}}}{y_{i,\text{exp}}} \right) \times 100\%.
\]

#### 3.2. Chemical reactions

In the model developed by Solbraa [7], the species OH\(^-\) and CO\(_3^{2-}\) were not taken into account. However, at very low CO\(_2\) liquid loadings (influence of OH\(^-\)-ions) and higher MDEA concentrations and/or high CO\(_2\) liquid loadings (influence of CO\(_3^{2-}\)-ions) these assumptions may lead to erroneous results. Therefore these two species and the relevant interaction parameters were incorporated in the E-EOS model. For the governing reaction equations and their equilibrium constants reference is made to Section 2.5.

#### 3.3. Binary molecular interaction parameters

#### 3.3.1. Overview

Before the quaternary system CO\(_2\)–MDEA–H\(_2\)O–CH\(_4\) can be simulated, first the following binary systems have to be studied and optimized:

- CO\(_2\)–H\(_2\)O: The Huron–Vidal binary interaction parameters for this system were found by fitting the parameters to experimental solubility data (222 data points) of CO\(_2\) in water. This work was carried out by Solbraa [7].
- H\(_2\)O–MDEA: In Solbraa’s original model 25 freezing point data of Chang et al. [17] have been used to determine the Huron–Vidal interaction parameters. In this work this experimental database was extended and three additional literature sources have been added. New Huron–Vidal interaction parameters were determined with the changed database.
- CO\(_2\)–MDEA: In Solbraa’s original model the Huron–Vidal interaction parameters were determined by fitting them
Table 3
Model predictions compared with experimental data for the MDEA–H2O system

<table>
<thead>
<tr>
<th>Reference</th>
<th>Solbraa’s model AAD [%]</th>
<th>This work AAD [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chang at al. [17]</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Xu et al. [20]</td>
<td>2.5</td>
<td>3.1</td>
</tr>
<tr>
<td>Voutsas et al. [21]</td>
<td>7.4</td>
<td>3.3</td>
</tr>
<tr>
<td>Posey [14]</td>
<td>37.3</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Huttenhuis et al. [15] concluded that the calculated physical solubility of CO2 in MDEA did not agree with experimental data, so the binary interaction parameter of this system was critically re-evaluated.

- CH4–CO2: van der Waals mixing rule was used for this non-polar system. The interaction parameter \( k_{ij} \) was the same as that used in Solbraa’s original model and was taken from Prausnitz et al. [18] and Reid et al. [19].

- CH4–H2O: The Huron–Vidal binary interaction parameters for this system were found by fitting the parameters to experimental solubility data (400 data points) of CH4 in water and water in CH4. This work was carried out by Solbraa [7].

- CH4–MDEA: In the Solbraa version of the model this molecular interaction parameter was determined by using it as a fitting parameter (together with the ionic fitting parameter MDEAH⁺–CH4) for the ionic system MDEA–H2O–CO2–CH4. In the new approach this interaction parameter is determined from experimental data of the ternary molecular system MDEA–H2O–CH4.

3.3.2. H2O–MDEA

In Solbraa’s original model freezing point data (25 data points) of Chang et al. [17] in a relatively small temperature range (262–273 K) have been used to determine the Huron–Vidal interaction parameters. In this work the three additional literature sources have been added so that a higher temperature range was covered (262–460 K). Xu et al. [20] (34 VLE data points), Voutsas et al. [21] (27 VLE data points) and Posey [14] (19 excess heat of mixing data points).

As can be seen in Table 3 the deviations for the water–MDEA system were significantly reduced by the new binary interaction parameters.

In Fig. 2 the calculated activity coefficient for water in the H2O–MDEA system is compared with the experimental data of Chang et al. [17]. As it can be seen from this figure, the calculated activity coefficient in the new model is significantly improved compared to Solbraa’s model, especially for the more concentrated MDEA solutions.

When molecular interaction parameters are fitted to binary data, sometimes multiple sets of parameters are obtained. For the MDEA–H2O mixture two sets of Huron–Vidal parameters (HV-I and HV-II) were obtained during the regression calculations. In Table 4 the two sets of Huron–Vidal parameters are presented and the thermodynamic consequences are further discussed:

In Figs. 3 and 4 the calculated activity coefficient of H2O and MDEA is presented for the two different sets of

Fig. 2. Activity coefficient of water in a MDEA–H2O mixture (263 < T < 273 K).

Table 4
Two sets of Huron–Vidal parameters for the MDEA–H2O system

<table>
<thead>
<tr>
<th>Comp. i</th>
<th>Comp. j</th>
<th>HV-I</th>
<th>HV-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDEA</td>
<td>H2O</td>
<td>0.208</td>
<td>0.270</td>
</tr>
<tr>
<td>H2O</td>
<td>MDEA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δσ_{ij} (J mol(^{-1}))</td>
<td>−9148</td>
<td>33219</td>
<td></td>
</tr>
<tr>
<td>Δσ_{ji} (J mol(^{-1}))</td>
<td>6095</td>
<td>−46531</td>
<td></td>
</tr>
<tr>
<td>Δσ_{ij}′′ (J mol(^{-1}) K(^{-1}))</td>
<td>42.35</td>
<td>−66.84</td>
<td></td>
</tr>
<tr>
<td>Δσ_{ji}′′ (J mol(^{-1}) K(^{-1}))</td>
<td>−49.93</td>
<td>91.29</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Calculated activity coefficient of water in a MDEA–H2O mixture at 40 °C for two different sets of Huron–Vidal parameters (HV-I and HV-II).

Fig. 4. Calculated activity coefficient of MDEA in a MDEA–H2O mixture at 40 °C for two different sets of Huron–Vidal parameters (HV-I and HV-II).
Huron–Vidal parameters as function of the mole fraction water at 40 °C.

From Figs. 3 and 4 it can be seen that the behaviour of both MDEA and H2O activity coefficient is predicted differently for the two sets of parameters. For commercial applications, the used MDEA concentrations results in values for the mole fraction water always above 0.85, so in this concentration range the difference in H2O activity coefficient predicted by both set of parameters is negligible. The activity coefficient of MDEA, however, is predicted completely different by the two sets of parameters. When the HV-I parameters are used a minimum in MDEA activity coefficient of 0.55 is predicted, while for the HV-II parameters a continuously decreasing activity (with increasing water concentration) is predicted by the model. So in diluted MDEA concentrations the calculated MDEA activity coefficient of the two models differ more than a factor of 5! The minimum in MDEA activity coefficient as function of concentration was also observed by Solbraa [7], Posey [14], Lee [22] and Austgen [23]. However, Austgen concluded that a better model representation of the ternary system (CO2–MDEA–H2O) of the model was achieved by adjusting all MDEA–H2O interaction parameters to zero instead of using the fitted parameters. Austgen, however, could not give a straightforward explanation for this unexpected observation. Contrary to the authors mentioned above, Poplsteinova et al. [24] calculated a continuously decreasing MDEA activity coefficient (with increasing H2O concentration), comparable with the model using parameters HV-II. In the present study it was decided to use the HV-I parameters in the model, because predictions of the MDEA activity coefficient of this model is in line with most of the other authors. Also the predicted activity coefficient of water at infinite dilution (pure MDEA) of the HV-I model is more in line with the other authors. However, future work is required to generate more experimental data in the commercially important MDEA concentrations range. Different types of data can be determined for the estimation of the Huron–Vidal parameters, however it has been demonstrated by Posey [14] that heat of mixing data and freezing point data are more suitable to predict the binary interaction for MDEA–H2O system.

3.3.3. CO2–MDEA

In the original model, the Huron–Vidal interaction parameters were determined by fitting them together with the ionic interaction parameters to ternary solubility data. As already discussed in a previous paper Huttenhuis et al. [15], the physical solubility of CO2 calculated by the model did not match with experimental data. The physical solubility of CO2 in MDEA cannot be measured directly, because there are always trace amounts of water present in pure MDEA. These small amounts of water will increase the CO2 solubility tremendously, due to the chemical reaction which will take place. So for the prediction of the physical solubility in aqueous MDEA, the CO2–N2O analogy is widely accepted in the literature. This theory is based on the fact that CO2 and N2O are rather similar molecules. The only difference between the molecules is, that N2O does not chemically (only physically) dissolve in aqueous MDEA. According to the CO2–N2O analogy the Henry’s constant (physically dissolved CO2) of CO2 in aqueous MDEA can be calculated as given by the formula below:

$$H_{CO_2,\text{aq, MDEA}} = \frac{H_{CO_2,\text{water}}}{H_{N_2O,\text{water}}} \times H_{N_2O,\text{aq, MDEA}}$$  \hspace{1cm} (19)

So the physical solubility of CO2 in aqueous MDEA can be determined by measuring the solubility of N2O in water and aqueous MDEA and the solubility of CO2 in water. In this, indirect, way binary interaction parameters for MDEA–CO2 can be obtained by using the physical solubility data of CO2 in aqueous MDEA derived from the equation above and the already determined binary interaction parameters of the MDEA–H2O and the CO2–H2O system. For the solubility of CO2 and N2O in water the empirical correlation of Jamal [25] was compared with the relation presented by Versteeg and van Swaaij [26]. The solubility predicted by both relations were comparable until a temperature of approximately 333 K. Above this temperature the Henry constant of N2O predicted by Versteeg was higher than the Henry constant calculated from the relation of Jamal. Therefore some additional experiments were carried out to verify, which relation was more correct. Experimental data of Jou et al. [27] were also used for the comparison, because in this work experiments where carried out at higher temperatures until 413 K. In Fig. 5 it can be seen that the new experimental data and the work of Jou et al. [27] are more in line with the relation of Jamal, so it was decided to use this correlation for the prediction of N2O and CO2 in water.

Fig. 5. Henry constant of N2O in water according relation of Jamal [25], Versteeg and van Swaaij [26], experimental data from Jou et al. [27] and experimental data from this work.

<table>
<thead>
<tr>
<th>Reference</th>
<th>T (K)</th>
<th>MDEA (wt.%)</th>
<th>Number of experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haimour and Sandall [28]</td>
<td>288–308</td>
<td>10–20</td>
<td>12</td>
</tr>
<tr>
<td>Jou et al. [29]</td>
<td>298–398</td>
<td>0–40</td>
<td>14</td>
</tr>
<tr>
<td>Versteeg and van Swaaij [26]</td>
<td>293–333</td>
<td>4–32</td>
<td>50</td>
</tr>
<tr>
<td>Li et al. [30]</td>
<td>303–313</td>
<td>30</td>
<td>3</td>
</tr>
<tr>
<td>Pawlak and Zarzycki [31]</td>
<td>293</td>
<td>0–100</td>
<td>9</td>
</tr>
</tbody>
</table>
The available volumetric data as specified above must be converted from volumetric to molar units, so the density of the solutions should be known. Therefore the correlation as presented by Al-Ghawas et al. [32] was used. With the above set of experimental data and correlations, new Huron–Vidal interaction parameters were determined for the CO2–MDEA binary system and the physical solubility of CO2 in aqueous MDEA was calculated and compared with the results of the original model and the experimental results of Pawlak and Zarzycki [31]. In Fig. 6 the results can be seen at 293 K and from this figure it can be concluded that the accuracy of the model is improved significantly with respect to the physical solubility of CO2 in aqueous MDEA.

All solubility data of N2O in aqueous MDEA from the experimental database (Table 5) were compared with results of the updated model. AAD and BIAS-deviation were, respectively, 2.7 and 0.2%.

3.3.4. CH4–MDEA

In the original model of Solbraa [7] both the molecular interaction parameter (CH4–MDEA) and the ionic interaction parameter (CH4–MDEAH+) were determined by regressing the model to experimental data of Addicks et al. [33] for the quaternary reactive system (CO2–MDEA–H2O–CH4). In this way two fitting parameters were determined by fitting them to one set of dependent experimental data. In this work a more sound fundamental approach is used. The molecular interaction parameter \( k_{ij} \) for MDEA–CH4 is determined by fitting the EOS model with a van der Waals mixing rule with experimental data for the molecular system CH4–MDEA–H2O (Jou et al. [34]). Because the CH4–H2O and MDEA–H2O binary interaction parameters were already determined, the CH4–MDEA parameter can be determined by regressing to the available experimental data. Jou et al. [34] determined the physical solubility of CH4 in a 3 M aqueous MDEA solution in the temperature interval 298–403 °C. In total 44 experiments were carried out. When the experimental data of Jou et al. [34] were compared with the model total AAD and BIAS-deviation were, respectively, 10.5 and 2.2%. In Fig. 7 the model results are compared with the experimental data at 298 and 348 K, respectively.

3.3.5. Summary

In the above paragraphs all binary molecular interactions which are applicable in the MDEA–H2O–CO2–CH4 system were discussed. In Table 6 the determined interaction parameters are presented.

3.4. Binary ionic interaction parameters

3.4.1. Ionic interaction parameters in MDEA–H2O–CO2 system

For the development of the electrolyte part of the EOS model the ionic interaction parameters \( W_{ij} \) have to be determined. As mentioned in Section 2.4, only the cation–molecule and the cation–anion interactions parameters have to be determined. For the ternary system MDEA–CO2–H2O the interaction of MDEAH+–ion with MDEA, H2O, OH−, CO2, HCO3− and CO32− should be determined. Because the concentration of OH−-ions in the system is normally very low, the MDEAH+–OH− binary interaction parameter was not fitted but estimated by the correlation given by Fürt and Renon [9]. So the remaining five fitting parameters were determined via the experimental VLE-database for the ternary system MDEA–CO2–H2O. It must be noted, however, that the experimental database as used by Solbraa [7] was adapted significantly. A detailed discussion of these changes is given by Huttenhuis et al. [15].

The experimental database as used for the determination of MDEAH+–interaction parameters is presented in Table 7. The database for the determination of the MDEAH+–interaction parameters consisted of 283 data points. When the distribution of process conditions of this database is studied the following conclusions can be drawn:

- Most of the experimental data (>30% of total experiments) were determined at conditions where the CO2 loading is lower than 0.1 mol CO2/mol amine).
- Most of the experimental data were determined at 313 and 373 K (respectively 27 and 17% of the total experiments)
- Most of the experimental data were determined at 25 and 30 wt.% MDEA (both 30% of total experiments)

When the new binary interaction parameters were determined the model results were compared with the experimental database
Table 6
Molecular interaction parameters

<table>
<thead>
<tr>
<th>Comp. $i$</th>
<th>CO$_2$</th>
<th>CO$_2$</th>
<th>CO$_2$</th>
<th>MDEA</th>
<th>MDEA</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. $j$</td>
<td>MDEA</td>
<td>H$_2$O</td>
<td>CH$_4$</td>
<td>MDEA</td>
<td>H$_2$O</td>
<td>CH$_4$</td>
</tr>
<tr>
<td>$k_{ij}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_{ji}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta_{ij}$ (J mol$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta_{ij}$ (J mol$^{-1}$ K$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta_{ij}$ (J mol$^{-1}$ K$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7
Literature references used for the fitting of the ionic parameters of the MDEA–CO$_2$–H$_2$O system

<table>
<thead>
<tr>
<th>Ref.</th>
<th>MDEA conc. (wt.%)</th>
<th>Temperature (K)</th>
<th>Liquid loading (mol CO$_2$/mol amine)</th>
<th>Number of points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lemoine et al. [35]</td>
<td>23.6</td>
<td>298</td>
<td>0.02–0.26</td>
<td>13</td>
</tr>
<tr>
<td>Austgen and Rochelle [36]</td>
<td>23.4</td>
<td>313</td>
<td>0.006–0.65</td>
<td>14</td>
</tr>
<tr>
<td>Kuranov et al. [37]</td>
<td>19.2</td>
<td>313</td>
<td>1.56–2.46</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>18.8</td>
<td>313, 333, 373, 413</td>
<td>0.36–2.62</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>32.1</td>
<td>313, 333, 393, 413</td>
<td>0.41–4.46</td>
<td>40</td>
</tr>
<tr>
<td>Rho et al. [38]</td>
<td>5</td>
<td>323</td>
<td>0.24–0.68</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>20.5</td>
<td>323, 348, 373</td>
<td>0.026–0.848</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>323, 348, 373</td>
<td>0.0087–0.385</td>
<td>26</td>
</tr>
<tr>
<td>Kamps et al. [16]</td>
<td>32.0</td>
<td>313</td>
<td>0.85–1.24</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>48.8</td>
<td>393</td>
<td>0.32–0.56</td>
<td>6</td>
</tr>
<tr>
<td>Huang and Ng [39]</td>
<td>23</td>
<td>313, 343, 373, 393</td>
<td>0.00334–1.34</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>313, 343, 373, 393</td>
<td>0.00119–1.16</td>
<td>37</td>
</tr>
<tr>
<td>Rogers et al. [40]</td>
<td>23</td>
<td>313, 323</td>
<td>0.000591–1.177</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>313</td>
<td>0.00025–0.037</td>
<td>14</td>
</tr>
</tbody>
</table>

3.4.2. Ionic interactions parameters in MDEA–H$_2$O–CO$_2$–CH$_4$ system

For the quaternary system CO$_2$–MDEA–H$_2$O–CH$_4$ four additional interaction parameters must be determined compared to the system without methane, i.e. the MDEA–CH$_4$ (Section 3.3.4), CO$_2$–CH$_4$ (Section 3.3.1), H$_2$O–CH$_4$ (Section 3.3.1) parameter and the MDEAH$^+$–CH$_4$ parameter. The binary molecular interaction parameters (MDEA–CH$_4$, CO$_2$–CH$_4$ and H$_2$O–CH$_4$) have already been determined as described in Section 3.3. So only one additional parameter, the MDEAH$^+$–CH$_4$ interaction parameter, was determined by regressing the model with experimental VLE data of Addicks et al. [33]. Addicks measured the CO$_2$ and CH$_4$ solubility in aqueous MDEA. In total 31 experimental data points were used for the parameter fitting. When the model was fitted to the experimental data of Addicks et al. [33]; the AAD and BIAS were 35 and 22%, respectively, for the partial pressures of CO$_2$ and 21.5 and −2.8% for the total pressure. Unfortunately, the data of Addicks could not be compared with experimental data from other authors, because this information is unique in its kind.

In Table 8 the ionic interaction parameters are presented.

Table 8
Ionic interaction parameters

<table>
<thead>
<tr>
<th>Comp. $i$</th>
<th>MDEAH$^+$</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>CO$_2$</td>
<td>H$_2$O</td>
<td>MDEA</td>
<td>HCO$_3^-$</td>
<td>CO$_3^{2-}$</td>
<td>CH$_4$</td>
</tr>
<tr>
<td>$W_{ij}$ (m$^3$ mol$^{-1}$)</td>
<td>2.48E − 04</td>
<td>4.09E − 04</td>
<td>1.95E − 03</td>
<td>−1.29E − 04</td>
<td>−3.58E − 04</td>
<td>4.93E − 04</td>
</tr>
</tbody>
</table>

4. Modeling results

4.1. Ternary system CO$_2$–MDEA–H$_2$O

The model CO$_2$–MDEA–H$_2$O has been validated with the experimental database for this ternary system. As described in Section 3.4 the AAD and BIAS were 24 and 8.3%, respectively. In Fig. 8, the parity plot with the experimental database of Table 7 is presented for different liquid loadings.

From this figure it can concluded that at low loadings, the partial pressure seems to be somewhat under predicted by the model. When looking to the data at a CO$_2$ partial pressure of approximately 1 kPa, it can be seen that the predictions for the higher liquid loadings (0.1–1) (at equal partial pressure) are relatively better than the predictions at low liquid loadings (0.01–0.1). So, it seems that the quality of the experimental data at low liquid loadings is more scattered compared with data at higher liquid loadings. In Fig. 9 the experimental data, used for the regression
of parameters of the present E-EOS model is compared for the different authors.

In Table 9 the results of this analysis are presented. Also the model predictions at different temperatures and different MDEA concentrations are presented in Table 9.

From Table 9 it can be concluded that model predictions are good when the liquid loading is above 0.1 mol CO₂/mol amine, because the BIAS-deviation in this area is only +1%. For low loadings (<0.1 mol/mol) the model is always under predicting the CO₂ partial pressure; BIAS-deviation in this area is more than +20% and even more than +30% for liquid loadings below 0.01 mol/mol. A relation between temperature and model predictions cannot be seen clearly. BIAS and AAD deviation are not changing systematically with temperature. The model predictions for MDEA concentration between 20–24% are very good (BIAS = −1%). However, at lower and higher MDEA concentrations the match between model results and experimental data is worse. When looking to the influence of the author on the model predictions it can be concluded that the match with experimental data of Austgen and Rochelle [36] and Kuranov et al. [37] are rather good, with respect to BIAS-deviation; It must be noted, however, that Kuranov did not measure solubility data at low liquid loadings; only high loading data were measured.
As it can be concluded from Table 9, Figs. 8 and 9, the electrolyte equation of state model used in this work, gives an under-prediction of the partial pressure CO2, i.e. an over-prediction of the gas solubility in the low loading area. This observation was also reported by Fürst and Planche [6], Austgen and Rochelle [36] and Weiland et al. [41]. It must be noted that the models used by these authors were different, so it is not clear at this state to determine exactly the phenomena that cause these under-predictions.

Generally, the spread in experimental determined solubility is much higher at lower loadings (<0.1), compared with the higher liquid loadings. So apparently the experimental accuracy in this loading range is substantially lower compared with the higher liquid loadings. In order to take this inaccuracy at lower liquid loadings into account in the presently developed E-EOS model, these were omitted from the database. Next new ionic interaction parameters ($W_{ij}$) were determined with the reduced experimental database excluding the data at loadings below 0.1. From an analysis of the results it was concluded that on average the model was not improved significantly. Still there was a large under-prediction of the CO2 partial pressure. Therefore the model with the ionic parameters determined with the whole database as presented in Table 7 was used for further study. It can also be concluded that at lower liquid loadings a need exists for better and more reliable experimental data.

As mentioned before one of the major advantages of a rigorous fundamentally more correct electrolyte E-EOS model compared to the more simplified models, is that the distribution of the different species present in the liquid phase can be calculated more accurately. Therefore the speciation calculated by the present model was compared with experimentally determined speciation carried out by Poplsteinova et al. [24]. Poplsteinova et al. measured the molecular and ionic concentrations at equilibrium conditions for the absorption of CO2 in different amine solutions with a NMR technique. In Fig. 10 experimental data of Poplsteinova et al. [24] are compared with the E-EOS model results.

From Figs. 10 and 11 it can be concluded that the speciation calculations of the present model are well in line with the experimental data of Poplsteinova et al. [24]. At higher liquid loadings (>0.8 mol/mol), a small over-prediction of MDEAH+ (Fig. 10) and HCO3− and an under-prediction of CO32− (Fig. 11) is seen; however the deviations are relatively small.

In Figs. 12 and 13 the activity coefficients as calculated by the E-EOS are presented for the various species at different liquid loadings. From this figure it can be seen that the activity of the MDEAH+ (Fig. 12) is decreasing and the activity of HCO3− (Fig. 13) is increasing with increasing CO2 liquid loading. The change in activity coefficient for the other species with liquid loading is relatively small. However, it must be concluded that for all species, excluding CO2, the activity coefficients are deviating substantially from unity. It has been proven that the reaction constant based on concentrations is not a true constant.
because it is dependent on the other non-reactive species present in the liquid phase. However when the reaction rate constant is based on activities instead of concentrations a “true” constant can be derived and all non-idealities of the system are incorporated in the activities of the reactive component. For example, the influence of the counter-ion (Li, Na and K) on the reaction between the hydroxide ion and carbon dioxide has been studied experimentally by Haubrock et al. [42].

4.2. Quaternary system CO\textsubscript{2}–MDEA–H\textsubscript{2}O–CH\textsubscript{4}

The system CO\textsubscript{2}–MDEA–H\textsubscript{2}O–CH\textsubscript{4} has been validated with the experimental data from Addicks et al. [33] and the experimental data determined by Huttenhuis et al. [15]. Results are given in Table 10.

As can be concluded from Table 10, the E-EOS model is under-predicting (BIAS > 0) the CO\textsubscript{2} partial pressure for both authors. In Figs. 14 and 15 the results of the E-EOS model are compared with the experimental data for two different amine concentrations (35 wt.% and 50 wt.%). As it can be seen from this figures, the prediction for the higher (50 wt.%) MDEA concentration (BIAS = +25.2%) is poorer, than the model predictions for 35 wt.% MDEA (BIAS = +5.5%). This was also seen for the solubility data of the ternary system (CO\textsubscript{2}–MDEA–H\textsubscript{2}O). As it can be seen from Table 9, the model predictions with MDEA concentrations of 20–24 wt.% (BIAS = −1%) are much better than the predictions for 47–50 wt.% (BIAS = 16%). A possible explanation for this different behaviour is that the CO\textsubscript{2}–N\textsubscript{2}O analogy used for the determination of the Huron–Vidal parameters of the CO\textsubscript{2}–MDEA system might not be applicable for the higher MDEA concentrations. The influence of methane on the solubility of CO\textsubscript{2} in the liquid phase is predicted correctly by the model. As can be seen from both the model and from the experiments, the CO\textsubscript{2} solubility decreases with increasing partial pressure of methane. Other thermodynamic models like Kent–Eisenberg [2], Debye–Hückel [43] and NRTL [44] model do not have this effect of inert gas and/or system pressure on the solubility, included in the same way for liquid and vapour phase.

In Fig. 16 the partial pressure, fugacity and fugacity coefficient of CO\textsubscript{2} are presented graphically as function of partial pressure methane. From this graph it can be seen that the CO\textsubscript{2} partial pressure is increasing (which is equivalent to decreasing CO\textsubscript{2} solubility) with the partial pressure methane at constant CO\textsubscript{2} liquid loadings. However, the CO\textsubscript{2} fugacity, remains fairly constant at the different methane partial pressures.

From Fig. 16 it can be concluded that the decreasing solubility of CO\textsubscript{2} at conditions with higher partial pressures of methane can be attributed by a decreasing fugacity coefficient of CO\textsubscript{2}.

5. Conclusions

In the present study an electrolyte equation of state model as developed by Solbraa [7] was systematically reviewed, optimized and validated with experimental data for the system MDEA–H\textsubscript{2}O–CO\textsubscript{2}–CH\textsubscript{4}. With this model excellent results were obtained and a lot of information can be derived. It has been proven (experimentally and by the model) that both the system pressure and/or partial pressure methane, respectively have a significantly effect on the solubility of CO\textsubscript{2} in aqueous MDEA solutions. A decrease in CO\textsubscript{2} solubility has been observed, when the partial pressure of methane is increased. As the partial pres-
sure CO\textsubscript{2} is increasing with the methane partial pressure, the CO\textsubscript{2} fugacity is less dependent of the methane partial pressure. So based on fugacities, it can be concluded that the CO\textsubscript{2} solubility seems only slightly dependent of methane partial pressure. At the moment it is not clear if this decrease in CO\textsubscript{2} solubility is caused by the increase in pressure of the system or that the additional methane is responsible for this phenomenon. Model predictions in general are in line with experimental data. At low CO\textsubscript{2} liquid loadings the predicted CO\textsubscript{2} partial pressure is lower than the experimental partial pressure. This conclusion is in line with most other authors. At lower MDEA concentrations (<30 wt.%) model predictions are better than at high MDEA concentrations. This phenomena may be caused by the fact the CO\textsubscript{2}–N\textsubscript{2}O analogy as used in this work is not applicable in more concentrated amine solutions.