Solubility of Carbon Dioxide and Hydrogen Sulfide in Aqueous N-Methyldiethanolamine Solutions

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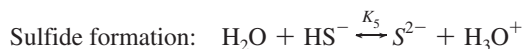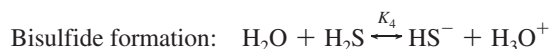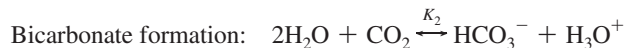**P. J. G. Huttenhuis,*,† N. J. Agrawal,† and G. F. Versteeg‡**

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In this work, 72 new experimental solubility data points for H_2S and CO_2 mixtures in aqueous N-methyldiethanol amine (MDEA) solutions at different methane partial pressures (up to 69 bara) are presented. They are correlated using an electrolyte equation of state (E-EOS) thermodynamic model. This model has already been used to estimate the CO_2 solubility in aqueous MDEA (Huttenhuis et al. *Fluid Phase Equilib.* 2008, *264*, 99−112) and the H_2S solubility in aqueous MDEA (Huttenhuis et al. *Int. J. Oil, Gas Coal Technol.* 2008, *1*, 399−424). Here, the model is further extended to predict the behavior of CO_2 and H_2S when they are present simultaneously in aqueous MDEA. The application of an equation of state is a new development for this type of system, i.e., of acid-gas−amine systems. The molecular interactions are described by Schwarzentruber et al.'s modification of the Redlich−Kwong−Soave equation of state, with terms added to account for ionic interactions in the liquid phase. The model is used to describe acid-gas solubility data for the CO_2−H_2S−MDEA−H_2O system reported in the open literature and experimental data reported here for the CO_2−H_2S−MDEA−H_2O−CH_4 system.

1. Introduction

Acid gases such as CO_2 and H_2S are commonly present in natural gas. In the past, research has focused on the development of solvents to remove H_2S selectively to low gas concentrations (of less than 10 ppm). To lower the operating costs for these processes, it was attractive not to remove the CO_2 that is also present in the natural gas. The H_2S concentration is usually much lower than the CO_2 concentration, so selective solvents were designed that have a high reaction rate with H_2S and a low reaction rate with CO_2 [e.g., N-methyldiethanol amine (MDEA)]. However, because of the greenhouse effect, research has recently been focused on the removal of CO_2 from gas streams. Acid components can be removed from gas streams in many ways. However, removal with aqueous alkanolamine solutions in an absorber−desorber system is most commonly used. To predict the mass transfer from gas to liquid, and thus the dimensions of the process equipment, the thermodynamics of the system need to be known accurately.

An alkanolamine−acid-gas system is a reactive absorption system, so chemical reactions have to be incorporated in the model. For the CO_2−H_2S−MDEA−H_2O−CH_4 system, the following chemical reactions occur

Water dissociation: $\quad 2H_2O \overset{K_1}{\longleftrightarrow} H_3O^+ + OH^-$

Bicarbonate formation: $\quad 2H_2O + CO_2 \overset{K_2}{\longleftrightarrow} HCO_3^- + H_3O^+$

Carbonate formation: $\quad H_2O + HCO_3^- \overset{K_3}{\longleftrightarrow} CO_3^{2-} + H_3O^+$

Bisulfide formation: $\quad H_2O + H_2S \overset{K_4}{\longleftrightarrow} HS^- + H_3O^+$

Sulfide formation: $\quad H_2O + HS^- \overset{K_5}{\longleftrightarrow} S^{2-} + H_3O^+$

MDEA protonation: $\quad H_2O + MDEAH^+ \overset{K_6}{\longleftrightarrow} MDEA + H_3O^+$

MDEA is a tertiary amine, i.e., it contains three nonhydrogen groups attached to the nitrogen atom. A tertiary amine can react only indirectly with CO_2 through a base-catalyzed reaction. This reaction is relatively slow compared to the reaction between a secondary or primary amine and CO_2. With primary/secondary amines, CO_2 can react directly, and carbamates are formed ($AmCOO^-$). However, a disadvantage of this (fast) carbamate formation reaction is that significantly higher amounts of energy are required to regenerate each mole of CO_2.

In the literature several thermodynamic models have been reported for alkanolamine−acid-gas systems. In this work, an electrolyte equation of state (E-EOS) is used to describe the CO_2−H_2S−MDEA−H_2O−CH_4 system. This model has already been applied to the systems CO_2−MDEA−H_2O−CH_4[1] and H_2S−MDEA−H_2O−CH_4.[2] The reason for the selection of this thermodynamic E-EOS model instead of the commonly used activity-based models (such as NRTL) is that extrapolation to other process conditions, extension to different types of inert components, and vapor−liquid equilibrium (VLE) predictions at high pressure seem to be feasible with the former.

To validate the E-EOS model, new experimental solubility data are required, which are presented in section 3.2. In total, 72 new solubility experiments are presented for the system CO_2−H_2S−MDEA−H_2O−CH_4. The influence of inert gas, in this case methane, on the acid gas was studied quantitatively for typical natural gas conditions. Acid-gas solubility data are usually limited to low pressures with no inert present; sometimes, low-pressure (1 bar) nitrogen is used as a makeup gas. Here, the acid-gas solubilities of CO_2 and H_2S simultaneously are measured for system pressures up to 69 bar with methane as the inert makeup gas.

First, the E-EOS model is briefly described. Then, the experimental method and solubility are presented. Finally, the

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Table 1. Ionic Interaction Parameters as Used in This Work[2]

component j^a	W_{ij} (m^3 mol^{-1})	component j^a	W_{ij} (m^3 mol^{-1})
MDEA	2.31×10^{-3}	CO$_2$	2.98×10^{-4}
H$_2$O	4.17×10^{-4}	HCO$_3^-$	-1.32×10^{-4}
H$_2$S	4.88×10^{-4}	CO$_3^{2-}$	-2.74×10^{-4}
HS$^-$	-1.49×10^{-4}	CH$_4$	5.77×10^{-4}

^{a} In all cases, component i is MDEAH$^+$.

Table 2. Chemicals Used in This Study

name	CAS number	purity	supplier
N-methyldiethanolamine (MDEA)	105-59-97	>99%	Acros
water (H$_2$O)	7732-18-5	demineralized	
hydrogen sulfide (H$_2$S)	7783-06-4	99.6%	Hoekloos
carbon dioxide (CO$_2$)	124-38-9	99.7%	Hoekloos
methane (CH$_4$)	74-82-8	99.5%	Hoekloos
nitrogen (N$_2$)	7727-37-9	99.99%	Hoekloos

E-EOS model is compared with data for the CO$_2$−H$_2$O−MDEA−H$_2$O system from the open literature and with new experimental data obtained in the presence of methane.

2. Description of Electrolyte Equation of State Model

In this study, an electrolyte equation of state (E-EOS) is used to describe the system CO$_2$−H$_2$S−MDEA−H$_2$O−CH$_4$. This model has already been applied to the single-acid-gas systems in previous work.[1] Schwarzentruber et al.'s modification[4] of the Redlich−Kwong−Soave EOS is used with a Huron−Vidal mixing rule.[5] To allow for ions in the liquid, additional (electrolyte) interactions are added to the molecular equation of state. The E-EOS is based on a Helmholtz energy that is a summation of molecular and ionic interactions. This approach was originally proposed by Fürst and Renon.[6]

Posey[7] found that mixed-gas equilibria can be fairly well predicted with a thermodynamic model using accurate single-gas parameters. Thus, when CO$_2$ and H$_2$S are present simultaneously, only one additional parameter is required compared with the single-gas E-EOS. Only the value of the CO$_2$−H$_2$S molecular interaction parameter needs to be determined. This parameter was determined at a value of 0.12 (using the van der Waals mixing rule) by regressing the model with the experimental data as described in section 4.1. During simulations, it appeared that the model results were not sensitive to the value of the CO$_2$−H$_2$S interaction parameter. The values for all other parameters used in the E-EOS model were identical to those used for the single-gas systems.[1,2,8]

The values of the ionic binary interaction parameters employed in this work are summarized in Table 1.

3. Experimental Section

3.1. Experimental Setup and Procedure. The chemicals used in this study are described in Table 2.

For the experimental determination of the solubility data, a 1 dm^3, intensively stirred Büchi reactor was used. In this reactor, it is possible to analyze the gas concentration and to take liquid samples. In Figure 1, a schematic representation of the experimental setup is presented.

The main parts of the reactor are a gas supply from which a certain amount of CO$_2$ and/or H$_2$S can be introduced; a reactor containing a stirrer, heating system, and liquid sampler; and a gas analysis system, whereby the H$_2$S concentration in the gas phase was measured in a Varian Micro GC CP-2003 instrument and the CO$_2$ concentration was measured with a MAIHAK S700 infrared analyzer.

During each experiment, the reactor was filled with approximately 0.5 L of solvent and degassed with a vacuum pump until the solvent vapor pressure was reached. Then, the solvent was preloaded with CO$_2$ and H$_2$S from the gas bombs, and the reactor was pressurized with methane up to the specified reactor pressure [6.9, 34.5, or 69 bara (bar absolute)]. The stirrer was started, a small (methane) sweep stream (approximately 200 NmL min^{-1}) was routed through the reactor, and the CO$_2$ and H$_2$S concentrations of the reactor outlet were analyzed with the infrared analyzer and gas chromatograph, respectively. When a constant (CO$_2$ + H$_2$S) concentration was measured (typically after 1 h), the reactor was closed, a liquid sample was taken, and the acid-gas concentration (CO$_2$ + H$_2$S) in the liquid was analyzed with a liquid-phase titration. To prevent any release of acid gas from the liquid sample, the sample was precontacted with a caustic agent. The gas-phase partial pressures were determined with the gas chromatograph (H$_2$S) and infrared analyzer (CO$_2$) and the pressure indicator in the reactor. The overall accuracy was approximately ±5%.

The H$_2$S concentration in the liquid was measured with an automated iodometric back-titration using thiosulfate, whereas the CO$_2$ concentration was measured with a back-titration using *tert*-butyl alcohol (TBAH). The inaccuracies of the two titration methods were determined by several calibrations using Na$_2$S and NaHCO$_3$, respectively, and appeared to be smaller than 2% in both cases. More details about these liquid titrations can be found in ref 8. With the TBAH titration method, the total amount of acid gas (CO$_2$ and H$_2$S) is determined and not the amount of CO$_2$ separately. Therefore, an excess amount of CuSO$_4$ was added to a vessel containing boiling sulfuric acid. In this way, all sulfur species precipitated irreversibly as CuS, but the amount of CO$_2$ present was not influenced. In the single-gas CO$_2$ experiments,[8] the TBAH liquid titration method (without using CuSO$_4$) appeared to be very accurate, with the results always being within 10% of the liquid loading determined from the amount of CO$_2$ added to the reactor (mass balance). However, for the mixed-gas experiments in this work, the difference between the titration and mass balance was more than 20% for CO$_2$. Therefore, it was decided to determine the CO$_2$ liquid loading from the mass balance instead of from the titration with TBAH. With this mass balance method, the accuracy was estimated to be within 10% in the low loading range (<0.1 mol of CO$_2$/mol of amine) and within 5% in the high loading range (>0.1 mol of CO$_2$/mol of amine).

3.2. Experimental Results. Some initial experiments were carried out to validate the experimental setup and procedures. From these experiments, it was concluded that the methods used were able to produce reliable solubility data for both H$_2$S and CO$_2$ in aqueous amine solvents. The results of the experiments were well in line with literature sources.

In this work, new experimental solubility data were obtained for two different solvents (35 and 50 wt % aqueous MDEA), at two temperatures (283 and 298 K) and at three different system pressures (6.9, 34.5, and 69 bara) with methane as an inert gas. In total, 72 data points were produced according to the matrix presented in Table 3.

The results of the solubility experiments are reported in Tables 4−7.

3.3. Discussion. As indicated in Table 4, the initial experiments were carried out with nitrogen as the makeup gas instead of methane. To check the influence of the type of inert gas, nitrogen was sent through the reactor, followed by methane, and then nitrogen again. It appeared that the switchover did not influence the CO$_2$ gas partial pressure. However, the H$_2$S
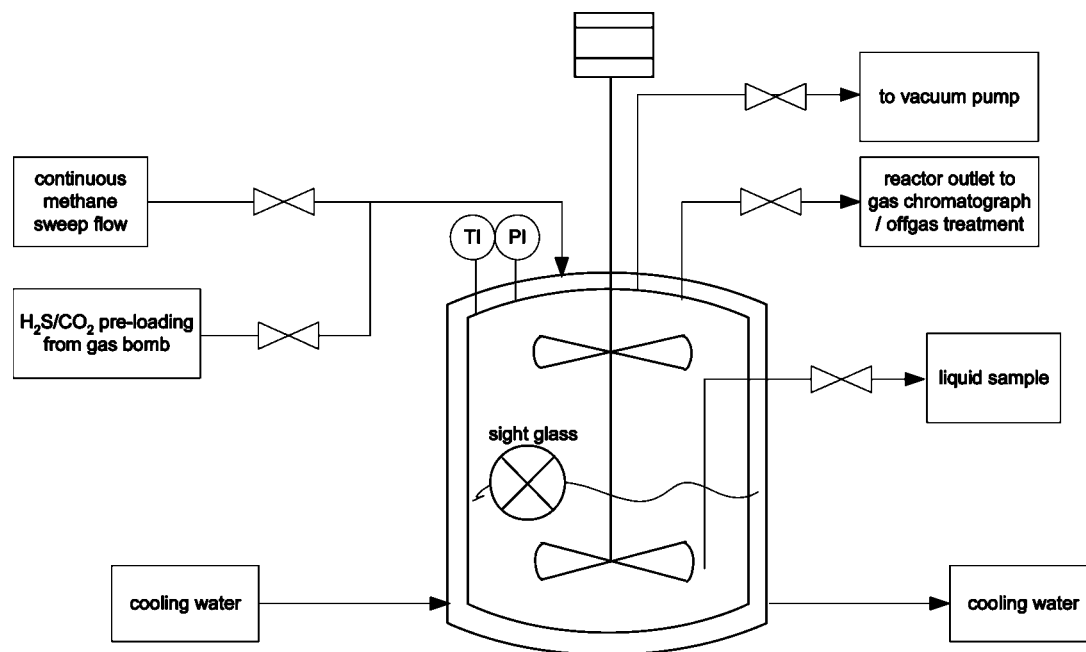
Figure 1. Schematic representation of the reactor.

Table 3. Experimental Matrix for the Solubility Experiments

parameter	units	values
temperature	K	283 and 298
MDEA concentration	wt %	35 and 50
system pressure	bara	6.9, 34.5, and 69
CO_2 liquid loading	mol of CO_2/mol of amine	0.05, 0.15, and 0.30
H_2S gas-phase concentration	ppm	200 and 2000[a]

[a] These gas concentrations are approximate; it was not possible to adjust them accurately.

Table 4. Experimental Solubility Data for CO_2 and H_2S Simultaneously in 35 wt % MDEA at 10 °C

P (bar)	CO_2 liquid loading (mol of CO_2/mol of amine)	P_{CO_2} (kPa)	H_2S liquid loading (mol of H_2S/mol of amine)	P_{H_2S} (kPa)	note
6.9	0.060	0.086	0.037	0.151	a
6.9	0.125	0.216	0.037	0.197	a
6.9	0.201	0.532	0.036	0.278	a
34.7	0.050	0.135	0.103	0.497	
35.7	0.152	0.568	0.084	0.803	a
34.5	0.396	3.02	0.033	0.610	a
69.0	0.050	0.207	0.169	1.78	
69.8	0.152	0.776	0.144	1.89	a
70.1	0.300	2.08	0.082	1.95	
6.9	0.061	0.180	0.145	1.00	a
7.2	0.164	0.667	0.139	1.44	a
7.0	0.325	2.07	0.143	2.24	a
34.8	0.050	0.310	0.351	5.41	
35.8	0.152	1.33	0.363	7.37	a
35.0	0.325	3.42	0.245	6.86	a
69.2	0.050	0.692	0.554	17.2	
69.7	0.152	4.26	0.592	35.2	a
70.0	0.325	7.57	0.468	22.7	a

[a] These mixed-gas experiments were carried out with nitrogen as the inert gas instead of methane. The measured H_2S gas concentrations of these experiments in nitrogen were corrected (multiplied by a factor of 1.3) to simulate the results with methane as the inert gas. For details, see section 3.3.

partial pressure was influenced at both high and low H_2S concentrations by the makeup gas used. When methane was used, the H_2S partial pressure was approximately 30% higher than when nitrogen was used. The experiments using nitrogen

Table 5. Experimental Solubility Data for CO_2 and H_2S Simultaneously in 35 wt % MDEA at 25 °C

P (bar)	CO_2 liquid loading (mol of CO_2/mol of amine)	P_{CO_2} (kPa)	H_2S liquid loading (mol of H_2S/mol of amine)	P_{H_2S} (kPa)
6.9	0.050	0.278	0.025	0.188
6.9	0.150	1.49	0.019	0.243
7.0	0.300	3.93	0.016	0.280
34.7	0.050	0.308	0.051	0.572
34.6	0.150	3.90	0.275	8.90
34.6	0.300	5.22	0.023	0.546
70.1	0.050	0.421	0.085	1.42
68.3	0.150	1.78	0.085	2.00
69.0	0.300	5.81	0.088	3.69
7.0	0.050	0.42	0.089	1.04
7.0	0.150	1.87	0.091	1.49
6.9	0.300	1.30	0.061	1.46
34.5	0.050	0.759	0.251	6.80
34.7	0.150	3.19	0.195	5.67
34.5	0.300	5.97	0.127	5.02
69.6	0.050	1.51	0.380	15.2
69.8	0.150	3.32	0.253	9.99
69.9	0.300	10.12	0.246	14.9

instead of methane as the makeup gas are indicated in Table 4. The H_2S phase partial pressures measured in nitrogen have been multiplied by a factor of 1.3 to allow them to be compared to those obtained using methane.

It was very difficult to compare and evaluate the data presented in the tables above. Moreover, a comparison with literature data is not possible because the presently determined data are unique. Figure 2 shows the influence of the CO_2 liquid loading on the H_2S solubility. The H_2S solubility data without CO_2 were taken from Huttenhuis et al.[2]

Figure 3 shows the CO_2 solubility in aqueous MDEA as a function of the H_2S liquid loading. For these experiments, the acid-gas partial pressure was found to increase with temperature, MDEA concentration, acid-gas liquid loading, and methane partial pressure. The effects are similar to those found for CO_2-only and H_2S-only. Additionally, it appears that the H_2S liquid loading decreased with increasing CO_2 liquid loading at constant H_2S partial pressure. For example, the H_2S liquid loading capacity decreased from 0.449 to 0.246 mol of H_2S/mol of amine

Table 6. Experimental Solubility Data for CO_2 and H_2S Simultaneously in 50 wt % MDEA at 10 °C

P (bar)	CO_2 liquid loading (mol of CO_2/mol of amine)	P_{CO_2} (kPa)	H_2S liquid loading (mol of H_2S/mol of amine)	P_{H_2S} (kPa)
7.0	0.050	0.131	0.024	0.127
6.9	0.150	0.760	0.020	0.200
7.1	0.300	2.11	0.012	0.126
35.0	0.050	0.182	0.046	0.392
34.6	0.150	0.872	0.032	0.398
35.7	0.300	2.88	0.029	0.532
68.6	0.050	0.322	0.128	1.72
68.3	0.150	1.11	0.063	1.11
69.2	0.300	3.29	0.050	1.23
6.9	0.050	0.228	0.122	1.17
7.0	0.150	0.810	0.066	0.760
7.0	0.300	2.68	0.049	0.807
34.5	0.050	0.531	0.364	8.56
36.8	0.150	1.60	0.223	4.88
35.1	0.300	3.91	0.158	4.44
69.0	0.050	0.863	0.446	18.49
69.0	0.150	3.02	0.404	16.44
69.0	0.300	6.97	0.302	15.40

Table 7. Experimental Solubility Data for CO_2 and H_2S Simultaneously in 50 wt % MDEA at 25 °C

P (bar)	CO_2 liquid loading (mol of CO_2/mol of amine)	P_{CO_2} (kPa)	H_2S liquid loading (mol of H_2S/mol of amine)	P_{H_2S} (kPa)
7.0	0.050	0.621	0.021	0.194
6.9	0.150	3.04	0.014	0.25
7.0	0.300	12.7	0.007	0.201
34.5	0.050	0.64	0.035	0.58
34.5	0.150	3.46	0.023	0.549
34.9	0.300	8.84	0.019	0.795
68.8	0.050	0.805	0.054	1.16
69.0	0.150	3.71	0.035	1.10
69.2	0.300	10.53	0.029	1.38
7.0	0.050	0.813	0.056	0.940
7.0	0.150	3.22	0.038	0.845
7.1	0.300	14.7	0.028	0.951
34.8	0.050	1.33	0.167	5.14
34.6	0.150	4.46	0.094	3.53
34.9	0.300	10.0	0.069	3.10
69.9	0.050	1.49	0.218	9.47
68.7	0.150	5.27	0.153	7.41
69.4	0.300	14.9	0.154	11.3

when the CO_2 liquid loading was increased from 0 to 0.3 mol of CO_2/mol of amine (P_{H_2S} = 14.9 kPa, 35 wt % MDEA, 298 K, 69 bara). The same can be concluded for the CO_2 solubility in aqueous MDEA. As can be seen in Figure 3, the CO_2 partial pressure increased with increasing H_2S liquid loading.

4. Model Results

4.1. System CO_2−H_2S−MDEA−H_2O. The E-EOS model for the CO_2−H_2S−MDEA−H_2O system was validated with the experimental solubility data in aqueous MDEA when CO_2 and H_2S were present simultaneously. The amount of experimental data for this system in the open literature is very limited. The following experimental solubility data were used to validate the model: solubility of CO_2 and H_2S simultaneously in 50 wt % MDEA at 313 and 373 K from Huang and Ng,[9] solubility of CO_2 and H_2S simultaneously in 35 wt % MDEA at 313 K from Jou et al.,[10] and solubility of CO_2 and H_2S simultaneously in 23 wt % MDEA at 313 and 323 K and in 50 wt % MDEA at 313 K from Bullin et al.[11]

Comparisons of the mixed-gas VLE data from open literature with the E-EOS calculations are presented as parity plots in Figure 4 (CO_2 solubility) and Figure 5 (H_2S solubility).

From Figures 4 and 5, it appears that the model gives good predictions for the solubilities of mixed gases in aqueous MDEA. At low partial pressures (<0.1 kPa), the model seems to overpredict the acid-gas partial pressure for both H_2S and CO_2. Especially for CO_2, the difference between the calculated and measured results of Bullin et al.[11] is significant. This was also concluded by Posey,[7] who used an NRTL model to describe the same system. In Table 8, the mean bias deviation (denoted BIAS) and absolute average deviation (AAD) are given for the different sets of data. The BIAS and AAD are defined as follows

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

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

From Table 8, it can be seen that the predictions of the E-EOS model differ considerably from the CO_2 solubility data of Bullin et al.;[11] i.e., the BIAS for these data is −121.4%. Therefore, the five experimental data points of Bulllin et al.[11] were omitted, and new BIAS and AAD values were calculated. The accuracy of the CO_2 solubility of the Bullin et al.[11] data increased significantly; specifically, the BIAS and AAD values changed from −121.4% to −19.3% and from 141.6% to 19.3%, respectively. The deletion of these five data points also resulted in increased deviations of the total experimental data set containing data of Huang and Ng,[9] Jou et al.,[10] and Bullin et al.[11]

The total BIAS (corrected for the Bullin et al.[11] data) for the H_2S solubility data is −27.3%, so the model overpredicts the H_2S partial pressure. This is not in line with the H_2S-only experiments (without CO_2), where a BIAS of +2% was found.[2] However, the BIAS of the data of Huang and Ng[9] is only −3.6%. The quality of the CO_2 experimental data is much better. The BIAS (corrected for the Bullin et al.[11] data) is 0.6%. However, there is some variation between the different research groups, because the BIAS is −19.3% for the (corrected) Bullin et al.[11] data, whereas for the Huang and Ng[9] data, the BIAS is +13.5%.

4.2. CO_2−H_2S−MDEA−H_2O−CH_4 System. The electrolyte equation of state as described in section 2 was further used to describe the experimental solubility data for the CO_2−H_2S−MDEA−H_2O−CH_4 system as presented in section 3.2. In Figures 6 and 7, these CO_2 and H_2S solubility data are compared with the E-EOS model predictions.

The BIAS and AAD values for the CO_2−H_2S−MDEA−H_2O−CH_4 system are presented in Table 9.

From Figures 6 and 7 and Table 9, it can be concluded that the solubilities of both H_2S and CO_2 in aqueous MDEA are predicted better by the E-EOS model for 35 wt % aqueous MDEA than for 50 wt % MDEA. The same conclusion was made for experiments with both CO_2-only[1] and H_2S-only[2] systems. In the single-gas studies,[1,2] it was suggested that the H_2S−N_2O and CO_2−N_2O analogy used in the model to calculate the H_2S−MDEA and CO_2−MDEA binary interaction parameters is less applicable at high amine concentrations. Kierzkowska-Pawlak and Zarzycki[12] studied the applicability of the CO_2 and N_2O analogy in a MDEA−ethanol system, in which both the N_2O and CO_2 dissolve physically only, because no chemical reaction can take place between the CO_2 and the solvent. In that study, it was concluded that the CO_2−N_2O
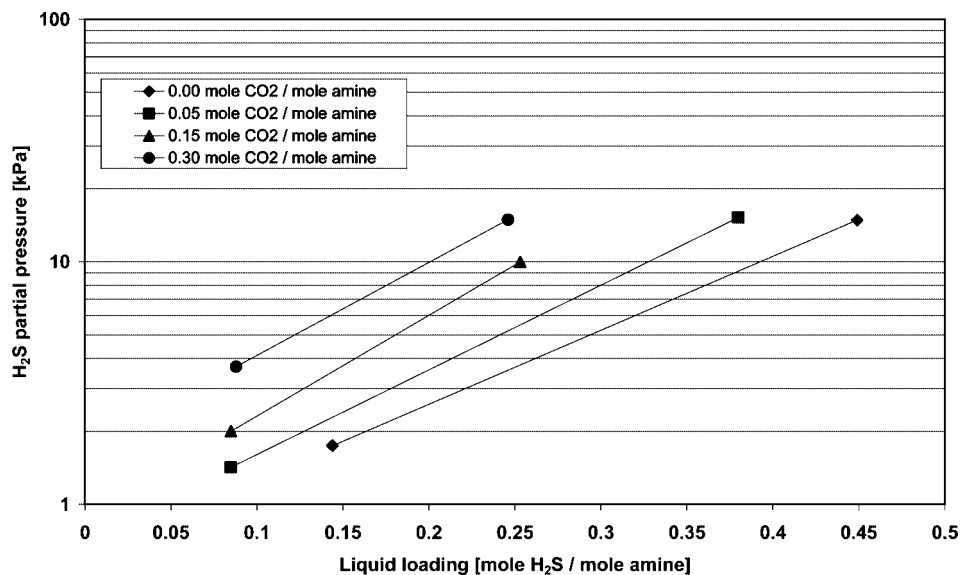
Figure 2. H_2S solubility in 35 wt % aqueous MDEA preloaded with CO_2 at concentrations (in moles of CO_2 per mole of amine) of 0,[2] 0.05, 0.15, and 0.3 (this work) at 298 K and 69 bara with methane as the makeup gas.
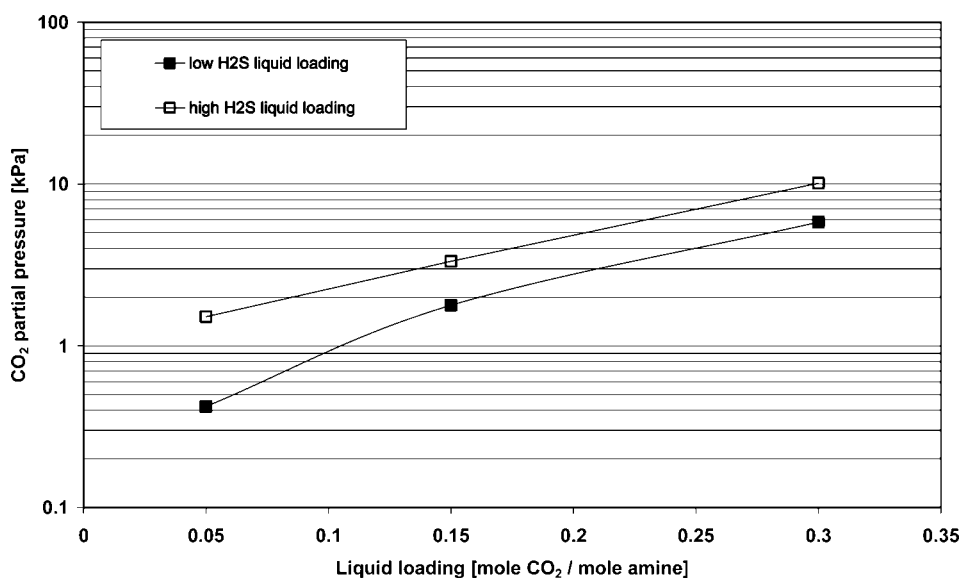

Figure 3. CO_2 solubility in 35 wt % aqueous MDEA preloaded with low (<0.09 mol of H_2S/mol of amine) and high (>0.24 mol of H_2S/mol of amine) concentrations H_2S at 298 K at 69 bara system pressure with methane as the makeup gas.

Table 8. AAD and BIAS Values for the Solubilities of CO_2 and H_2S Simultaneously in Aqueous MDEA

	number of points	BIAS (%)		AAD (%)	
		H_2S	CO_2	H_2S	CO_2
Jou et al.[10]	91	−34.5	−4.0	36.9	22.6
Huang and Ng[9]	16	−3.6	13.5	19.9	24.3
Bullin et al.[11]	21	−26.1	−121.4	41.3	141.6
Bullin et al.[11] corrected[a]	16	−40.5	−19.3	40.5	19.3
total	128	−26.6	−18.8	35.2	42.2
total corrected for Bullin et al.[11] data[a]	123	−27.3	0.6	36.3	23.6

[a] Five experimental data points of Bulin et al.[11] with AAD > 250% (CO_2 solubility) were omitted.

analogy is not applicable over the whole amine concentration. The N_2O solubility in ethanol solutions of MDEA decreases with increasing amine concentration, whereas the CO_2 solubility increases. So again, it appears that attention should be paid to this CO_2–N_2O analogy at high amine concentrations. However, more research is needed to study the physical solubility of CO_2

in aqueous amines. From Table 9, it can also be seen that the predictions at 283 K are better than those at 298 K. This was also found for the H_2S-only experiments in the H_2S–MDEA–H_2O–CH_4 system.[2]

In previous works, the influence of methane on the H_2S and CO_2 solubilities in aqueous MDEA was studied quantitatively for CO_2-only and H_2S-only systems.[1,2] It was concluded that the individual acid-gas solubilities (CO_2 or H_2S) decreased with increasing methane partial pressure. This behavior was thought to be due a decrease in the acid-gas fugacity coefficient with increasing methane partial pressure. In this work, simulations with the E-EOS model were carried out to study the influence of CH_4, CO_2, and H_2S on the acid-gas solubility in aqueous MDEA with both CO_2 and H_2S present simultaneously. From the experimental data presented in this work (see section 3.2), the influence of methane on the acid-gas solubility could not be derived directly, because the experiments were carried out at constant H_2S gas concentration, instead of constant H_2S partial
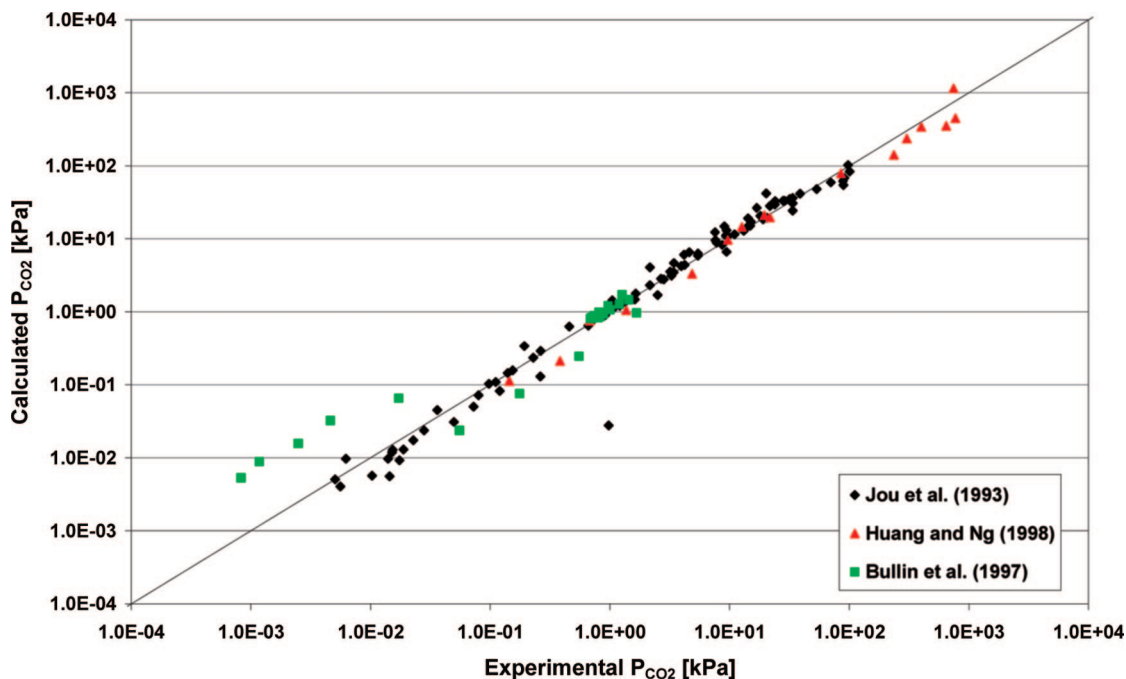
Figure 4. Parity plot of the CO_2 solubility for the system $H_2S-CO_2-MDEA-H_2O$ (see refs 9–11).
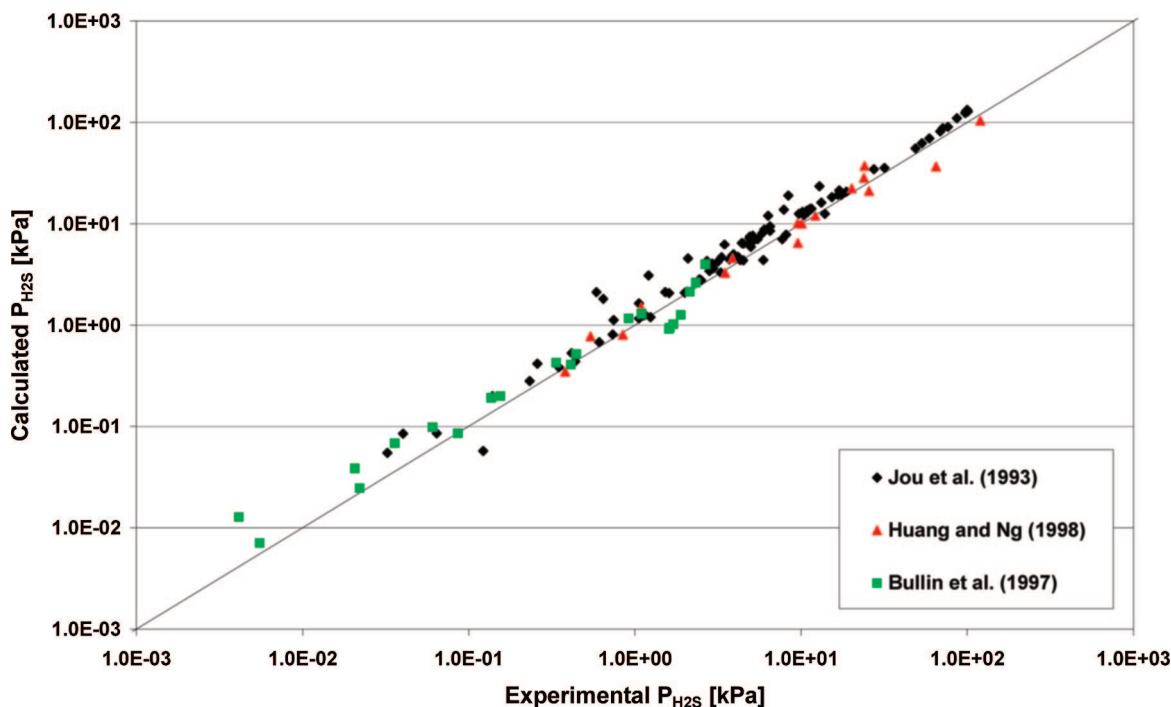

Figure 5. Parity plot of the H_2S solubility for the system $H_2S-CO_2-MDEA-H_2O$ (see refs 9–11).

pressure. In Table 10, the (acid) gas partial pressures, fugacities, and fugacity coefficients are summarized for the different simulations.

In Figure 8, the partial pressures and fugacity coefficients of H_2S and CO_2 as calculated with the E-EOS model are presented as functions of the methane partial pressure for constant acid-gas loading.

The fugacity coefficients of both H_2S and CO_2 decrease with increasing methane partial pressure, whereas the acid-gas partial pressure increases. At low methane partial pressures, the fugacity coefficients approach unity. The influence of the methane partial pressure on the H_2S fugacity coefficient is slightly higher than that on the CO_2 coefficient. As was concluded in previous

works,[1,2] a lower acid-gas fugacity coefficient results in a higher acid-gas partial pressure and thus a lower acid-gas solubility. Therefore, it can be concluded that, also in the mixed-gas experiments, the acid-gas solubility decreases with increasing methane partial pressure. The solubility of H_2S is more affected by the increasing methane partial pressure than the solubility of CO_2; for example, at a methane partial pressure of 69 bara, the H_2S fugacity coefficient is 0.715, whereas the CO_2 fugacity coefficient equals 0.751 (see Table 10).

Table 10 shows the calculated results for higher CO_2 and H_2S loadings (0.3 instead of 0.1 mol of acid gas/mol of amine). It appears that there is no influence of the acid-gas liquid loading on the acid-gas fugacity coefficient, when the acid-gas liquid
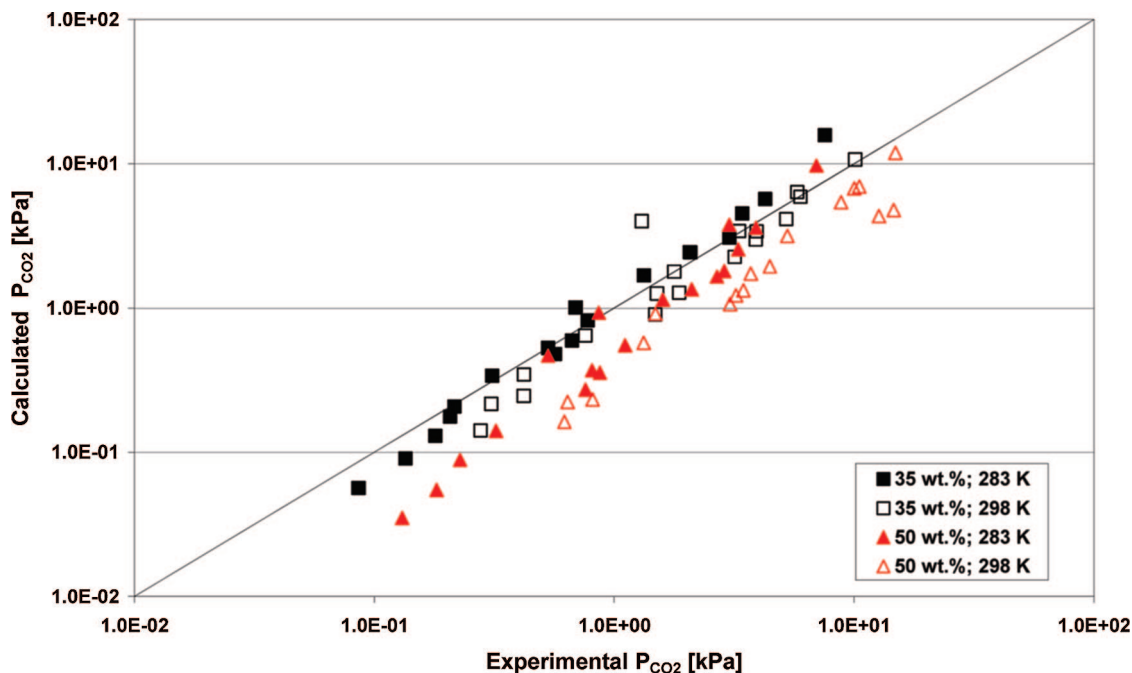
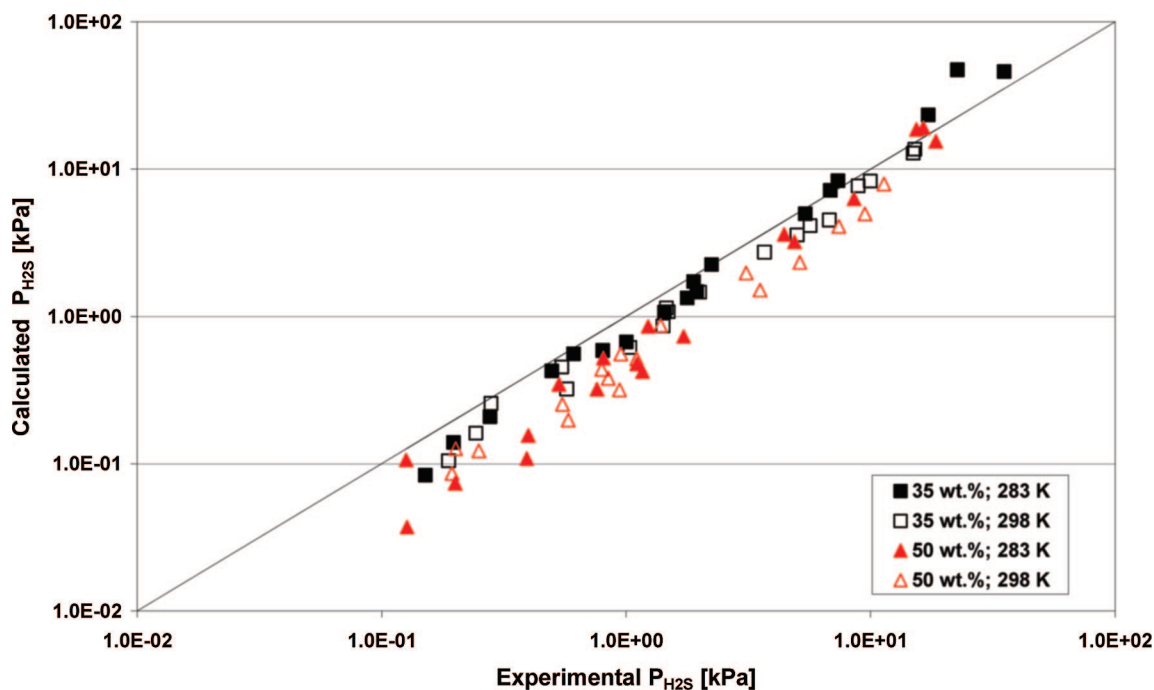**Figure 6.** Parity plot of the CO_2 solubility for the system $CO_2-H_2S-MDEA-H_2O-CH_4$ (this work).

Figure 7. Parity plot of the H_2S solubility for the system $CO_2-H_2S-MDEA-H_2O-CH_4$ (this work).

Table 9. AAD and BIAS Values for the Solubilities of CO_2 and H_2S in the $CO_2-H_2S-MDEA-H_2O-CH_4$ System

		BIAS (%)		AAD (%)	
	number of points	H_2S	CO_2	H_2S	CO_2
35 wt % MDEA, 283 K	18	4.5	−8.7	25.9	24.3
35 wt % MDEA, 298 K	18	26.3	5.8	26.3	30.7
50 wt % MDEA, 283 K	18	37.7	33.0	41.8	41.3
50 wt % MDEA, 298 K	17	48.9	53.1	48.9	53.1
total	71	29.1	20.4	35.5	37.1

loading is increased from 0.1 to 0.3 mol of acid gas/mol of amine. The H_2S and CO_2 fugacity coefficients are the same for H_2S and/or CO_2 liquid loadings of 0.1 and 0.3 mol of acid gas/mol of amine. However, it should be noted that the H_2S

solubility decreases with increasing CO_2 liquid loading and vice versa (see Figures 2 and 3), because part of the amine capacity is consumed by the acid gas.

5. Conclusions

In this study, the solubilities of CO_2 and H_2S, when present simultaneously in aqueous MDEA, have been studied experimentally and theoretically. This is with methane acting as inert component. Seventy-two new datapoints are presented for 35 and 50 wt % aqueous MDEA at 283 and 298 K. The methane partial pressure was varied from 6.9 to 69 bar. The H_2S partial pressure increased significantly with increasing CO_2 liquid loading; that is, the capacity of the solvent for H_2S capture
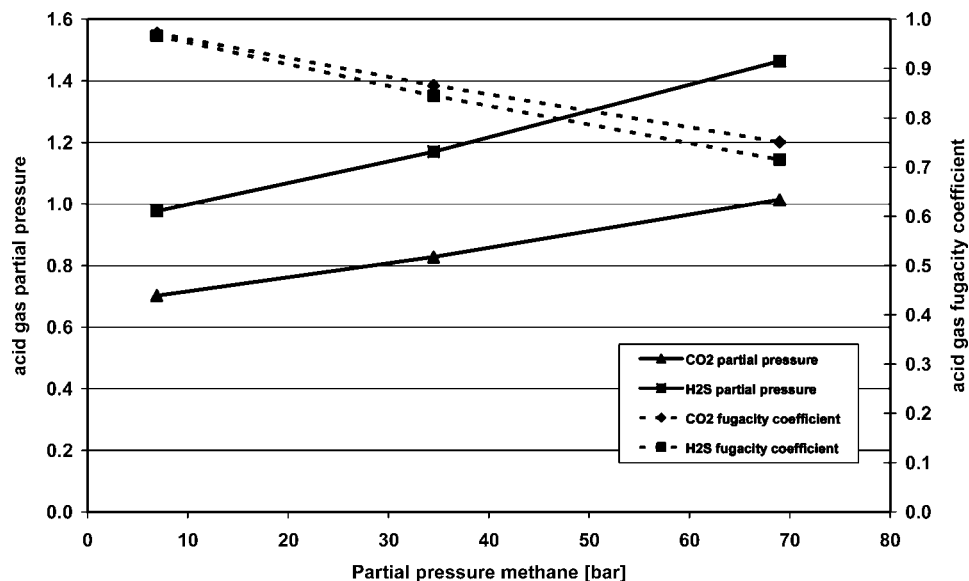
Figure 8. H_2S and CO_2 acid-gas fugacity coefficients as functions of the methane partial pressure as calculated by the E-EOS model for the $CO_2-H_2S-MDEA-H_2O-CH_4$ system. Conditions: CO_2 liquid loading = 0.1 mol/mol of amine, H_2S liquid loading = 0.1 mol/mol of amine, 35 wt % aqueous MDEA, 298 K.

Table 10. CO_2 and H_2S Solubilities in 35 wt % Aqueous MDEA at 298 K as Calculated by the E-EOS Model

CO_2 loading (mol of CO_2/mol of amine)	H_2S loading (mol of H_2S/mol of amine)	partial pressure			fugacity		fugacity coefficient	
		P_{CH_4} (bar)	P_{H_2S} (kPa)	P_{CO_2} (kPa)	f_{H_2S} (kPa)	f_{CO_2} (kPa)	φ_{H_2S}	φ_{CO_2}
0.1	0.1	6.9	0.98	0.70	0.94	0.68	0.967	0.972
0.1	0.1	34.5	1.17	0.83	0.99	0.72	0.845	0.866
0.1	0.1	69	1.46	1.01	1.05	0.76	0.715	0.751
0.1	0.3	6.9	6.42	1.56	6.20	1.51	0.967	0.972
0.1	0.3	34.5	7.71	1.84	6.51	1.59	0.845	0.866
0.1	0.3	69	9.67	2.26	6.91	1.69	0.714	0.751
0.3	0.1	6.9	2.14	4.56	2.07	4.43	0.967	0.972
0.3	0.1	34.5	2.57	5.39	2.17	4.66	0.845	0.866
0.3	0.1	69	3.22	6.62	2.30	4.97	0.715	0.751
0.3	0.3	6.9	12.25	8.69	11.83	8.44	0.966	0.972
0.3	0.3	34.5	14.74	10.29	12.44	8.91	0.844	0.865
0.3	0.3	69	18.54	12.67	13.24	9.51	0.714	0.750

decreased. During the experiments, it appeared that the type of inert gas (nitrogen or methane) did influence the H_2S solubility. However, the CO_2 partial pressure was not influenced by the type of inert gas. The experimental results were compared with an electrolyte equation of state that describes both gas and liquid. The equation includes terms to account for ionic species that are present in the liquid. Calculations with this E-EOS model showed that the fugacity coefficient of H_2S is more sensitive to increasing methane partial pressure than the fugacity coefficient of CO_2. Previously,[1,2] it was also concluded that a decreasing acid-gas fugacity coefficient could be responsible for the decreasing acid-gas solubility with increasing methane partial pressure. Thus, a probable explanation for the above-mentioned different behaviors of CO_2 and H_2S depending on inert gas type could be that the fugacity coefficient of H_2S is more sensitive to inert gas type (nitrogen or methane) than the fugacity coefficient of CO_2. However, the influence of the type of gas on the acid-gas solubility needs to be studied further.

The E-EOS model developed here was compared with experimental data in the literature for the $CO_2-H_2S-MDEA-H_2O$ system. The scatter in the different sets of data is fairly high. Therefore, more solubility experiments need to be carried out, in which CO_2 and H_2S are present simultaneously. The BIAS values for CO_2 and H_2S obtained with the E-EOS model are -0.6% and -27.3%, respectively.

The E-EOS model was also compared with experimental data for the $CO_2-H_2S-MDEA-H_2O-CH_4$ system from this work (section 3.2). The BIAS values for CO_2 and H_2S are 20.4% and 29.1%, respectively. Predictions at low MDEA concentration (35 wt %) and low temperature (283 K) are better than those at higher MDEA concentration and temperature. Also, the influence of the inert gas on this acid-gas solubility needs to be studied in more detail.

List of Symbols

AAD = absolute average deviation (%)
AMCOO⁻ = carbamate
BIAS = mean BIAS deviation (%)
E-EOS = electrolyte equation of state
MDEA = N-methyldiethanol amine
TBAH = *tert*-butyl alcohol

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