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Published in:
International Journal of Oil, Gas and Coal Technology

DOI:
[10.1504/IJOGCT.2008.020370](https://doi.org/10.1504/IJOGCT.2008.020370)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2008

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Huttenhuis, P. J. G., Agrawal, N. J., & Versteeg, G. F. (2008). The solubility of hydrogen sulfide in aqueous N-methyldiethanolamine solutions. *International Journal of Oil, Gas and Coal Technology*, 1(4), 399-424.
DOI: 10.1504/IJOGCT.2008.020370

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The solubility of hydrogen sulfide in aqueous N-methyldiethanolamine solutions

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Abstract: In this work the electrolyte equation of state as developed previously for the system MDEA-H₂O-CO₂-CH₄ [Huttenhuis et al. (2008), pp.99–112] was further developed for the system MDEA-H₂O-H₂S-CH₄. With this thermodynamic equilibrium model the total solubility of hydrogen sulfide and the speciation in aqueous solutions of N-methyldiethanolamine can be described quantitatively. The model results were compared to experimental H₂S solubility data in aqueous MDEA in absence and presence of methane respectively. The application of equation of state models for this kind of acid gas – amine systems is a rather new development in the literature. An accurate description is difficult for this kind of complex systems with significant amount of both molecular and ionic species present in the liquid phase. The Schwarzenuber's modification of the Redlich-Kwong-Soave EOS with a Huron-Vidal mixing rule is used as molecular part of the equation of state and ionic interactions terms are added to account for non-idealities caused by these interactions. With the new developed model a comparison with experimental data as presented was made. [Received: February 11, 2008; Accepted: June 1, 2008]

Keywords: hydrogen sulfide; N-methyldiethanolamine; solubility; electrolyte equation of state; gas treating.

Reference to this paper should be made as follows: Huttenhuis, P.J.G., Agrawal, N.J. and Versteeg, G.F. (2008) 'The solubility of hydrogen sulfide in aqueous N-methyldiethanolamine solutions', *Int. J. Oil, Gas and Coal Technology*, Vol. 1, No. 4, pp.399–424.

Biographical notes: Patrick Huttenhuis finished his Master thesis in Chemical Engineering at the University of Twente in 1995. After finishing his studies, he started his professional career as a Process Engineer at Jacobs Engineering. In this period, he worked on process simulations and conducted numerous conceptual studies for the chemical and gas treating industry. Since 2002, he has been working as a Senior Process Engineer for Procede Group B.V. His main focus has been the removal of acid components from several industrial gas streams.

Neeraj Agrawal is currently a PhD candidate in Chemical and Biomolecular Engineering Department of University of Pennsylvania. He holds a MS in Chemical Engineering from University of Twente and BS from University of

Mumbai. After finishing his MS, he was associated with Procede Group B.V. working on the development of equation of state thermodynamic models for acid-gas absorption in amines.

Geert Versteeg finished his Master thesis about the reaction kinetics between carbon dioxide and aqueous alkanolamine solutions at the University of Twente in 1982. In 1987, he finished his PhD thesis and he became a staff member of the Chemical Engineering Science group. He co-authored more than 150 scientific publications and patents and was Supervisor of more than 30 PhD projects. From 1992 to 2007, he was active as Professor in the same research group. In January 1993, he founded the company Procede where he is still active as Senior Scientist. In 2008, he was appointed as Professor at the State University of Groningen.

1 Introduction

Acid components like CO₂ and H₂S are normally (selectively) removed to a certain extent in natural and industrial gas streams, due to environmental or operational reasons. Absorption – regeneration process with an aqueous amine solution is commonly used for this kind of purification processes. The acid gas containing process stream enters at the bottom in the absorber where it is contacted counter-currently with a lean aqueous amine solution. In the absorber the acid gas is absorbed to the liquid phase where it is chemically converted to non volatile ionic species. The gas stream leaving the top of the absorber contains a significant lower acid gas concentration. The acid gas loaded solvent from the absorber is heated and/or depressurised and routed to a stripper where the solvent is regenerated and re-routed to the absorber. Thermodynamic data, mass transfer properties and the rate of the chemical reactions should be known for a robust process design of the above mentioned process system. Especially reliable thermodynamic data are valuable to prevent costly over-design factors of process equipment, which are currently applied for these kinds of complex acid gas – alkanolamine systems. In this work a rigorous thermodynamic model (an electrolyte equation of state) is used to predict the H₂S solubility in an aqueous MDEA solution at elevated methane pressure. In general the acid gas solubility is determined in absence of high partial pressures of inert components like nitrogen or hydrocarbons. However, in absorbers in the gas industry normally high methane pressures are encountered, so it is important to study the influence of hydrocarbons on the acid gas solubility. The thermodynamic model developed in this study has been validated with experimental data for the MDEA-H₂O-H₂S-CH₄ system as presented by Huttenhuis et al. (2007).

2 Description of electrolyte equation of state model

In the equation of state approach the same equations are used for both the vapour and liquid phase, i.e. the electrolyte equation of state (E-EOS). In the present work Schwarzenrüber et al.'s (1989) modification of the Redlich-Kwong-Soave EOS with a Huron and Vidal (1979) mixing rule is used. Additional interactions were added to this equation of state due to the presence of ions in the liquid phase as originally proposed by

Fürst and Renon (1993). A major advantage of this approach is that complex multi-component systems can be described quantitatively by studying less complex systems containing a smaller number of components. In former work of Huttenhuis et al. (2008) the system CO₂-MDEA-H₂O-CH₄ was described with the E-EOS approach and in this work the system H₂S-MDEA-H₂O-CH₄ is dealt with. Therefore the parameters to describe the system MDEA-H₂O-CH₄ are already known from the system CO₂-MDEA-H₂O-CH₄ and used in the newly developed model. Therefore, only additional pure component and interaction parameters due to the presence of H₂S and its relating ionic species are required.

The electrolyte equation of state used in this study can be reflected by the equation below:

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

In this equation the Helmholtz energy is calculated as the summation of five independent terms. The first two terms are described with the molecular equation of state – in the present case the Redlich-Kwong-Soave EOS modified by Schwarzenhuber et al. (1989) (ScRK-EOS). To account for interactions between molecules the Huron-Vidal mixing rule is used, because this mixing rule can also be used for highly non-ideal (polar) molecular systems, like MDEA-H₂O. In this mixing rule in total five interaction parameters are required for each binary molecular system. Another advantage of this Huron-Vidal mixing rule is that it can easily be converted to the van der Waals mixing rule using only one interaction parameter per binary pair. The other terms added to the Helmholtz expression are due to the interactions caused by the presence of ions in the system. For a detailed description of the E-EOS model used in this work reference is made to Huttenhuis et al. (2008).

3 Model development

3.1 Former work

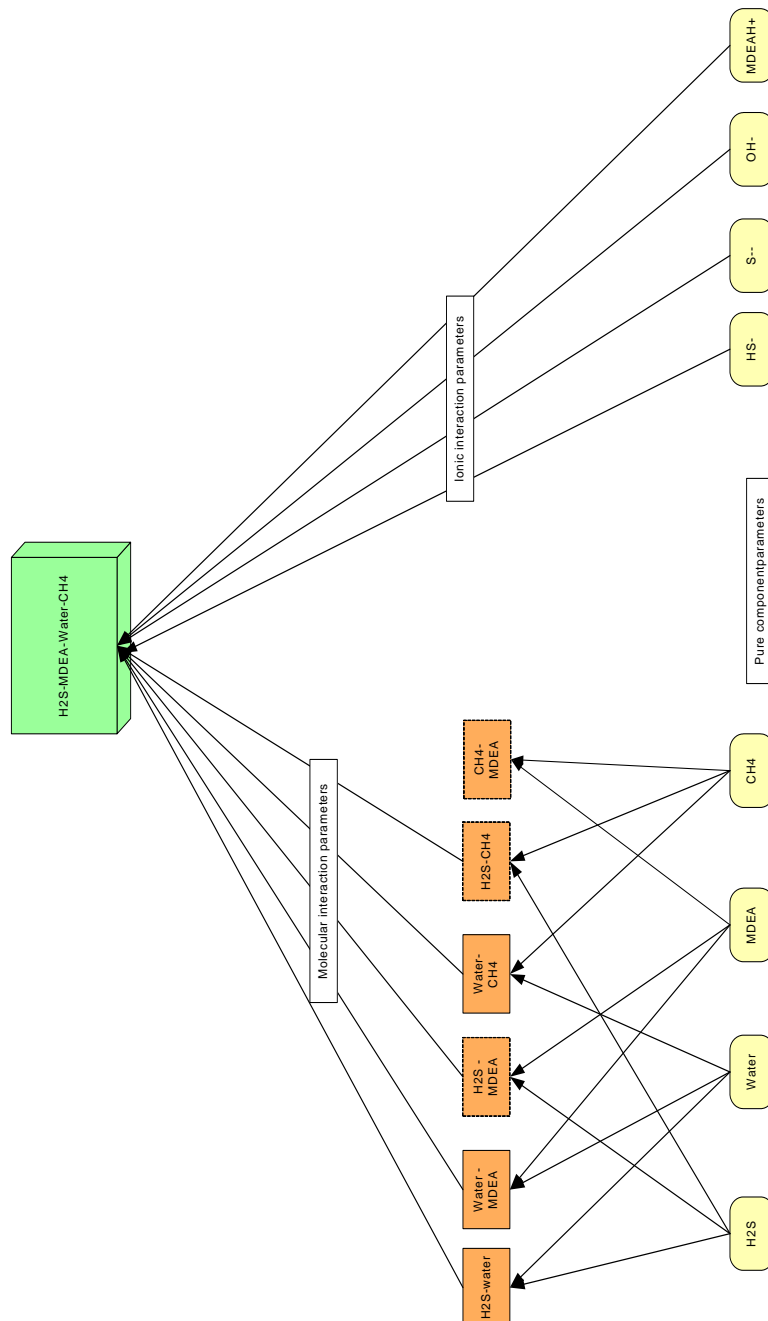
As described above the system MDEA-H₂O-CH₄ (part of the H₂S-MDEA-H₂O-CH₄ system) was already described quantitatively by the model presented in a former publication (Huttenhuis et al., 2008). Only additional pure component and interaction parameters due to the presence of H₂S and related ionic species in the system are required.

The following additional information is required to account for the presence of H₂S in the system:

- pure component parameters of H₂S, HS⁻ and S²⁻
- molecular interactions of the binary systems: H₂S-MDEA, H₂S-H₂O and H₂S-CH₄
- ionic interaction parameters: H₂S-MDEAH⁺, HS⁻-MDEAH⁺, S²⁻-MDEAH⁺.

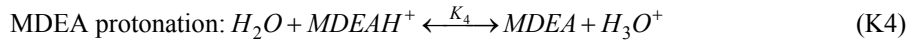
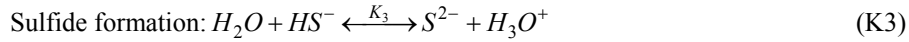
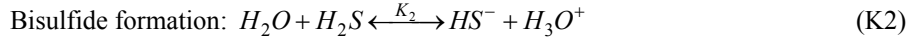
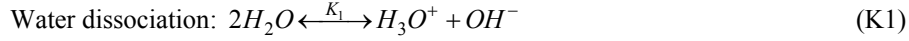
In the scheme shown in Figure 1 a schematic overview of the involved pure and binary parameters is presented for the H₂S-MDEA-H₂O-CH₄ system.

Figure 1 Overview of the interactions involved in the E-EOS model for the system H₂S-MDEA-H₂O-CH₄ (see online version for colours)



3.2 Chemical reactions

When the hydrogen sulfide absorbs in the liquid phase several acid-base reactions will take place and ionic species will be formed. For the H₂S-MDEA-H₂O-CH₄ system the following reactions will take place in the liquid phase:



The relation between equilibrium constant (K_x) and temperature is given by the relation as presented below:

$$\ln K_x = A + \frac{B}{T} + C \ln T \quad (2)$$

The relevant parameters for the equilibrium constants as used in the model are given in Table 1.

Table 1 Parameters for calculation of chemical equilibrium constants of system H₂S-MDEA-H₂O

Reaction	A	B	C	T [K]	Reference
K1	132.899	-13445.9	-22.4773	273–498	Austgen et al. (1991)
K2	214.582	-12995.4	-33.5471	273–423	Austgen et al. (1991)
K3	-32.0	-3338.0	0.0	287–343	Austgen et al. (1991)
K4	-77.262	-1116.5	10.06	278–423	Huttenhuis et al. (2007)

The K1 and K4 relations were the same as used by Huttenhuis et al. (2008) for the system MDEA-H₂O-CO₂.

In this work all chemical equilibrium constants are defined in the mole fraction scale with as reference state infinite dilution in water for all species. The concentration H₃O⁺-ions is neglected, because the mole fraction of this component is very low for this kind of systems. The thermodynamic model is able to calculate the mole fraction in both the gas and liquid phase of the following species: H₂O, OH⁻, H₂S, HS⁻, S²⁻, MDEA, MDEAH⁺ and CH₄.

3.3 Pure component model

In the MDEA-H₂O-H₂S-CH₄ system the following species are present: MDEA, MDEAH⁺, H₂O, H₃O⁺, OH⁻, H₂S, HS⁻, S²⁻, CH₄. The pure component parameters of these components are the same as used by Huttenhuis et al. (2008) except the data in Table 2, which were taken from Vallée et al. (1999):

Table 2 Pure component parameters

		H_2S	HS^-	S^{2-}
M	[gram.mole ⁻¹]	34.08	33.08	32.08
T _C	[K]	100.05		
P _C	[bar]	89.37		
ω	[-]	0.1		
p ₁		0.01857		
p ₂		0		
p ₃		-2.078		
σ	[10 ⁻¹⁰ m]	3.62	3.6	3.5
d ⁽⁰⁾		2		
d ⁽¹⁾		0		
d ⁽²⁾		0		
d ⁽³⁾		0		

3.4 Binary molecular interaction parameters

3.4.1 Overview

For the determination of the binary molecular interaction parameters, the same approach as presented by Huttenhuis et al. (2008) was followed in this work. Before simulating the quaternary system H₂S-MDEA-H₂O-CH₄, the following binary systems have to be studied and optimised:

- H₂S-H₂O: For this system the binary interaction data were determined from the three following sources: Selleck et al.(1952), Lee and Mather (1977) and Clarke and Glew (1971).
- H₂S-MDEA: For this molecular binary system no experimental data are available, because it is difficult to measure the physical solubility of H₂S in pure MDEA, because trace amounts of water which are always present in the MDEA increases the solubility significantly due to the occurring chemical reactions. Therefore, the N₂O analogy was used as frequently applied for CO₂.
- CH₄-H₂S: In this work the van der Waals equation was used with an interaction parameter $k_{ij} = 0.08$ (Reid et al., 1988).
- CH₄-MDEA; H₂O-MDEA; CH₄-H₂O: For these binary molecular systems the same interaction parameters as used by Huttenhuis et al. (2008) were incorporated in the model.

3.4.2 H₂S-H₂O

From an evaluation it was concluded that the experimental data of the following sources were consistent: Selleck et al. (1952), Lee and Mather (1977) and Clarke and Glew (1971). Lee and Mather (1977) measured the total system pressure at a specified temperature and H₂S liquid concentration. Selleck et al. (1952) and Clarke and Glew

(1971) measured both the system pressure and the H₂S vapour concentration. In the paper of Selleck et al. (1952) also extrapolated data and experimental data with two liquid phases are presented, however these are not used in this work, because our E-EOS model could not deal with two liquid phases. The experimental data (both system pressure and vapour concentration) were used to determine the binary Huron-Vidal parameters of the H₂S-H₂O system. The experimental conditions of the above mentioned literature sources and the comparison with the EOS model is presented in Table 3.

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

	<i>P</i> [bar]	<i>T</i> [°C]	<i>Data</i>	<i>Model results</i>			
				<i>Pressure</i> [bara]		<i>y</i> _{H₂S} [-]	
				<i>BIAS</i> [%]	<i>AAD</i> [%]	<i>BIAS</i> [%]	<i>AAD</i> [%]
Clarke and Glew (1971)	0.5–0.95	273–323	36	–4.0	4.4	–0.04	0.15
Lee and Mather (1977)	1.5–66.7	283–453	325	0.64	3.0	n.a.	n.a.
Selleck et al. (1952)	6.9–69	278–333	26	3.2	4.8	–0.11	0.40
Total	0.5–69	273–453	387	0.36	3.2	–0.07	0.25

Figure 2 Total pressure as function of H₂S liquid concentration for the H₂S-H₂O system; model results compared with experimental data of Lee and Mather (1977)

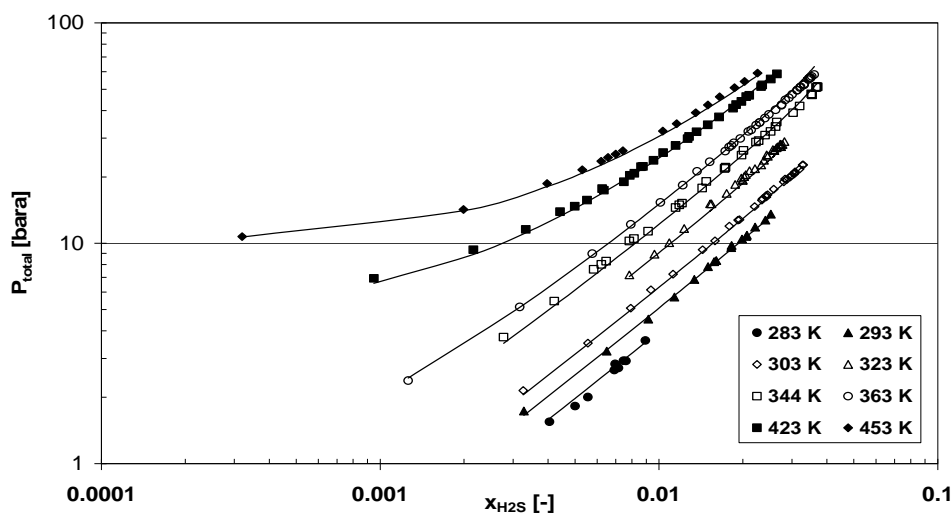
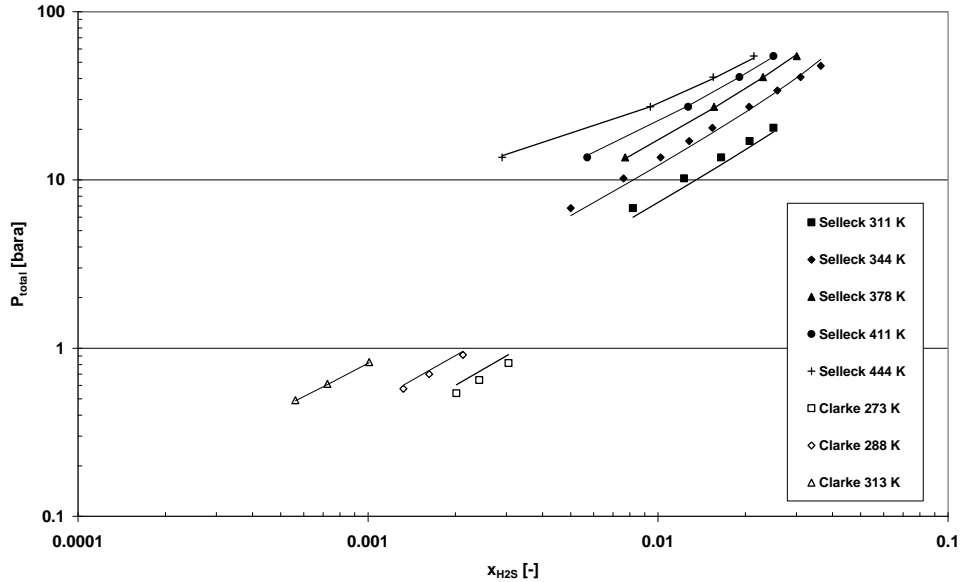


Figure 3 Total pressure as function of H₂S liquid concentration for the H₂S-H₂O system; model results compared with experimental data of Selleck et al. (1952) and Clarke and Glew (1971)



The AAD and BIAS are defined as presented in the equation below:

$$AAD = \frac{1}{n} \sum_{i=1}^n \left| \frac{P_{acidgas,exp} - P_{acidgas,calc}}{P_{acidgas,exp}} \right| * 100\% \quad \quad \quad BIAS = \frac{1}{n} \sum_{i=1}^n \frac{P_{acidgas,exp} - P_{acidgas,calc}}{P_{acidgas,exp}} * 100\%$$

From Table 3 it can be concluded that the model results are well in line with all three literature sources. In Figure 2 the experimental data as determined by Lee and Mather (1977) are presented graphically compared with the model results. In Figure 3, the experimental data of Selleck et al (1952) and Clarke and Glew (1971) are compared with the model. Due to the small temperature interval (5K) at which data of Clarke and Glew are measured not all data are presented in the graph; however for the model regression all experimental data have been used.

3.4.3 H₂S-MDEA

For this molecular binary system no direct experimental data can be used, because it is difficult to measure the physical solubility of H₂S in MDEA, because very small trace amounts of water present in the MDEA will cause significant chemical interactions and the formation of ionic species and for the H₂S-MDEA system only the binary molecular interactions should be determined. Therefore the same approach was used as in previous work (Huttenhuis et al., 2008). The physical solubility of H₂S in aqueous MDEA was determined from the N₂O analogy as frequently used to determine the physical solubility of CO₂ in different reactive solvents. According to this H₂S-N₂O analogy the physical solubility of H₂S in aqueous MDEA can be calculated in the following manner:

$$H_{H_2S, aq.MDEA} = \frac{H_{H_2S, water}}{H_{N_2O, water}} * H_{N_2O, aq.MDEA} \quad (3)$$

The experimental data for the solubility of N₂O in water and N₂O in aqueous MDEA were taken from previous work (Huttenhuis et al., 2008) and the solubility of H₂S in water was taken from the data of Clarke and Glew (1971), Lee and Mather (1977) and Selleck et al. (1952) for the H₂S-H₂O system (refer to Section 3.4.2).

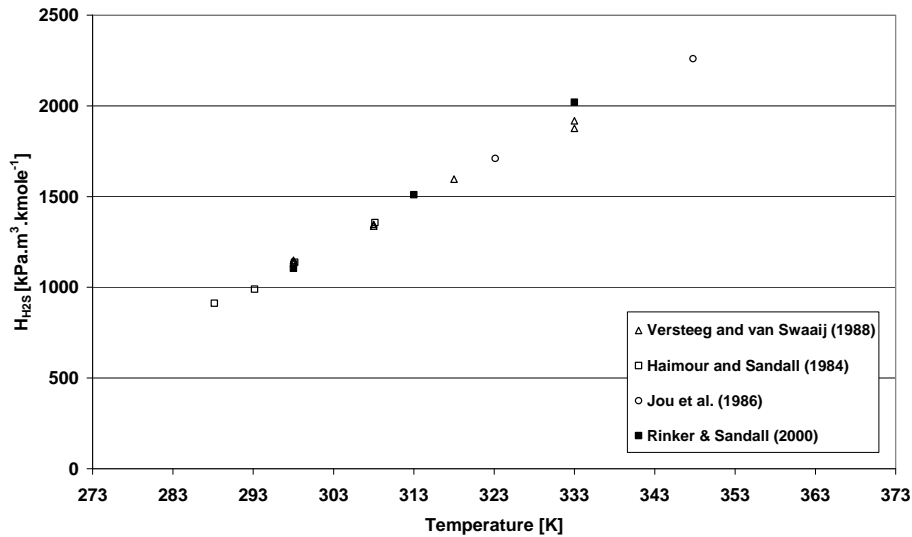
The physical solubility of H₂S in aqueous MDEA can be calculated, when the interaction parameters of the following binary molecular systems are determined: MDEA-H₂O, H₂S-H₂O and H₂S-MDEA. So in the present case the unknown binary interaction parameters of the H₂S-MDEA system can be calculated, when the binary molecular parameters of H₂S-H₂O (refer to Section 3.4.2) and MDEA-H₂O (Huttenhuis et al., 2008) and the physical solubility of H₂S in aqueous MDEA (see above) are determined. The physical solubility of N₂O in water was based on the relation developed by Jamal (2002). The physical solubility of N₂O in aqueous MDEA was based on experimental data produced by the following authors:

- Versteeg and van Swaaij (1988)
- Haimour and Sandall (1984)
- Jou et al. (1986)
- Li and Mather (1994)
- Pawlak and Zarzycki (2002).

In the work carried out by Rinker and Sandall (2000) the physical solubility of H₂S was determined by neutralising the aqueous MDEA solvent with HCl. In Figure 4, the calculated physical solubility of H₂S using the N₂O analogy (based on experimental data of Versteeg and van Swaaij, 1988; Haimour and Sandall, 1984; Jou et al., 1986) is compared with the experimental data in neutralised aqueous MDEA as reported by Rinker and Sandall (2000).

From Figure 4 it can be concluded that the physical solubility of H₂S in aqueous MDEA using the N₂O analogy (Versteeg and van Swaaij, 1988; Haimour and Sandall, 1984; Jou et al., 1986) is very well in line with the physical solubility determined in neutralised aqueous MDEA (Rinker and Sandall, 2000).

When the new binary interaction parameters for the H₂S-MDEA system were regressed, the calculated (from the experimental data) physical solubility of H₂S in aqueous MDEA was compared with the physical solubility calculated by the updated EOS model and results were good (BIAS = 0.61% and AAD=8.8%).

Figure 4 Physical solubility of H₂S in aqueous 20 wt.% MDEA as function of temperature

3.4.4 H₂S-CH₄

During the model simulations it was concluded that the calculated H₂S solubility was not sensitive for the value of the molecular interaction parameter of the H₂S-CH₄ binary system. Therefore it was decided to use a value of 0.08 for the binary interaction parameter k_{ij} of the van der Waal mixing rule, based on a binary interaction parameter k_{ij} for the binary system H₂S-propane (Reid et al., 1988).

3.4.5 Summary

In this chapter all relevant molecular interaction parameters are determined which are necessary to describe the total system H₂S-MDEA-H₂O-CH₄. These parameters are presented in Table 4.

The binary molecular interaction parameters MDEA-H₂O, MDEA-CH₄ and H₂O-CH₄ were derived from systems containing no acid gas (CO₂ or H₂S), so the same values as used in previous work (Huttenhuis et al., 2008) were used for these interaction parameters.

Table 4 Binary molecular interaction parameters

<i>comp.i</i>	<i>H₂S</i>	<i>H₂S</i>	<i>H₂S</i>	<i>MDEA</i>	<i>MDEA</i>	<i>H₂O</i>
<i>comp.j</i>	<i>MDEA</i>	<i>H₂O</i>	<i>CH₄</i>	<i>H₂O</i>	<i>CH₄</i>	<i>CH₄</i>
$k_{ij} [-]$	–	–	0.08	–	0.600	–
$a_{ij} [-]$	–0.907	0.104	–	0.208	–	0.150
$\Delta'g_{ij} [Jmol^{-1}]$	5567	26082	–	–9148	–	–1028
$\Delta'g_{ji} [Jmol^{-1}]$	2928	–2148	–	6095	–	40532
$\Delta'g_{ij} [Jmol^{-1}K^{-1}]$	–2.44	–18.45	–	42.35	–	17.40
$\Delta'g_{ji} [Jmol^{-1}K^{-1}]$	15.11	5.76	–	–49.93	–	–54.45
<i>reference</i>	This work	This work	This work	Huttenhuis et al. (2008)	Huttenhuis et al. (2008)	Huttenhuis et al. (2008)

3.5 Binary ionic interaction parameters

3.5.1 Ionic interaction parameters in MDEA-H₂S-H₂O system

Following the work of Fürst and Renon (1993), only the cation-anion and cation-molecular ionic interaction parameters are regressed in the model. The cation-cation, anion-anion and anion-molecular interactions are neglected. To describe the ternary system H₂S-MDEA-H₂O, the following ionic interaction parameters should be determined:

- MDEAH⁺ – MDEA
- MDEAH⁺ – H₂O
- MDEAH⁺ – H₂S
- MDEAH⁺ – HS[–]
- MDEAH⁺ – S^{2–}

The first two interaction parameters (MDEAH⁺-MDEA and MDEAH⁺-H₂O) are independent of the acid gas type. These interaction parameters have already been regressed in previous work for the CO₂-MDEA-H₂O system (Huttenhuis et al., 2008). However, the other ionic interaction parameters, which are H₂S specific, should be derived from experimentally obtained H₂S solubility data (VLE data) as presented in literature. Before using the published experimental data of various research groups, a consistency check was carried out on the applicability of the data. The MDEA-H₂S-H₂O solubility data of the following authors were reviewed with a mutual and internal consistency tests: Maddox et al. (1987), Lemoine et al. (2000), Huang and Ng (1998), Kamps et al. (2001), Kuranov et al. (1996), MacGregor and Mather (1991), Rogers et al. (1998), Sidi-Boumedine et al. (2004), Jou et al. (1982; 1993), Li and Shen (1993).

An overview of the experimental data used to determine the ionic interaction parameters in this work is presented in Table 5.

Table 5 Literature references used for the fitting of the ionic parameters of the H₂S-MDEA-H₂O system

<i>Reference</i>	<i>MDEA conc. [wt.%]</i>	<i>Temperature [K]</i>	<i>Liquid loading [mole H₂S/mole amine]</i>	<i>Number of points [-]</i>
Lemoine et al. (2000)	11.8	298	0.01–0.26	16
	23.6	313	0.015–0.15	13
Maddox et al. (1987)	11.8	298	0.64–2.17	19
	20	311, 339, 389	0.18–1.59	30
Huang and Ng (1998)	23.1	313, 373, 393	0.003–0.20	8
	50	313, 343, 373, 393	0.003–1.74	33
Kamps et al. (2001)	48.8	313, 353, 393	0.15–1.43	26
Kuranov et al. (1996)	18.7	313, 333, 373, 393, 413	0.50–1.93	35
	32.2	333, 373, 393, 413	0.48–1.63	36
MacGregor and Mather (1991)	20.9	313	0.13–1.73	27
Rogers et al. (1998)	23	313	0.013–0.31	12
	50	313	0.0022–0.093	10
Sidi-Boumedine et al. (2004)	46.8	313, 373	0.039–1.12	26

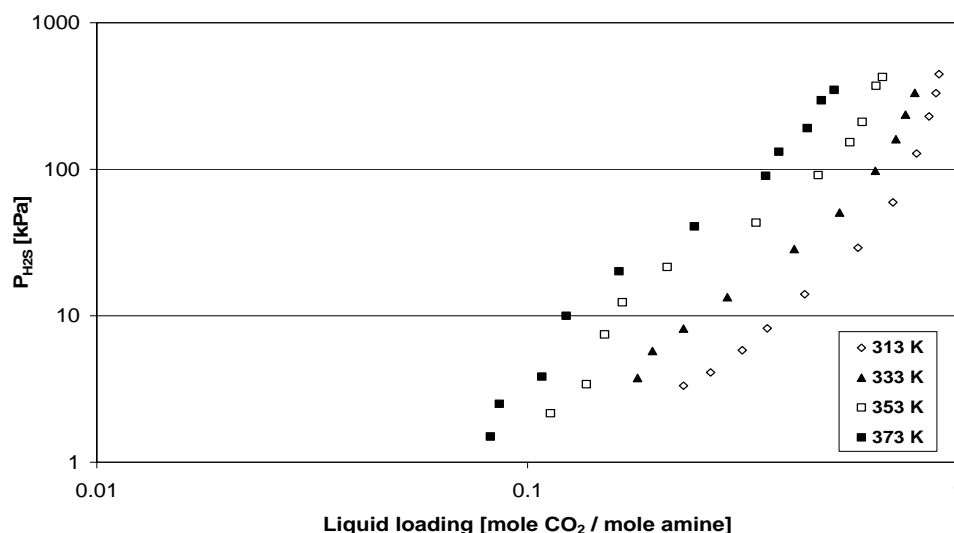
Note: Total 291 data points

The data of Jou et al. (1982; 1993) and Li and Shen (1993) were not included in the experimental database which was used to determine the ionic interaction parameters for the following reasons:

- When the presented experimental data of Jou et al. (1982) at 313K were compared for self-consistency, it was concluded that there was almost no difference in H₂S solubility between 35 wt.% and 49 wt.% aqueous MDEA. This seems questionable, because at fixed loading and temperature; the acid gas partial pressure increases with the MDEA concentration (refer to Chunxi and Fürst, 2000).
- Data of Jou et al. (1993) in 50 wt % MDEA were not consistent at loadings below 0.05. The trend of a log-log graph of the liquid loading versus H₂S partial pressure at low loadings should be almost linear and this was not the case for the data of Jou et al. (1993). There was also a mutual inconsistency seen when Jou's experimental data were compared with experimental data of Lemoine et al. (2000), Huang and Ng (1998) and Rogers et al. (1998). For more details reference is made to Huttenhuis et al. (2007).
- Data of Li and Shen (1993) at higher temperature are highly non-linear at elevated temperatures as can be seen in Figure 5. In general, at low loadings (< 0.3), a linear

relation between the logarithm of the partial pressure and the gas loading exists for acid gas – aqueous alkanolamine systems (refer to Chunxi, and Fürst, 2000).

Figure 5 Solubility of H₂S in 2.57 M aqueous MDEA at different temperatures



Source: Li and Shen (1993)

To determine the ionic interaction parameters for the system MDEA-H₂O-H₂S the relevant interaction parameters were regressed simultaneously with the ionic interaction parameters for the system MDEA-H₂O-CO₂, which were already derived in our former work (Huttenhuis et al., 2008). A similar approach of ‘simultaneously regression’ procedure was used by Chunxi and Fürst (2000). As the S²⁻ concentration in general will be very low, due to the low dissociation constant of the bisulfide ion, the influence of the MDEAH⁺ - S²⁻ ionic interaction parameter is assumed to be small. Therefore, this parameter is not regressed in this work. Instead, this ionic interaction parameter was calculated with the correlation proposed by Chunxi and Fürst (2000). The total experimental database used during the regression consists of the H₂S solubility database (Table 5) and the CO₂ solubility database described in previous work (Huttenhuis et al., 2008). From the simultaneous regression with single CO₂ and single H₂S solubility data, the following values for the ionic binary interaction parameters were derived (Table 6):

Table 6 Ionic interaction parameters regressed with solubility data of H₂S in aqueous MDEA and CO₂ in aqueous MDEA simultaneously

comp.i	MDEAH ⁺	MDEAH ⁺	MDEAH ⁺	MDEAH ⁺	MDEAH ⁺	MDEAH ⁺	MDEAH ⁺
comp.j	MDEA	H ₂ O	H ₂ S	HS ⁻	CO ₂	HCO ₃ ⁻	CO ₃ ²⁻
W _{ij} [m ³ mol ⁻¹]	2.31E-03	4.17E-04	4.88E-04	-1.49E-04	2.98E-04	-1.32E-04	-2.74E-04

When the ionic interaction parameters of the MDEA-H₂O-CO₂ system (MDEAH⁺-MDEA, MDEAH⁺-H₂O, MDEAH⁺-CO₂, MDEAH⁺HCO₃⁻ and MDEAH⁺-CO₃²⁻) which were already derived from the CO₂ single gas experiments in our former work (Table 7)

were compared with the values derived in this work (Table 6), it was concluded that changes in both acid gas independent (MDEAH⁺-MDEA and MDEAH⁺-H₂O) and dependent (MDEAH⁺-CO₂, MDEAH⁺-HCO₃⁻ and MDEAH⁺-CO₃²⁻) interaction parameters were negligible.

Table 7 Ionic interaction parameters regressed with solubility data of CO₂ in aqueous MDEA

comp.i	MDEAH ⁺	MDEAH ⁺	MDEAH ⁺	MDEAH ⁺	MDEAH ⁺
comp.j	MDEA	H ₂ O	CO ₂	HCO ₃ ⁻	CO ₃ ²⁻
W _{ij} [m ³ mol ⁻¹]	1.95E-03	4.09E-04	2.48E-04	-1.29E-04	-3.58E-04

Source: Huttenhuis et al. (2008)

The value of the MDEAH⁺-MDEA interaction parameter increased 18%, while the MDEAH⁺-H₂O interaction parameters increased only 2%.

Also the values of the CO₂ specific interaction parameters (MDEAH⁺-CO₂, MDEAH⁺-HCO₃⁻, MDEAH⁺-CO₃²⁻) did not alter significantly, due to the addition of the single gas H₂S data in the regression procedure. Maximum change was seen for the MDEAH⁺-CO₃²⁻ interaction parameter which showed an increment of 23%. However, owing to the very low concentrations of CO₃²⁻ in loaded amine solutions the value of this parameter will have only a minor influence on the overall results of the E-EOS model. The predicted CO₂ single gas solubility of the E-EOS model with the new ionic interaction parameters (W_{ij}) were compared with the experimental single gas CO₂ solubility data as mentioned in the previous paper (Huttenhuis et al., 2008). The conclusion of this comparison was that similar results were derived with the new interaction parameters. The calculated AAD and BIAS for the CO₂ single gas experiments were changed from 24% (Huttenhuis et al., 2008) to 25 % (this work) and 8.3% (Huttenhuis et al., 2008) to 8.4% (this work) respectively. The AAD and BIAS for the H₂S single gas experiments were respectively 26 and 2.1% (this work).

3.5.2 Ionic interactions parameters in H₂S-MDEA-H₂O-CH₄ system

Only one additional ionic interaction parameter is required when methane is added to the H₂S-MDEA-H₂O system, i.e. the MDEAH⁺-CH₄ ionic interaction parameter, however this parameter has been determined in a previous study (Huttenhuis et al., 2008). The value of this parameter has been determined by regressing this interaction parameter with experimental solubility data of Addicks (2002), who measured the solubility of CO₂ in aqueous MDEA at elevated methane partial pressure. However due to the new (CO₂) ionic interaction parameters determined in this work, as described in Section 3.5.1 the regression of this parameter with Addick's experimental solubility data has been repeated. This MDEAH⁺-CH₄ ion interaction parameter changed marginally from 4.93E-04 to 5.77E-04.

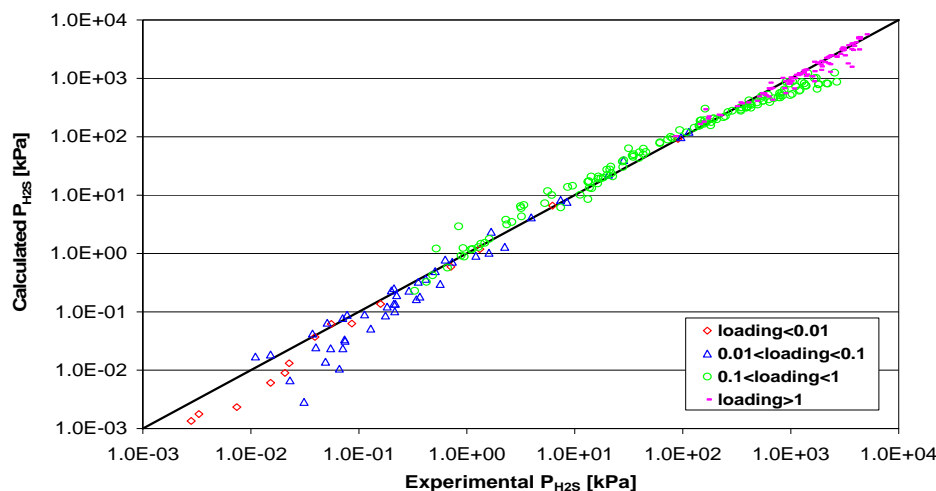
3.5.3 Summary

All relevant ionic interaction parameters have been determined to characterise the H₂S-MDEA-H₂O-CH₄ system. It must be noted that the ionic interaction parameters which were used to describe the system CO₂-MDEA-H₂O-CH₄ as determined in a previous paper (Huttenhuis et al., 2008) were changed marginally.

4 Modeling results

4.1 Ternary system H_2S -MDEA- H_2O

Figure 6 Parity plot for different H_2S liquid loadings (mole H_2S /mole amine) (see online version for colours)



When all input parameters of the electrolyte equation of state model have been derived, new model calculations were carried out to validate the model to the experimental database as reflected in Table 5. The calculated AAD and BIAS between model and experimental data were respectively 26 and 2%. In Figure 6, a parity plot of the H_2S solubility data is presented for different H_2S liquid loadings.

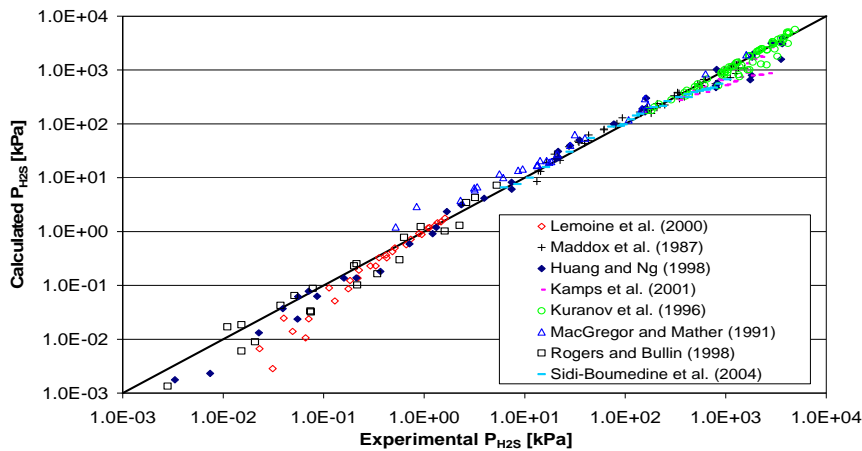
From Figure 6, it can be concluded that at low loadings (<0.1 mole H_2S / mole amine) the model predict H_2S partial pressures which are consistently lower as compared to the experimental data. The same conclusion was made in previous work where the CO_2 -MDEA- H_2O system was studied (Huttenhuis et al., 2008). Both the AAD and BIAS deviation decreased significantly for H_2S liquid loading above 0.1 mole H_2S / mole amine. It was remarkable to see that for the intermediate loadings ($0.1 < \text{loading} < 1$) a negative BIAS was derived for the low partial pressures and for the higher partial pressure a positive BIAS deviation was resulting. The best model results were derived in very high H_2S liquid loadings (loading > 1); in this regime the calculated BIAS was zero for the 96 experimental data points. The influence of temperature and MDEA concentration on the model performance was also analysed, however no clear conclusion could be drawn from this comparison. One remarkable observation is that at intermediate temperature (311–313K) and intermediate MDEA concentrations (20–24 wt.%) a negative BIAS ($P_{\text{exp}} < P_{\text{model}}$) was noticed, while for all other conditions positive BIAS deviations were seen (refer to Table 8).

Table 8 BIAS (left column) and AAD deviation (right column) (%) for the experimental data points as function of liquid loading, temperature, MDEA concentration and author

Liquid loading [mole H ₂ S/mole amine]	<0.01 (14)		0.01–0.1 (45)		0.1–1 (136)		>1 (96)	
	32	34	19	34	–5	31	0	14
Temperature (K)	298–299 (35)		311–313 (121)		333–353 (41)		373–413 (94)	
	8	27	–11	30	14	19	11	22
Concentration MDEA [wt.%]	12 (35)		20–24 (125)		32 (36)		47–50 (95)	
	8	27	–16	26	11	17	20	29
Author	Lemoine et al. (2000) (29)		Maddox et al. (1987) (49)		Huang and Ng. (1998) (41)		Kamps et al. (2001) (26)	
	25	28	–5	17	6	29	31	31
Author	Kuranov et al. (1996) (71)		MacGregor and Mather (1991) (27)		Rogers et al. (1998) (22)		Sidi-Boumedine et al. (2004) (26)	
	4	13	–60	60	8	38	9	17

Note: Number of experimental data points is given in brackets.

In Figure 7 the model E-EOS predictions are compared with the experimental data of the different research groups.

Figure 7 Parity plot for different research groups (see online version for colours)

From Figure 7, it can be concluded that the model is underpredicting the H₂S partial pressure for all authors (Rogers et al., 1998; Huang and Ng 1998; Lemoine et al., 2000) at partial pressures lower than 1 kPa (low H₂S liquid loadings). Also, a lot of scatter is seen in these range for all authors (AAD > 25 %). Most likely explanation for the observed phenomena is the assumption that the used MDEA was contaminated with small amounts of primary and/or secondary amines. These contaminants usually have a higher pKa and therefore reduce the experimentally observed equilibrium partial pressures, especially at low loadings.

In the intermediate region ($1 < P_{\text{H}_2\text{S}} < 1000$ kPa) the experimental data of MacGregor and Mather (1991) are remarkable. The BIAS and AAD for this data set were respectively -60 and +60%; for all of their experimental data the experimentally determined H₂S partial pressures are substantially lower compared to the model estimations. This is not in line with the experimental solubility data of the other authors, which showed good model predictions for intermediate H₂S partial pressures and positive BIAS deviations for low and high partial pressures. The same conclusion was presented by Huttenhuis et al. (2008) with respect to the work of Jou et al. (1982; 1993) who measured the solubility of CO₂ in aqueous MDEA. It was concluded by Huttenhuis that the solubility data of Jou et al. showed CO₂ partial pressures which were significantly lower compared to the results of other authors at similar process conditions. MacGregor and Mather (1991) measured the solubility of H₂S in 20.9 wt.% MDEA at 313K; so the influence of their data on the model predictions is the reason that negative BIAS deviations were seen in the intermediate temperature range 311–313K and intermediate MDEA concentrations (20–24 wt.%). When the data of MacGregor and Mather (1991) were excluded from the AAD and BIAS calculations as reflected in Table 8, the respective BIAS deviations for the temperature range (311–313K) and MDEA concentration (20–24 wt.%) decreased from respectively -11 to +4% and -16 to -4% (respectively BIAS and AAD)! When these deviations are compared to those calculated in previous work Huttenhuis et al. (2008) for the CO₂-MDEA-H₂O system, it can be concluded that the accuracy of the model for H₂S is similar to the CO₂ results. According to the model simulations for the different data sources, it can be seen that the best matching was obtained for the experimental data of Maddox et al. (1987) and Kuranov et al. (1996), however, it should be noted that for these two sources experiments were carried out at relatively high acid gas partial pressures. These experiments are in general less difficult than the low acid gas partial pressure experiments.

One of the key advantages of the E-EOS model to less rigorous models is that the activity coefficient and speciation of each component in the liquid phase can be calculated. This speciation is important when detailed rate based absorption models are required to predict the mass transfer rate in e.g. gas treating equipment. In Figure 8, (MDEA and MDEAH⁺) and Figure 9 (H₂S and HS⁻) the speciation for the species, in a 35 wt.% aqueous MDEA solution at 313K is calculated with the E-EOS model.

The calculated mole fractions of the S²⁻-ion in the liquid phase were lower than 10⁻⁹ for all liquid loadings, so this species has been omitted in Figure 9. Due to this low concentration of S²⁻-ion it can be seen that the fractions of the MDEAH⁺-ion are almost identical to the fraction HS⁻-ions. In Figure 10 and Figure 11, the calculated activity coefficients are presented for all species present in the H₂S-MDEA-H₂O system.

Figure 8 Speciation of MDEA species in 35 wt.% MDEA at 313K calculated by the E-EOS model (see online version for colours)

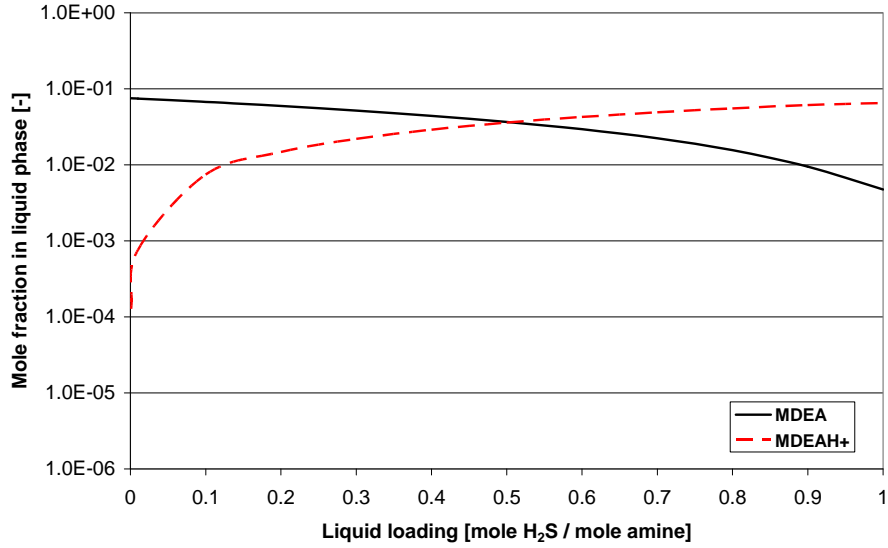


Figure 9 Speciation of H₂S species in 35 wt % MDEA at 313K calculated by the E-EOS model (see online version for colours)

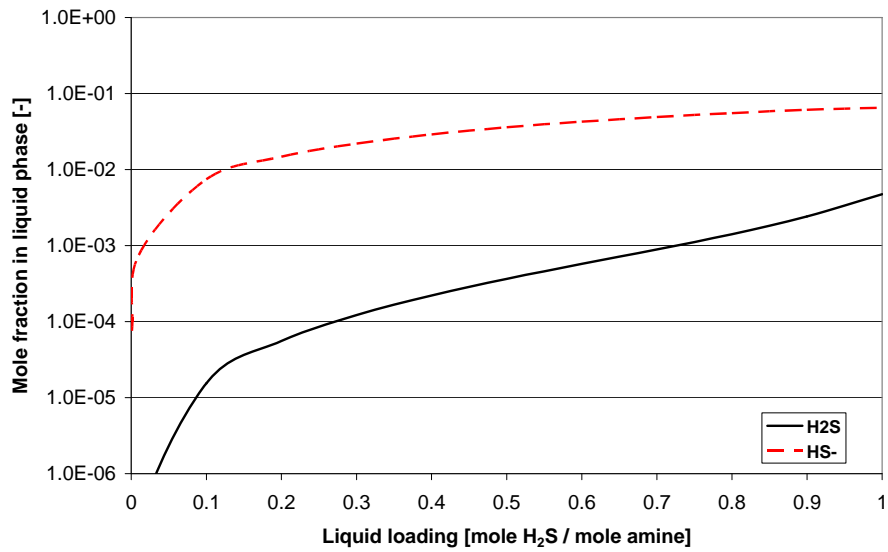


Figure 10 Activity coefficient of MDEA species in 35 wt.% MDEA at 313K calculated by the E-EOS model (see online version for colours)

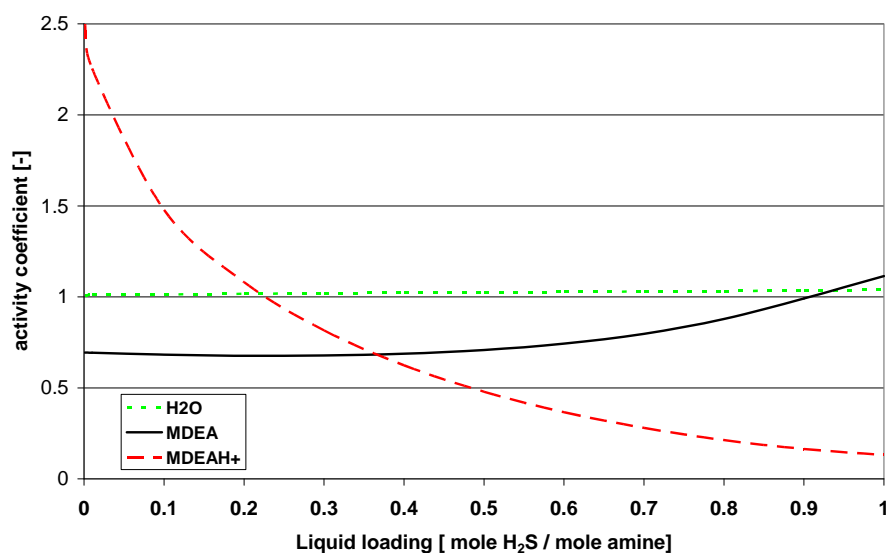
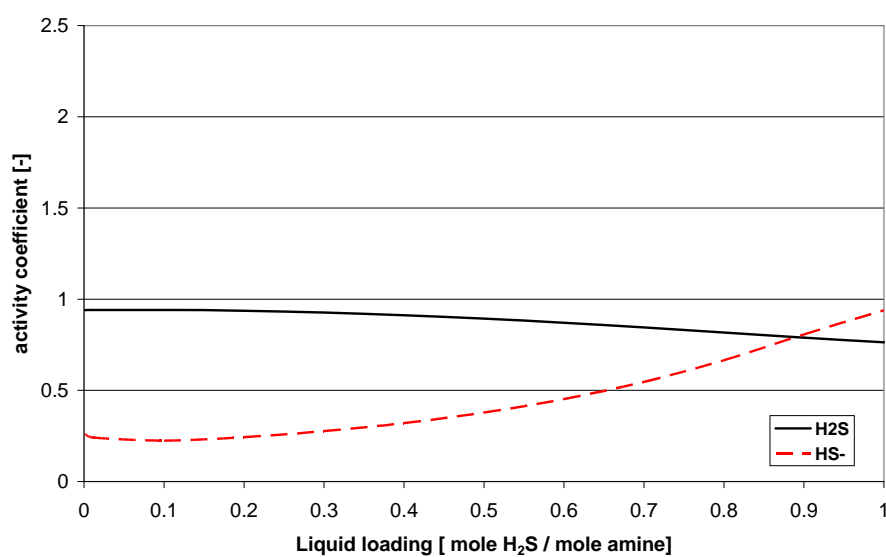


Figure 11 Activity coefficient of H₂S species in 35 wt.% MDEA at 313K calculated by the E-EOS model (see online version for colours)

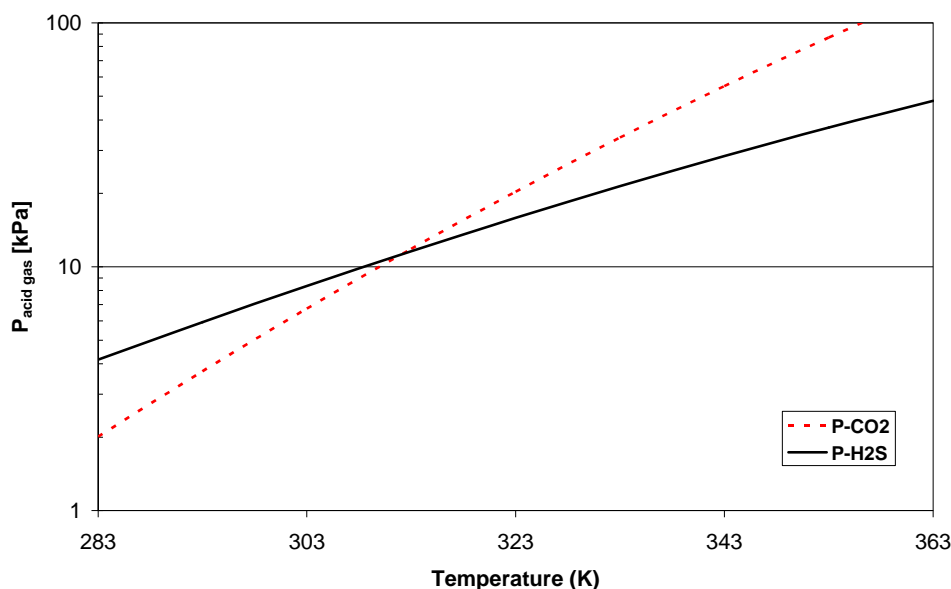


From Figure 10 and Figure 11 it can be concluded that MDEAH⁺ activity coefficient decreases and the HS⁻ activity coefficient increases as H₂S liquid loading increases. For the other species present in the liquid phase, the influence of the H₂S liquid loading on the activity coefficient is less pronounced. The activity of H₂O and H₂S are rather close to unity over a wide range of liquid loadings. However, the MDEA activity is lower than

unity at low loadings and, remarkably, increases with the loading and at 0.9 it even becomes larger than 1. The same behaviour for the activity and speciation was seen in the system $\text{CO}_2\text{-H}_2\text{O-MDEA}$ (Huttenhuis et al., 2008). Main difference is that the concentration S^{2-} in the liquid phase can be neglected completely over the entire range of H_2S liquid loadings and in case of CO_2 the CO_3^{2-} concentrations are significant. This can be explained by the difference in dissociation constant of HS^- and HCO_3^- . The dissociation constant (pKa) of HS^- is more than two points higher (lower dissociation in alkaline solutions) than the pKa of HCO_3^- .

In Figure 12, the H_2S partial pressure as calculated with the E-EOS model is calculated for 35 wt.% aqueous MDEA solution loaded with a liquid loading of 0.5 as a function of temperature. The same calculations have been carried out for the solubility of CO_2 in aqueous MDEA with the model previously developed (Huttenhuis et al., 2008).

Figure 12 Calculated partial pressure CO_2 and H_2S in 35 wt.% MDEA at an acid gas liquid loading of 0.5 mole acid gas/mole amine (see online version for colours)

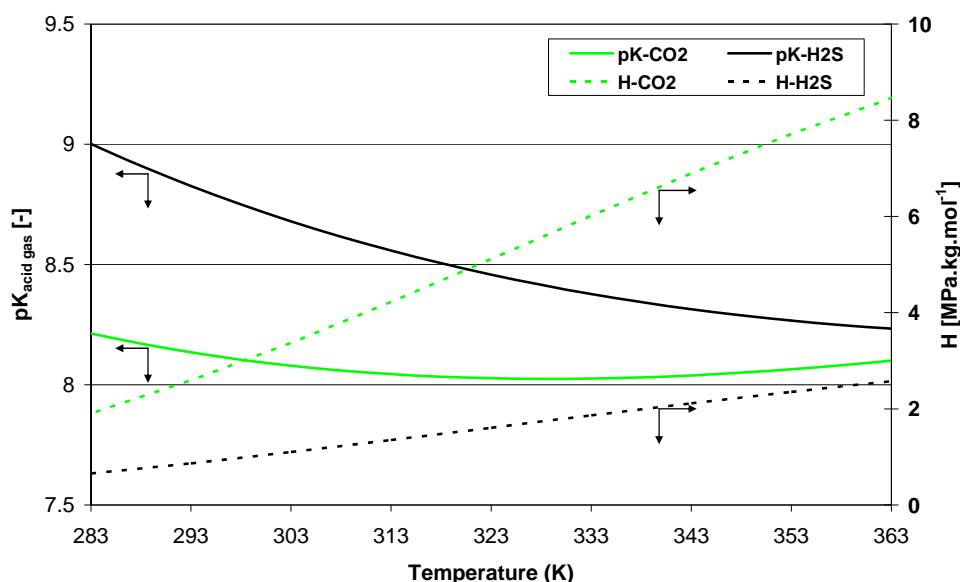


From Figure 12 it can be concluded that at 313K, H_2S and CO_2 solubilities are comparable in 35 wt.% MDEA. With increasing temperature the acid gas solubility for H_2S becomes higher than for CO_2 . The above mentioned effect can be explained by the influence of the temperature on the acid gas dissociation constant and physical solubility for both acid gases in the liquid phase respectively. In Figure 13, the dissociation constant (pKa) and the Henry's constant in water is presented graphically as function of temperature for both H_2S and CO_2 .

In Figure 13, it can be seen that over the temperature range 283–363 K, the pKa of CO_2 is lower than H_2S (i.e. CO_2 is a stronger acid), meaning that more molecular CO_2 will dissociate to ionic species in water. On the other hand, the Henry's constant of CO_2 in water is higher than H_2S in water, i.e. the solubility of CO_2 in water is lower than that of H_2S in water. According to the N_2O analogy as mentioned in Section 3.4.3, the acid gas solubility in water can be correlated to the physical solubility in aqueous MDEA,

when the N_2O solubility in water and aqueous MDEA are known. So from the Henry's constant presented in Figure 13 it can be concluded that the physical solubility in H_2S in aqueous MDEA is substantially higher than the physical solubility of CO_2 . So due to the lower acidity of H_2S and the higher physical solubility in aqueous MDEA compared to CO_2 , it is possible that the total solubility (both physical and chemical respectively) between CO_2 and H_2S are equal as is seen in Figure 12 at 313K. From Figure 13, it can also be seen that with increasing temperatures the difference in dissociation constants of CO_2 and H_2S becomes less, however, the difference in physical solubility between CO_2 and H_2S increases with temperature. Owing to the above mentioned consideration the total solubility of H_2S in aqueous MDEA will be higher than in CO_2 at elevated temperature. This is in line with the equilibrium – loading simulations of the E-EOS model as can be seen in Figure 12.

Figure 13 Acid gas dissociation constant (see online version for colours)



Source: pK- CO_2 based on molefractions (Posey and Rochelle, 1997)
 pK- H_2S based on molefractions (Austgen et al., 1991)
 Henry's constant in water (Kuranov et al., 1996)

4.2 Quaternary system H_2S -MDEA- H_2O - CH_4

To study the influence of methane on the solubility of H_2S in aqueous MDEA the following additional parameters are required:

- Pure component parameters of methane (Huttenhuis et al., 2008).
- Molecular binary interaction parameters CH_4 -MDEA and CH_4 - H_2O . Values for these parameters were taken from Huttenhuis et al. (2008).

- Ionic binary interaction parameter $\text{CH}_4\text{-MDEAH}^+$. The value for this parameter was taken from Huttenhuis et al. (2008) and slightly modified in this work (refer to Section 3.5.2).
- Molecular binary interaction parameter $\text{CH}_4\text{-H}_2\text{S}$. A value of 0.08 was taken as stated in Section 3.4.4. It appeared that the calculated H_2S solubility was very insensitive for the value of this parameter.

The electrolyte equation of state was compared with the experimental solubility data of H_2S in aqueous MDEA at different partial pressures methane as reported by Huttenhuis et al. (2007). Huttenhuis et al. (2007) measured the solubility of H_2S in aqueous 35–50 wt.% MDEA at 10 and 25°C with methane as make-up gas up to a methane partial pressure of 69 bar. In this work, from the experimental data, it was concluded that the H_2S solubility decreased with increasing methane partial pressure. The experimental data of Huttenhuis et al. (2007), a total of 30 experiments with varying temperatures, MDEA concentrations, H_2S loadings and CH_4 partial pressures, was compared to the outcome of the E-EOS simulations. The results are reflected in Table 9.

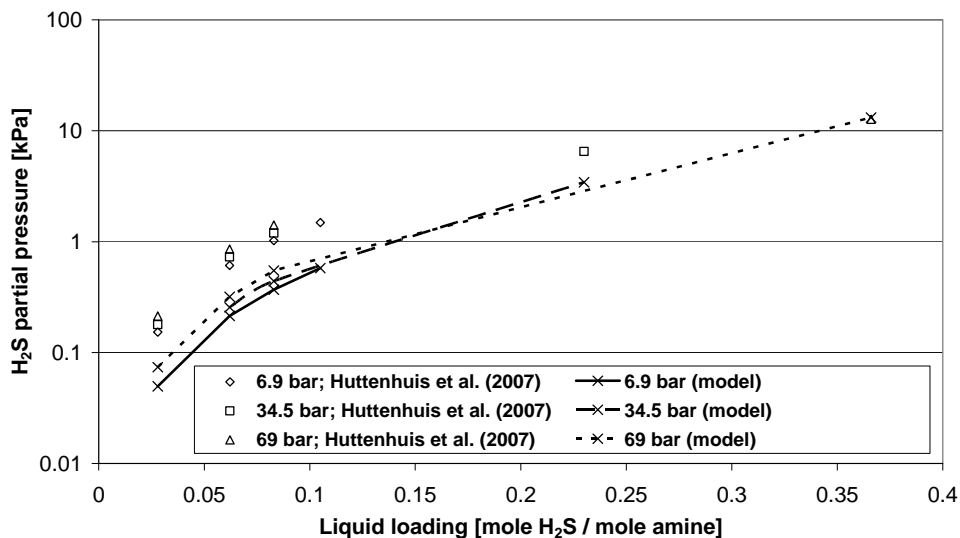
Table 9 Number of experimental data (Huttenhuis et al., 2007), BIAS and AAD for the H_2S solubility in aqueous MDEA and methane partial pressure up to 69 bar

	<i>data</i>	<i>BIAS [%]</i>	<i>AAD [%]</i>
Overall	30	40	44
35 wt.% MDEA	12	17	26
50 wt.% MDEA	18	55	55
10°C	12	45	48
25°C	18	37	40
6.9 bar CH_4	10	55	55
34.5 bar CH_4	10	33	38
69 bar CH_4	10	31	38

From Table 9, it can be concluded that the model calculates significantly lower H_2S partial equilibrium pressures for all process conditions. The overall BIAS and AAD deviations for all 30 experimental data points were 40% and 44% respectively. Best model results were derived at low temperature (10 °C), low MDEA concentration (35 wt.%) and high partial pressure methane (69 bar). When the results of these single gas H_2S experiments are compared with the single gas CO_2 work as reported by Huttenhuis et al. (2008) the same trends were seen. Also, in the CO_2 work the model was calculating lower acid gas partial pressures. Moreover, the model predictions at 35 wt.% MDEA were significantly better than the predictions at 50 wt.% MDEA. This was also seen for the model predictions for the system $\text{H}_2\text{S}\text{-MDEA}\text{-H}_2\text{O}$ as reported in Section 4.1. However, model results of the CO_2 work (overall BIAS was 16%) were better than the H_2S model calculations in this work. It was concluded that the $\text{CO}_2\text{-N}_2\text{O}$ analogy as used by Huttenhuis et al. (2008) to regress the $\text{CO}_2\text{-MDEA}$ molecular binary interaction parameter might be less applicable for higher MDEA concentrations. The same may be concluded for the $\text{H}_2\text{S}\text{-N}_2\text{O}$ analogy as used in this work to regress the $\text{H}_2\text{S}\text{-MDEA}$ molecular binary interaction parameter.

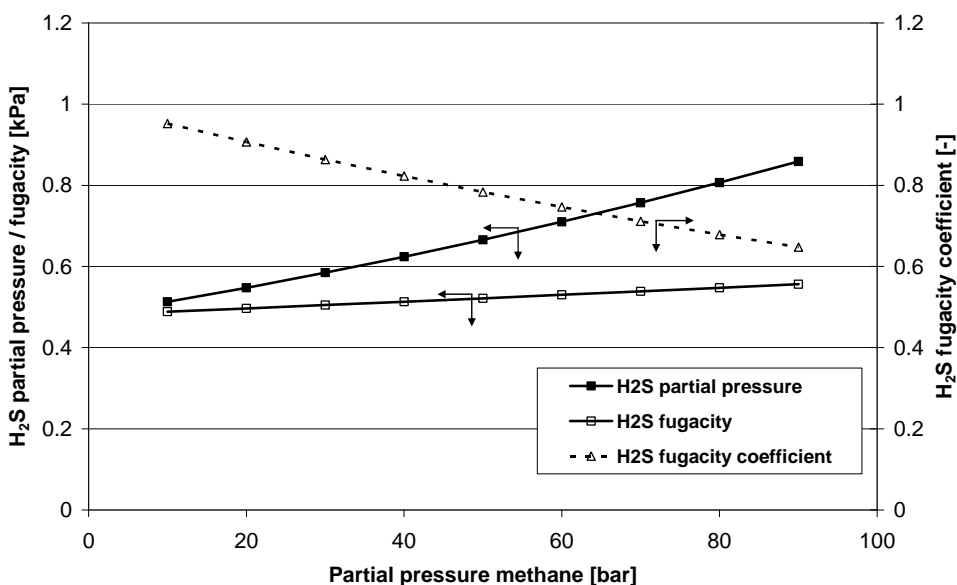
In Figure 14, the experimental H₂S solubility as measured by Huttenhuis et al. (2007) is compared graphically with the calculations of the E-EOS model.

Figure 14 Solubility of H₂S in 50 wt.% MDEA at 298K and different partial pressure methane



From this figure it can be concluded that the E-EOS model is predicting significantly lower the H₂S solubilities in the entire range. However, the influence of methane on the solubility is predicted correctly by the model. If the partial pressure methane increases the H₂S solubility in aqueous MDEA decreases.

Figure 15 Partial pressure, fugacity and fugacity coefficient of H₂S in 35 wt.% MDEA at 25°C at a liquid loading of 0.1 mole H₂S/mole amine



In Figure 15, the partial pressure, the fugacity and the fugacity coefficient of H₂S are presented in a 35 wt.% MDEA solvent and a liquid loading of 0.1 as function of methane partial pressure. From this figure it can be seen that the H₂S partial pressure is a strong function of the methane partial pressure. However, from Figure 15 it can also be seen that the H₂S fugacity is more or less independent of the methane partial pressure. So the reason for the H₂S decreasing solubility at increasing methane partial pressure may be caused mainly by the decreasing fugacity coefficient of H₂S. From the above mentioned considerations it is expected that the model predictions may be improved by incorporating additional experimental data from different research groups for the determination of the interaction parameters. Especially experimental solubility data with methane are lacking in literature. The ionic interaction parameter MDEAH⁺-CH₄ has been based on experimental data of Addicks (2002) and the molecular interaction parameter MDEA-CH₄ was based on data of Jou et al. (1998).

5 Conclusions

In the present study an electrolyte equation of state model as developed by Huttenhuis et al (2008) for the system CO₂-MDEA-H₂O-CH₄ was further developed for the system H₂S-MDEA-H₂O-CH₄. The model was validated with experimental solubility data of H₂S in aqueous MDEA in absence and presence of methane as a make-up gas. For both the system H₂S-MDEA-H₂O and H₂S-MDEA-H₂O-CH₄ the model was under-predicting the acid gas partial pressure (i.e. over-predicting the acid gas solubility), however, model predictions for the system in absence of methane were better. It was seen both experimentally and from model calculations that an increase in partial pressure methane resulted in a decrease of H₂S solubility in the aqueous MDEA. From this work it was concluded that this decreasing solubility was caused by a decreasing H₂S fugacity coefficient at increasing methane partial pressure. More experimental data are required to improve the accuracy of the E-EOS model. Especially additional acid gas solubility data with high methane partial pressures are required, because in this study only one single source could be used for model validations.

Acknowledgements

Even Solbraa is greatly acknowledged for his support with the development of the E-EOS model used in this work.

Nomenclature

A	Helmholtz energy	[J]
AAD	Absolute average deviation	[%]
BIAS	Mean BIAS deviation	[%]
d	Coefficients for dielectric constant	
g	Interaction parameter in Huron-Vidal mixing rule	[J m ⁻³]
H	Henry's coefficient	[kPa.m ³ .kmole ⁻¹]
K	Chemical equilibrium constant	[-]
k	Binary (molecular) interaction parameter	[-]
MDEA	N-methyldiethanol amine	[-]
M	Molecular mass	[gram.mol ⁻¹]
n	Mole number	[mole]
P	(partial) Pressure	[Pa]
p ₁ , p ₂ , p ₃	polarity parameters	[-]
R	Gas constant	[J mole ⁻¹ K ⁻¹]
T	Temperature	[K]
W	Binary ionic interaction parameter	[m ³ .mol ⁻¹]
x	Liquid mole fraction	[-]
y	Vapour mole fraction	[-]
<i>Greek letters</i>		
α	Binary nonrandomness parameter in Huron-Vidal mixing rule	[-]
σ	Ionic/molecular diameter	[m]
ω	Accentric factor	[-]

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