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Gas solubility of H_2S and CO_2 in aqueous solutions of *N*-methyldiethanolamine

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Abstract

Alkanolamine processes are used in the industry to remove acid gases, like CO_2, H_2S and other sulphur components, from natural gas and industrial gas streams. In this process the acid components react with the basic alkanolamine solution via an exothermic, reversible reaction in a gas/liquid absorber. The composition of these amine solutions is continuously changed to optimise the (selective) removal of the several acid components. For the design of gas treating equipment accurate mass transfer, reaction kinetics and solubility data of acid gases in aqueous alkanolamine solutions are required. In this paper new solubility data of H_2S and CO_2 in aqueous MDEA at different conditions encountered in modern gas treating facilities are presented. The experimental pressure and temperature were varied from 6.9 to 69 bar (methane was used as make-up gas) and from 10 to 25 °C respectively. These new solubility data were evaluated and correlated with an Electrolyte Equation of State Model (EOS) as originally proposed by Fürst and Renon [Fürst, W., Renon, H., 1993. Representation of Excess Properties of Electrolyte Solutions Using a New Equation of State. AIChE J., 39 (2), pp. 335.]. The application of Equation of State Models for the prediction of VLE data for reactive, ionic systems is a rather new development in this field.
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Keywords: Chemical absorption; Carbon dioxide; Hydrogen sulphide; Alkanolamines; Vapour liquid equilibrium

1. Introduction

Acid gases like CO_2, H_2S and other sulphuric components are usually to some extent present in natural gas and industrial gases. They may have to be removed (selectively) from these gas streams for operational, economical or environmental reasons. One of the most commonly used processes for the removal of acid components is absorption in alkanolamine based solvents. In this process the acidic components react with an alkanolamine absorption liquid via an exothermic, re-

versible reaction in a gas/liquid contactor. In a following process step the acidic components are removed from the solvent in a regenerator, usually at low pressure and/or high temperature. For the design of such process systems reliable solubility data of acid gases in aqueous alkanolamine solutions are indispensable. In the present study new obtained solubility data of CO_2 and H_2S in aqueous MDEA solutions will be presented.

The ability of an alkanolamine solution to remove acidic gases is determined by the acid gas solubility, the reaction rate and the mass transfer properties. In this study the experimental determined solubility data of CO_2 and H_2S in aqueous MDEA solutions will be presented at temperatures of 283 and 298 K, acid gas partial pressures

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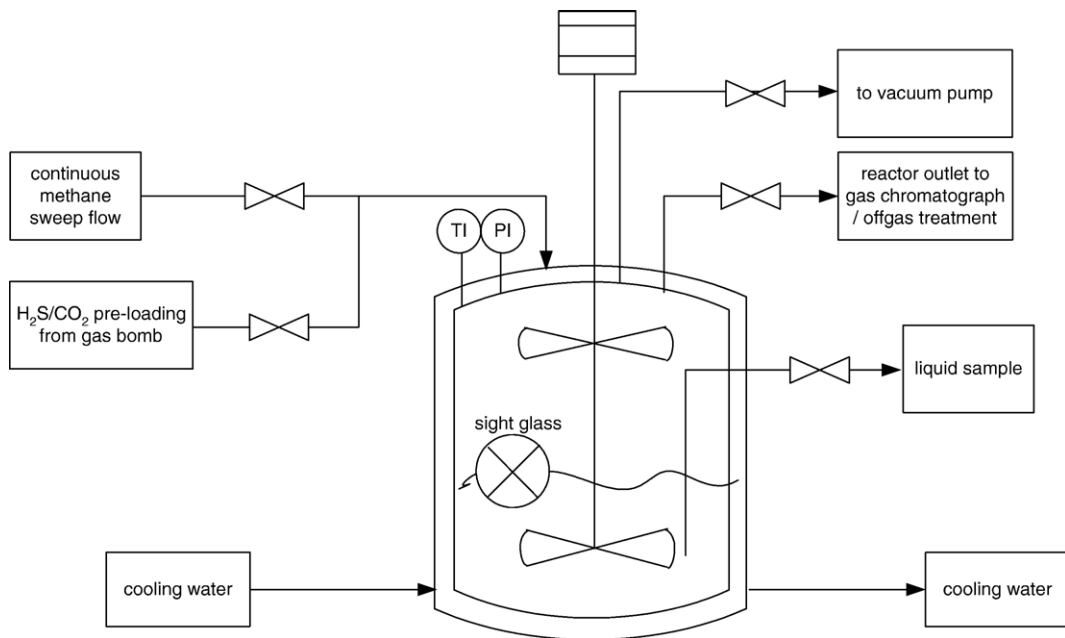*E-mail address:* patrick.huttenhuis@procede.nl (P.J.G. Huttenhuis).

Fig. 1. Schematic representation of the reactor.

0.05–10 kPa and a total system pressure of 6.9–69 bar with methane as make-up gas. In open literature normally only the partial pressure acid gas is specified and not the total system pressure, because experiments are carried out at low pressure. In this study the influence of the total system pressure (with methane as make-up gas) on the acid gas solubility is also shown. This system pressure is an important parameter, because normally there is a substantial difference in total system pressures between an industrial absorber (70–100 bar) and a regenerator (2–3 bar). So if the system pressure influences the acid gas solubility, the low pressure experimental solubility data cannot be used in the high pressure absorber. Also the measured acid gas solubility data at relatively low temperatures of 283 and 298 K are scarce. The new obtained solubility data are used to develop and validate an electrolyte Equation of State Model that can be used to predict the equilibria for these treating processes.

2. Experimental

For all experiments demineralised water was used. N-methyldiethanolamine (purity > 99%) was supplied by
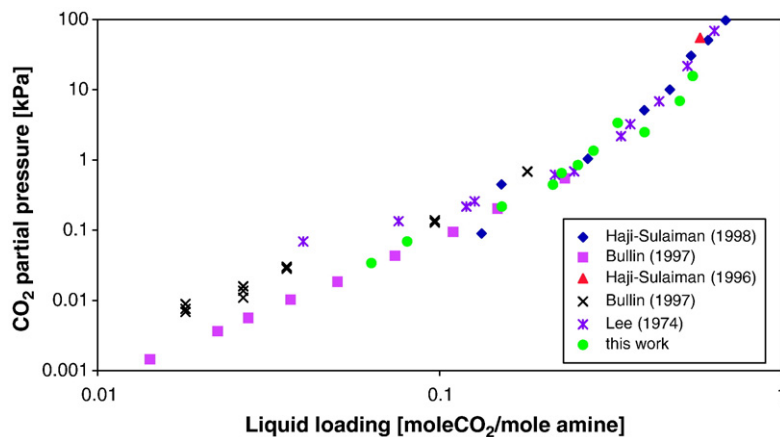

Fig. 2. Validation experiments for the solubility of CO_2 in 20 wt.% DEA at 323 K.

Table 1
Experimental solubility data of CO_2 in an aqueous solution of 35 wt.% MDEA

T=283 K			T=298 K		
P (bar)	α (mol/mol)	P_{CO_2} (kPa)	P (bar)	α (mol/mol)	P_{CO_2} (kPa)
6.9	0.048	0.054	6.9	0.048	0.170
	0.143	0.314		0.048	0.168
	0.276	1.000		0.143	1.001
	0.325	1.324		0.270	3.037
34.5	0.143	0.385	34.5	0.048	0.198
	0.275	1.237		0.048	0.195
	0.319	1.658		0.143	1.204
69.0	0.140	0.482		0.276	3.728
	0.275	1.448		0.327	4.815
	0.320	2.141	69.0	0.047	0.245
				0.047	0.235
				0.143	1.340
				0.279	4.408
				0.316	6.121

Acros. Hydrogen sulfide, (purity > 99.6%), Carbon dioxide (purity > 99.7%) and Methane (purity > 99.5%) were supplied by Hoekloos.

For the experimental determination of the gas solubility data an intensively stirred, 1 l, Büchi reactor located at the laboratories of Procede was used. A drawing of the used reactor system is presented in Fig. 1. From this reactor both gas and liquid samples were withdrawn and analysed.

The set-up basically consisted of three parts:

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

With this set-up it was possible to measure the total H_2S and CO_2 concentration in both the gas and the liquid phase independently. As it was also possible to determine the total amount of added H_2S or CO_2 to the reactor a mass balance check was made to determine the accuracy of the experiments. During an experiment the reactor filled with approximately 0.5 l aqueous amine solution was evacuated until the vapour pressure of the solution was reached. A predefined amount of acid gas was routed to the reactor. The partial pressure methane was increased to the required total system pressure. While the reactor content was highly stirred, a small sweep stream methane (approximately 200 Nml min^{-1}) was routed through the reactor and the outlet was analysed in a Gas Chromatograph for acid gas composition. When equilibrium was reached the reactor was blocked and a small liquid sample was taken and the amount of acid gas in it was analysed with a suitable liquid phase titration technique. The CO_2 content was measured with an automated organic acid–base titration and the H_2S content was measured with an automated iodometric back titration with thiosulfate. The liquid sample containing CO_2 was added to a vessel containing boiling sulfuric acid. The high acidity and high temperature and addition of a small nitrogen purge flow caused that the CO_2 was completely stripped from the sample. A reflux cooler was used to prevent contamination of CO_2 with sulfuric acid and water. The CO_2 was routed to a second vessel containing MEA and an organic solvent (DMF). In this vessel the CO_2 was captured by the MEA and subsequently the pH dropped. The total amount of CO_2 was determined by keeping the MEA solution at its original pH with a strong base (TBAH). For the determination of the amount H_2S in the liquid sample, an excess amount of iodine was added to react with H_2S in an acid solution. The amount of excess iodine was determined by using sodium thiosulphate. Both titration methods were calibrated extensively with samples containing a known amount of Na_2CO_3 and Na_2S respectively.

When the acid gas partial pressure and liquid loading were determined a consecutive experiment at a higher liquid loading was started. The reactor was depressurized and an additional amount of acid gas from the gas bomb was added to the reactor. For each experiment it was verified that the amount of acid gas removed during the

Table 2
Experimental solubility data of CO_2 in an aqueous solution of 50 wt.% MDEA

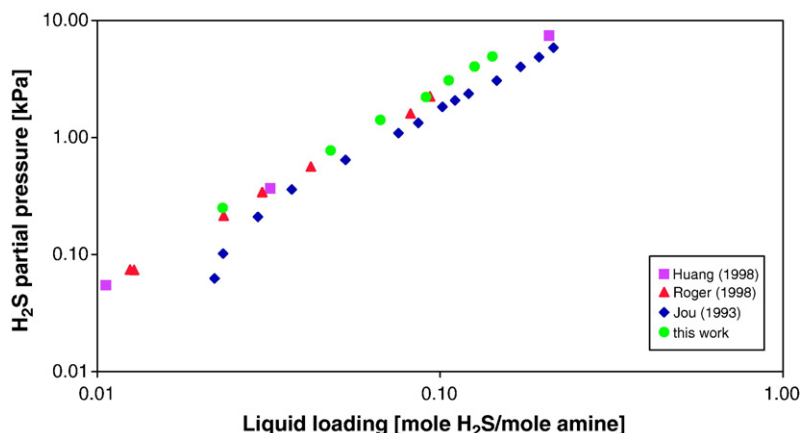| T=283 K			T=298 K		
P (bar)	α (mol/mol)	P_{CO_2} (kPa)	P (bar)	α (mol/mol)	P_{CO_2} (kPa)
6.9	0.144	0.671	6.9	0.047	0.441
	0.270	1.754		0.111	2.379
	0.428	3.848		0.139	2.143
34.5	0.150	0.781		0.238	7.206
	0.273	2.103		0.265	5.492
	0.428	5.036		0.287	7.773
69.0	0.152	0.939		0.424	37.07
	0.275	2.695		0.551	70.29
	0.409	5.887		0.700	212.57
			34.5	0.048	0.487
				0.141	2.698
				0.272	7.315
				0.887	180.73
				0.936	986.80
				1.105	351.37
			69.0	0.047	0.570
				0.128	3.092
				0.272	8.720

Fig. 3. Validation experiments for the solubility of H_2S in 50 wt.% MDEA at 313 K.

depressurizing phase was neglectable compared to the total amount of acid gas absorbed by the alkanolamine solution.

3. Results

3.1. Experiments with CO_2

In order to establish the accuracy of the experimental technique, set-up and procedures, some validation experiments were carried out and the results were compared with CO_2 solubility data available in the literature. The validation experiments were carried out with a 20 wt.% aqueous diethanolamine (DEA) solution at 323 K, because at these conditions a huge amount of experimental data are available. The results of the measured data are compared to data of Haji-Sulaiman and Aroua (1996), Bullin et al. (1997) and Lee et al. (1974). A comparison is presented in Fig. 2.

Fig. 2 illustrates some scatter in literature data among the different authors. The newly obtained values are in good agreement with the other data presented in Fig. 2. At higher liquid loadings (>0.4 mol/mol) the measured CO_2 partial pressure are lower than that measured by Haji-Sulaiman et al. (1998) and Lee et al. (1974), how-

ever, most of the experiments presented in the present study were carried out at lower liquid loadings. It appears that the data of Lee et al. (1974) demonstrate substantial deviations in the low loading range. From Fig. 2, it can be concluded that our experimental set-up was able to reproduce results that are well in line with an existing literature data for a CO_2–DEA system.

New solubility data of CO_2 were obtained for two different amine solutions (35 and 50 wt.% MDEA) at two temperatures (283 and 298 K) and three system pressures (6.9, 34.5 and 69 bar) with methane as make-up gas. The experimental data are given in Table 1 (35 wt.% MDEA) and Table 2 (50 wt.% MDEA).

3.2. Experiments with H_2S

Initially, validation runs were carried out with 50 wt.% MDEA at 313 K and 3.5 bar (nitrogen as make-up gas). The results of these experiments are compared with

Table 3
Experimental solubility data of H_2S in an aqueous solution of 35 wt.% MDEA

T=283 K			T=298 K		
P (bar)	α (mol/mol)	P_{H_2S} (kPa)	P (bar)	α (mol/mol)	P_{H_2S} (kPa)
6.9	0.052	0.141	6.9	0.042	0.156
	0.171	1.057		0.165	1.495
34.5	0.112	0.638	34.5	0.102	0.707
	0.575	14.976		0.391	8.542
69.0	0.172	1.691	69.0	0.144	1.745
	0.574	18.982		0.449	14.838

Table 4
Experimental solubility data of H_2S in an aqueous solution of 50 wt.% MDEA

T=283 K			T=298 K		
P (bar)	α (mol/mol)	P_{H_2S} (kPa)	P (bar)	α (mol/mol)	P_{H_2S} (kPa)
6.9	0.081	0.486	6.9	0.028	0.153
	0.125	1.137		0.062	0.609
34.5	0.095	0.828		0.083	1.024
	0.365	8.349		0.105	1.484
69.0	0.132	1.760	34.5	0.028	0.179
	0.447	17.250		0.062	0.727
				0.083	1.19
				0.230	6.51
			69.0	0.028	0.21
				0.062	0.856
				0.083	1.411
				0.366	12.715

literature data from Huang and Ng (1998), Rogers et al. (1998) and Jou et al. (1993). A comparison of the present experimental data with the literature data is given in Fig. 3.

The literature data from Jou et al. (1993) differ significantly and systematically from the other literature sources and the present, new acquired data. Data by Jou demonstrate also a different trend especially in the low loading range. For this reason, the accuracy of these data is questionable; it seems straightforward to explain this difference by the influence of contaminations (primary and/or secondary amines) on the solubility of aqueous MDEA, however if this is the reason the effect would vanish at higher liquid loadings and this is not the case.

New solubility of H_2S were obtained for two different blends (35 and 50 wt.% MDEA) at two temperatures (283 and 298 K) and three pressures (6.9, 34.5 and 69 bar). The experimental data are given in Table 3 (35 wt.% MDEA) and Table 4 (50 wt.% MDEA).

3.3. Discussion

From the CO_2 and H_2S data in the above mentioned tables the following observations can be made. The acid gas partial pressure increases (solubility decreases) with:

- increasing liquid loading (and constant temperature, pressure and amine concentration)
- increasing temperature (and constant liquid loading, pressure and amine concentration)
- increasing amine concentration in the liquid phase (and constant temperature, pressure and liquid loading.

These observations are well in line with data presented by other authors in this field.

It can also be concluded that the solubility of H_2S and/or CO_2 is substantially affected by the methane partial pressure. Increasing the methane partial pressure results in a pronounced decrease of the solubility of the acidic component. This is line with the results of the experiments carried out by Addicks (2002). He measured the solubility of CO_2 and CH_4 in aqueous MDEA at pressures up to 200 bar. At the moment it is not known if the changing acid gas solubility is caused by the increased system pressure or by the presence of methane in the system.

4. Validation of model

4.1. General model description

The experimental results are compared with an electrolyte equation of state model (EOS), originally proposed by Fürst and Renon (1993). In this model the same equations, based on an equation of state, are used for both the liquid and vapour phase. The model can be extrapolated and the speciation of the components occurring in the liquid phase can be calculated. Moreover the solubility of physically dissolved hydrocarbons (i.e. methane) can be calculated. This is very important for the design of high pressure gas treating equipment and for the mass transfer calculations.

The model used in the present work is that originally developed by Solbraa (2002). Details about the model can be found in his work. In this paper the main equation and most important model parameters are given. This electrolyte equation of state was derived from an expression of the Helmholtz energy (Eq. (1)) with a non-electrolyte part (RF and SR1) and an electrolyte part (SR2, LR and BORN).

$$\left(\frac{A^{\mathrm{R}}}{\mathrm{RT}}\right) = \left(\frac{A^{\mathrm{R}}}{\mathrm{RT}}\right)_{\mathrm{RF}} + \left(\frac{A^{\mathrm{R}}}{\mathrm{RT}}\right)_{\mathrm{SR1}} + \left(\frac{A^{\mathrm{R}}}{\mathrm{RT}}\right)_{\mathrm{SR2}} + \left(\frac{A^{\mathrm{R}}}{\mathrm{RT}}\right)_{\mathrm{LR}} + \left(\frac{A^{\mathrm{R}}}{\mathrm{RT}}\right)_{\mathrm{BORN}} \tag{1}$$

The first two terms, resp. repulsive forces (RF) and attractive short range interactions (SR1), are given by the molecular part of the equation of state. This model was based on a cubic equation of state (Schwarzentruber et al. (1989) modification of the Redlich–Kwong EOS) with a Huron–Vidal mixing rule. Most important parameters of this part of the model are the critical properties, Schwarzentruber parameters and molecular (Huron–Vidal) interaction parameters. These molecular interaction parameters are determined by fitting experimental molecular binary data with the EOS model.

To account for electrolyte systems three ionic terms were included in the model: a short-range ionic term (SR2), a long range ionic term (LR) and a Born term. The third term of the model is predicting the short range ionic interactions. The most important parameters of this interaction are the molecular and ionic diameter and the ionic binary interaction parameters. These ionic interaction parameters are determined by fitting the EOS model with experimental solubility data for the system CO_2–MDEA–H_2O. In this work only the interactions cations–molecules and cations–anions were taken into account. Most important parameter of the 4th term in the Electrolyte Equation of State Model (long range ionic attractive forces) is the dielectric constant of the solvent.

A Born term has been added to correct the standard states of ions. This term gives the solvation energy of an ion in a dielectric medium, relatively to vacuum. The
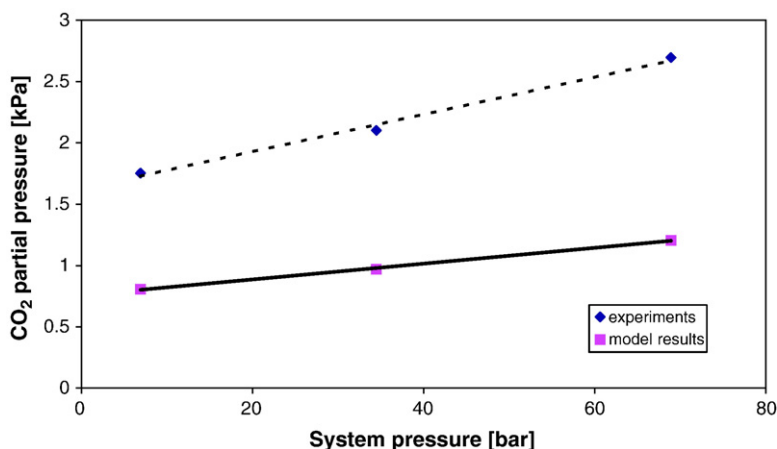
Fig. 4. Influence of partial pressure methane for both EOS model and experiments in case of CO_2–MDEA–water–methane experiments ($T=283$ K, 50 wt.% MDEA, liquid loading$=0.27$ mol CO_2/mol amine).

Born term is an important parameter for modelling both liquid and vapour phase with an EOS model, because this parameter is responsible for the phenomena that ions stay in the liquid phase mainly. Fürst and Renon (1993) did not use the Born term in their original publication, but it has been added in a later paper on LLE in electrolyte systems (Zuo et al., 2000). Solbraa (2002) developed his EOS model for CO_2–MDEA–water system. The model was also validated by Solbraa for a high pressure system (100–200 bar) of CO_2–MDEA–water–methane.
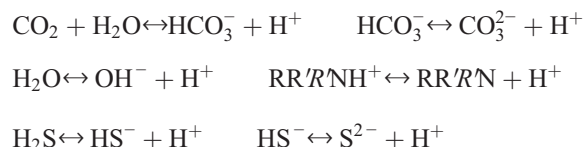
In this EOS model the following parameters have to be obtained:

- Molecular and ionic parameters, like critical data and polar parameters. These data are independent of the

model and can be found in open literature, measured independently or estimated.
- Binary and ionic interactions parameters. These parameters are related to the model and should be determined via fitting procedures or estimations.

The following chemical reactions occur in an aqueous MDEA solution when CO_2 and H_2S are present:

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \qquad HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

$$H_2O \leftrightarrow OH^- + H^+ \qquad RR'R'NH^+ \leftrightarrow RR'R'N + H^+$$

$$H_2S \leftrightarrow HS^- + H^+ \qquad HS^- \leftrightarrow S^{2-} + H^+$$

Where R corresponds to a methyl group and R′ to an ethanol group.

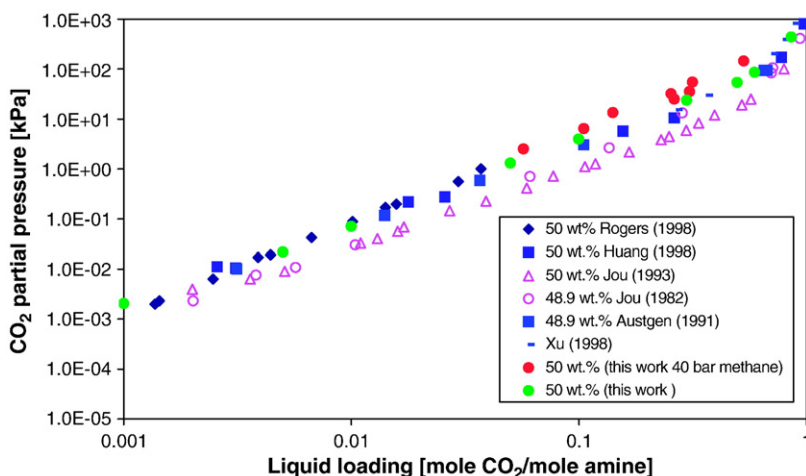

Fig. 5. Literature data of CO_2–MDEA–H_2O system at 40 °C and with 50 wt.% MDEA.

4.2. Validation of original Solbraa model

The results of the CO_2 experiments of this work were directly compared to the EOS model of Solbraa (2002). A large systematic deviation was observed between the experimental results and the predictions of the EOS model. The EOS was always underestimating the CO_2 partial pressure. Both the AAD (Eq. (2)) and BIAS (Eq. (3)) compared with these experiments were 40% respectively.

$$AAD = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{Y_{i,\exp} - y_{i,\text{calc}}}{y_{i,\exp}} \right| *100\% \qquad (2)$$

$$BIAS = \frac{1}{n} \sum_{i=1}^{n} \frac{y_{i,\exp} - y_{i,\text{calc}}}{y_{i,\exp}} *100\% \qquad (3)$$

In the following paragraphs the reason for this big difference in model predictions and experimental results is discussed.

In Fig. 4 the influence of the methane partial pressure can be seen for both the experiments and the EOS model.

From Fig. 4 it can be concluded that the slope of both graphs (influence of methane partial pressure) are rather similar, i.e. a (pseudo) proportional relation exists between total system pressure and CO_2 partial pressure, but the intercept with the y-axis in case of the experiments is much higher than calculated by the model. The results at system pressure zero bar can be compared with results at zero partial pressure methane. It was concluded that the large deviations between model and experiments were not caused by the input parameters and properties of methane in the model, but were caused by the values

applied for the ternary system CO_2–MDEA–water. For this reason the determination and fitting procedure of the ionic parameters of the CO_2–MDEA–water system as carried out by Solbraa (2002) was critically reviewed. The relevant ionic parameters in this system were fitted against experimental data available in open literature.

4.3. Influence of experimental database

In Fig. 5 an overview of available literature for 50 wt.% MDEA at 40 °C is presented graphically.

From this figure it can be concluded that a lot of scatter exists in the literature data. The results of the present experiments are well in line with a large group of literature sources. However the data of Jou et al. (1982,1993) give CO_2 partial pressures, that are substantially lower than the other literature sources. This observation was also seen at other conditions; Data by Jou in general have a lower partial pressure CO_2 (higher CO_2 solubility), which also was seen in Fig. 3 (validation of H_2S experiments). An explanation of this systematically under-prediction of the acid gas partial pressure by Jou could be that the MDEA used by Jou contained a certain amount of impurities, like primary and secondary amines. These small amounts of amines can have a remarkable influence on the measured acid gas solubility. However influence of amine impurities on the solubility should vanish at higher liquid loadings and that is not seen in Fig. 5, so the real reason is not known at this stage. The database used by Solbraa (2002) for the determination of the ionic interaction parameters of the CO_2–MDEA–water system was for a main part (approximately 35%) based on data by Jou'; so a critical review of available literature data has been carried out and a new reliable data were included in the

Table 5
Literature references used for the fitting of the ionic parameters of the CO_2–MDEA–water system

| Reference	MDEA conc. (wt.%.)	Temperature (K)	Liquid loading (mol CO_2/mol amine)	Number of points (−)
Lemoine et al. (2000)	23.6	298	0.02–0.26	13
Austgen and Rochelle (1991)	23.4	313	0.006–0.65	14
Kuranov et al. (1996)	19.2	313	1.56–2.46	9
	18.8	313,333,373,413	0.36–2.62	32
	32.1	313,333,373,393,413	0.41–4.46	40
Rho et al. (1997)	20.5	323,348,373	0.026–0.848	32
	50	323,348,373	0.0087–0.385	26
Kamps et al. (2001)	32.0	313	0.85–1.24	5
	48.8	313,353,393	0.12–1.15	23
Huang and Ng (1998)	23	313,343,373,393	0.00334–1.34	29
	50	313,343,373,393	0.00119–1.16	37
Rogers et al. (1998)	23	313	0.000591–.1177	14
	23	323	0.001–0.07	6

database. The following modifications to the original database of Solbraa (2002) were incorporated:

- All data of Jou et al. (1982, and 1991) were deleted. As mentioned before these data showed a systematically under-prediction of acid gas partial pressure.
- All data of Bhairi (1984) were deleted. These data showed a strange behaviour at low loadings (no straight line of log–log graph of partial pressure versus liquid loading).
- All data of Chakma (1987) were deleted due to assumptions which have been made in the experimental procedure. The experiments of Chakma were carried out at high temperatures (373–473 K) and no corrections for change in liquid density and water evaporation were made. Also possible degradation of MDEA at these high temperatures was not taken into account.
- Data of Rho et al. (1997) measured with 5 wt.% and 75 wt.% MDEA were deleted. These results cannot be validated and model simplifications, like neglecting CO_3^{2-} and OH^- concentrations are not valid under these conditions.
- Recent data of Kamps et al. (2001), Rogers et al. (1998) and Huang and Ng (1998) were included. Low loading data of Rogers et al. (1998) at 50 wt.% MDEA and 40 °C were not used, because these data were measured at very low loadings (<0.004 mol CO_2/mol amine) and at these conditions the model assumption that concentration of OH^- ions may be neglected is not correct.

An analyse of the quality of the solubility data of CO_2 and H_2S in MDEA available in open literature is presented by Weiland et al. (1993). In this work the experimental solubility data (until year 1992) were compared with the Deshmukh–Mather thermodynamic model. When experimental data deviate more than factor 3 from the model result, the data were qualified as not good. Compared with the database used in our work Weiland concluded that 25% of the data of Jou et al. (1982) were not fulfilling the criterium. In contradiction with the conclusion in this work, the data of Chakma and Meisen (1987) and Bhairi (1984) were qualified as good.
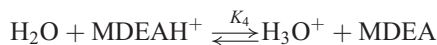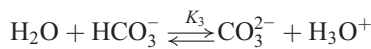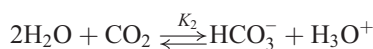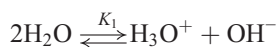
Incorporation of the above described modifications resulted in the database as reflected in Table 5.

When the predictions of the original model of Solbraa (2002) were compared with the experimental data as specified in Table 5, it appeared that the BIAS and AAD were respectively 19.8% and 26.7%. For this reason a new fit with the database of Table 5 was carried out to get new values for the following ionic interaction parameters:

$$MDEA^+-MDEA, MDEA^+$$
$$-H_2O, MDEA^+$$
$$-CO_2, MDEA^+-HCO_3^-.$$
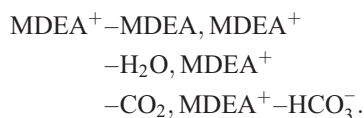
4.4. Influence of MDEA dissociation constant (Ka)

In an aqueous MDEA solution with CO_2 present the following chemical reactions will occur:

$$2H_2O \xrightleftharpoons{K_1} H_3O^+ + OH^-$$

$$2H_2O + CO_2 \xrightleftharpoons{K_2} HCO_3^- + H_3O^+$$

$$H_2O + HCO_3^- \xrightleftharpoons{K_3} CO_3^{2-} + H_3O^+$$

$$H_2O + MDEAH^+ \xrightleftharpoons{K_4} H_3O^+ + MDEA$$

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

$$\ln K_x = A + \frac{B}{T} + C\ln T \tag{4}$$

The relevant parameters for the equilibrium constants as used by Solbraa (2002) are given in Table 6.

The formation of carbonate-ions is normally limited so reaction K_3 is neglected. Also the formation of OH^- ions is neglected (reaction K_1); this assumption may not be correct in very low liquid loadings. So only reaction K_2 and K_4 are incorporated in the EOS model. The most important reaction in the system is the protonation of MDEA to MDEAH$^+$. The fit of Posey (1995) which was

Table 6
Parameters for calculation of the chemical equilibrium constants of the system CO_2–MDEA–H_2O

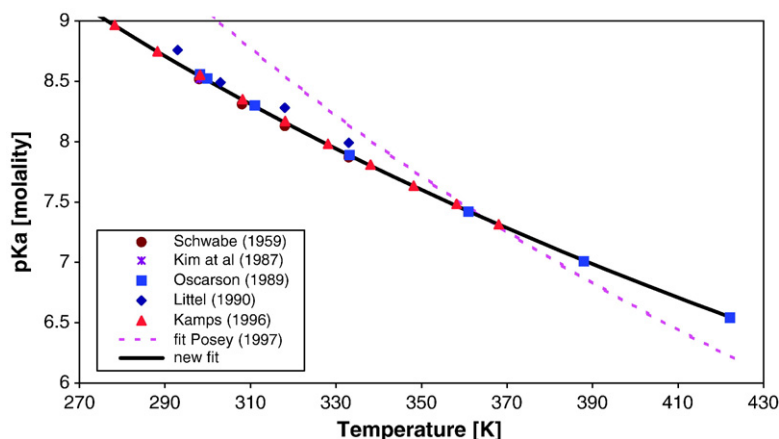| Reaction	A	B	C	T (K)	Reference
K_1	132.899	−13445.9	−22.4773	273−498	Posey (1995)
K_2	231.465	−12092.1	−36.7816	273−498	Posey (1995)
K_3	216.049	−12431.7	−35.4819	273−498	Posey (1995)
K_4	−56.2	−4044.8	7.848	298−419	Posey (1995)

Fig. 6. pK_a of MDEA as a function of temperature.

used by Solbraa (2002) was based on experiments carried out by Schwabe et al. (1959), Kim et al. (1987) and Oscarson et al. (1989). In Fig. 6 the pK_a measured by different authors is given as function of temperature and compared with the fit of Posey (1995). For the fit of Posey a unit conversion from mole fraction to molality has been incorporated.

The experimental data measured by Schwabe et al. (1959), Kim et al. (1987), Oscarson et al. (1989), Littel et al. (1990) and Kamps and Maurer (1996) as presented in Fig. 6 are at reference state infinite dilution for MDEA. However, the data used in work of Posey are based on another reference state namely pure MDEA. The following relation is applicable between the equilibrium constant at reference state infinite dilution (Ka_1) and reference state pure MDEA (Ka_2):

$$\gamma_{MDEA}^{\infty} = \frac{Ka_2}{Ka_1} \qquad (5)$$

where γ_{MDEA}^{∞} is called the normalized activity coefficient. A new fit was prepared from the available literature data given in Fig. 6, because in our model reference state infinite dilution is used as reference state for all components except water. Only the data of Littel et al. (1990), were not used, because these results were not completely in line with the other results. The fitted equation was of the same type as the equations given by Posey (1995) (refer to Eq. (4)). The new fit resulted in the following fit parameters:

This equation is based on reference state infinite dilution. A conversion from molality scale (experiments) to mole fraction scale (fit equation) has been incorporated. Now the normalized activity coefficient as used by Posey can be calculated and compared with the activity coefficient as calculated by the EOS model.

It appeared that these two activity coefficients did not match. At 40 °C the two values matched very well, but at higher and lower temperatures, the deviations increased above 50%. For this reason it was decided to use the new fit relation for the dissociation of MDEA as described in Table 7. This new relation is then used in the model with reference state infinite dilution. The new fit is included in Fig. 6. With this new relation for the dissociation of MDEA, new ionic interaction parameters of the system (CO_2–MDEA–water) have been determined with the modified database as described in Table 5.

4.5. Influence of binary interaction parameters

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

There was a significant under prediction of the partial pressure CO_2 of the model in these cases. At lower MDEA concentrations the fit of the model resulted in satisfactory results. A comparison between model results and experimental data is presented for 50 wt.% MDEA (Fig. 7) and 23 wt.% MDEA (Fig. 8).

Table 7
New fit parameters for calculation of MDEA dissociation constant

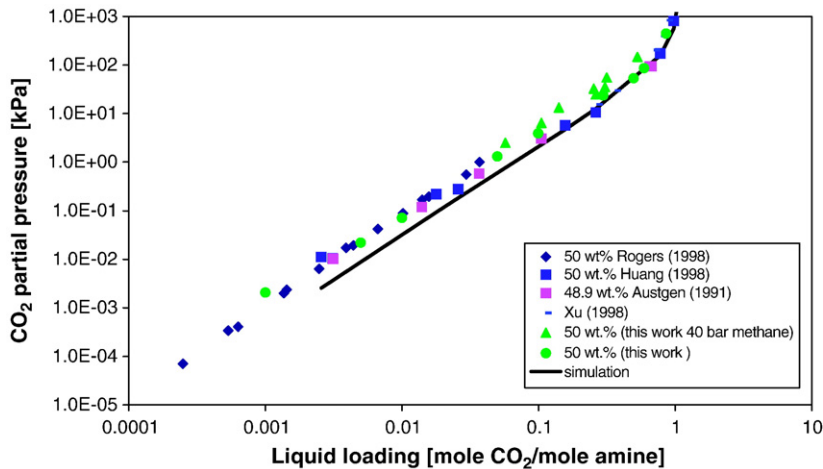| Reaction	A	B	C	T (K)
K_4	−77.262	−1116.5	10.06	278–423

Fig. 7. Model results compared with experimental data for 50 wt.% MDEA at 40 °C.

When the physical solubility (solubility without reaction) of CO_2 in the aqueous MDEA solution calculated by the model was compared with experimental results (using the CO_2–N_2O analogy) the graph as presented in Fig. 9 was obtained (experiments of Pawlak and Zarzycki (2002) have been converted from N_2O to CO_2 solubility using N_2O–CO_2 analogy).

Because chemical reaction will take place simultaneously, the physical solubility of CO_2 in aqueous MDEA cannot be measured directly and hence the CO_2–N_2O analogy was used. This theory is widely used in literature and experimentally proven to be reliable for MDEA concentrations up to approximately 30 wt.%. In view of the similarities with regard to configuration, molecular volume and electronic structure N_2O is often used as a non reacting gas to estimate the physical properties of CO_2 (Versteeg and van Swaaij, 1988). With this analogy the

physical solubility (Henry's constant H) for CO_2 in aq. MDEA is calculated in the following way:

$$H_{CO_2,aq.MDEA} = \frac{H_{CO_2,water}}{H_{N_2O,water}} * H_{N_2O,aq.MDEA} \qquad (6)$$

From Fig. 9 it can be seen that the estimation of the physical solubility by the EOS-model is completely contradictory to the experimental results. The model predicts a maximum in solubility (minimum in H) as a function of MDEA concentration and the experiments show a minimum solubility. The maximum error is seen at approximately 50 wt.% MDEA. The physical solubility of CO_2 in MDEA is mainly determined by the binary interaction parameters. Because no binary data are available for the system CO_2–MDEA to determine these parameters the interaction parameters were used
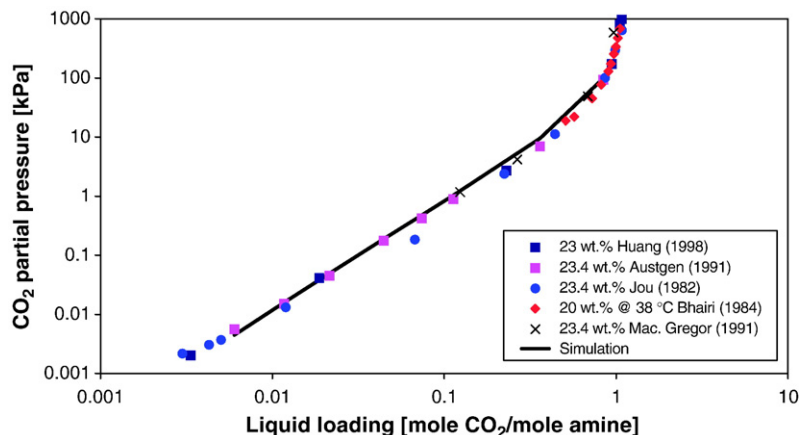

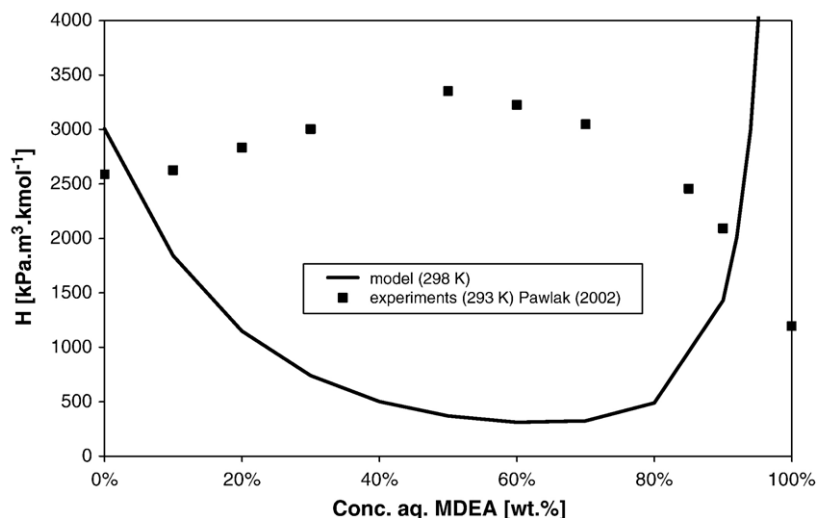Fig. 8. Model results compared with experimental data for 23 wt.% MDEA at 40 °C.

Fig. 9. Physical solubility of CO_2 in aqueous MDEA.

as a fit parameter in the ternary system (CO_2–water–MDEA). So probably the calculated fit parameter from this fit is inline with the data for the ternary ionic system, but does not agree with the data from the binary system. A new approach to obtain a better value for this interaction parameter was proposed. The interaction parameters of the CO_2–MDEA system will be determined by fitting this value with the experimental data available of the N_2O solubility in aqueous MDEA and applying the N_2O–CO_2 analogy to these data. This new approach will be carried out in the coming period.

5. Conclusions and recommendations

In the present study new solubility data of CO_2 and H_2S in aqueous MDEA were presented. Experiments were carried out in an intensively stirred reactor at elevated pressures up to 69 bar (methane as make-up gas). From these experiments it is concluded that an increasing methane partial pressure resulted in a higher acid gas partial pressure.

The results of the CO_2 experiments were used to validate an electrolyte equation of state (EOS) model. The EOS model as developed by Solbraa (2002) was improved in the following aspects:

- The database used for the determination of ionic parameters for the CO_2–MDEA–water was reviewed and modified.
- The equation for calculation of the dissociation of MDEA was modified. Instead of using the equation of Posey (1995), which was based on reference state

pure MDEA a new fit equation was developed based on reference state infinite dilution.

The modified model was not able to estimate the CO_2 partial pressure satisfactorily. When the physical solubility of CO_2 in aqueous MDEA was compared with experimental data, a large deviation was observed. Most likely the binary interaction parameter of CO_2–MDEA, which was fitted during the fit of the reactive system of CO_2–MDEA–water was not correct. A new method is proposed to fit this parameter with the experimental data of the N_2O solubility in aqueous MDEA.

The results of the EOS model until now look very promising and the development will be continued, however as for every other model the input parameters are not known as sufficiently accurate. The model is very sensitive for the binary interaction parameters and if they can not be determined accurate from data available in the literature, additional experiments have to be carried out.

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

- Formation of carbonate will be included in the model. This reaction will become important in case of high MDEA concentrations and/or high acid gas liquid loadings.
- Formation of OH^- ions will be included in the model. This reaction will become important in case of low acid gas liquid loadings.
- Critical review of binary interaction coefficients and additional experiments if not enough literature data are available will be carried out.

- Model will be extended to predict the system H_2S–MDEA–H_2O–CH_4.
- Model will be extended to predict the system H_2S–CO_2–MDEA–H_2O–CH_4.
- Model will be extended to predict the system H_2S–CO_2–MDEA–other amine–H_2O–CH_4.

Notation

A^R	Residual Helmholtz energy (J)
DEA	DiEthanol Amine (−)
MDEA	*N*-MethylDiethanol Amine (−)
MEA	MonoEthanol Amine (−)
DMF	DiMethylFormamide (−)
TBAH	TetraButylAmmonium Hydroxide (−)
P	(partial) Pressure (kPa)
AAD	Absolute Average Deviation (%)
BIAS	Mean BIAS Deviation (%)
K	Chemical equilibrium constant (−)
H	Henry's coefficient (kPa m^3 kmol^{-1})

Greek letters

α	Acid gas liquid loading (mol acid gas/mol amine)
γ	Activity coefficient (−)

Sub/super-scripts

i,j,I,n,x	Index
exp	Experiments
calc	Calculated by model
∞	Infinite dilution in water
Aq	Aqueous

Acknowledgements

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