



## Solubility of hydrogen sulfide in aqueous solutions of *N*-methyldiethanolamine at high pressures



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### ABSTRACT

A static-analytic method was used to measure the H<sub>2</sub>S solubility in 50 wt% MDEA and in presence of methane as a makeup gas. The solubility was measured at 7000 kPa total pressure, and at 50 and 70 °C, for H<sub>2</sub>S partial pressures from 31 to 974 kPa. Measurements were also performed at 1500 kPa total pressure and 50 °C for H<sub>2</sub>S partial pressure span of 53–386 kPa. The measured data were compared to predictions using the Extended UNIQUAC model. The experimental data showed that the total pressure has a significant effect on H<sub>2</sub>S solubility in aqueous MDEA. The observed effect is shown to be dominated by the non-ideality of the gas, and it could be predicted by the pressure effect on the fugacity coefficient of H<sub>2</sub>S in the gas phase. The experimental data from this work are compared and shown to be consistent with earlier published data.

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### 1. Introduction

A large portion of the world's natural gas resources comprises high amounts of CO<sub>2</sub> and H<sub>2</sub>S (acid gases). CO<sub>2</sub> has to be removed from the natural gas because of transport requirements and sale gas specifications. Dependent on product quality, CO<sub>2</sub> typically needs to be reduced to 2.5 mol% for sale gas specifications or to 0.005 mol% for production of liquefied natural gas. H<sub>2</sub>S generally needs to be reduced to around 0.0005 mol% because of its high toxicity.

Aqueous solutions containing alkanolamines are widely used for the removal of acid gases from natural gas. The absorption process is classified as chemical absorption, since acid gases and aqueous alkanolamine solution react partly and create non-volatile ionic species in the liquid phase. Among alkanolamine based solvents, aqueous MDEA or an aqueous mixture containing MDEA is often preferred for acid gas treating. Aqueous MDEA is

advantageous because it can selectively remove H<sub>2</sub>S from a gas that also contains CO<sub>2</sub>. The selectivity of absorption is due to the higher rate of the reaction of MDEA with H<sub>2</sub>S than the reaction of MDEA with CO<sub>2</sub> (Anufrikov et al. [1]). By adding a second amine which reacts fast with CO<sub>2</sub>, like piperazine or MEA, MDEA-based solvents may also be tailored for deep CO<sub>2</sub> removal. Compared to other amines, MDEA is more stable, less volatile and less corrosive; it also has lower heat of reaction and higher absorption capacity (Anufrikov et al. [1]).

To design natural gas cleaning processes, equilibrium, thermal effects and kinetics of mass transfer and of chemical reactions at industrial conditions are required (Prausnitz et al. [2]). In general, acid gas solubility data in alkanolamines are limited to low pressures, where there is no inert gas like nitrogen or hydrocarbons present. Despite this fact, the natural gas treatment industry typically has hydrocarbons such as methane present in the absorber column and the absorber operates at high pressures (up to around 10,000 kPa) whereas the regenerator operating pressure is low (around 100–300 kPa). Therefore, it is crucial to investigate the effect of high pressure on the acid gas partial pressure and acid gas solubility.

In this study, vapor–liquid equilibrium (VLE) data for mixtures of H<sub>2</sub>S, CH<sub>4</sub>, MDEA and H<sub>2</sub>O are presented at two different total pressures, 1500 and 7000 kPa. The data at 7000 kPa were measured for partial pressures of H<sub>2</sub>S from 31 to 974 kPa and at 50 and 70 °C.

Abbreviations: VLE, vapor–liquid equilibrium; AARD, average absolute relative deviation; MDEA, *N*-methyldiethanolamine; H<sub>2</sub>S, hydrogen sulfide; CH<sub>4</sub>, methane; CO<sub>2</sub>, carbon dioxide; HCl, hydrochloric acid; NaOH, sodium hydroxide; UNIQUAC, UNiversal QUAsi Chemical thermodynamic model; M, molarity; T, temperature; N, number of data; Calc., calculated; Exp., experimental.

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## Nomenclature

### Symbols

$G^E$	Excess Gibbs energy
$P_{H_2S}$	$H_2S$ partial pressure
$P_{total}$	Total pressure
$P_{cr}$	Critical pressure
$T_{cr}$	Critical temperature
$\omega$	Acentric factor

Measured data at 1500 kPa are presented at 50 °C for  $H_2S$  partial pressure varies from 53 to 386 kPa. The concentration of the aqueous MDEA solution is 50 wt% for all the experiments. Moreover, the obtained data are compared to the predictions of the Extended UNIQUAC model by Sadegh et al. [3], and the effect of methane presence on  $H_2S$  partial pressure and  $H_2S$  solubility in aqueous MDEA is investigated.

## 2. Status of the experimental knowledge

Existing literature data reveal a gap in  $H_2S$  solubility in aqueous MDEA at high pressures, in the presence of methane. One objective of this work is to obtain complementary required points where there is a lack of data in the open literature. Most of the data available in the open literature are presented as acid gas partial pressure without specifying the total pressure, because the data were measured at low total pressures (Huttenhuis et al. [4]). A bibliographic study over the experimental vapor–liquid equilibrium data available in the open literature for the  $H_2S$ –MDEA– $H_2O$  and the  $H_2S$ – $CH_4$ –MDEA– $H_2O$  systems is presented in Table 1.

As it can be seen in Table 1, there are only few measured  $H_2S$  solubilities at high total pressure (Ter Maat et al. [15], Huttenhuis et al. [4] and Dicko et al. [16]). Thus there is a need for more data at high total pressures corresponding to the typical absorber pressure in amine based gas sweetening processes. There is a significant discrepancy in the  $H_2S$  solubility data measured at low total pressure. The effect of the total system pressure on the  $H_2S$  solubility is comparable in size, or smaller, than the discrepancy. It is therefore not possible to study the pressure effect by comparing low pressure and high pressure data from different literature sources. In this study, experiments were therefore performed at both high (7000 kPa) and low (1500 kPa) total pressure. The

experiments at 1500 and 7000 kPa were carried out in the same apparatus and in exactly the same way in order to isolate the pressure effect from other factors that may affect the experiments. Similar investigations were done by Huttenhuis et al. [4], Ter Maat et al. [15] and Dicko et al. [16], but less extensive than in this study.

## 3. Experimental

### 3.1. Chemicals

The chemicals used in this work include MDEA (Merck,  $\geq 98\%$  pure),  $H_2S$  (Yara,  $\geq 99\%$  pure) and  $CH_4$  (Yara,  $\geq 99\%$  pure). All chemicals were used without any further purification.

### 3.2. Apparatus

The experiments were done in the apparatus shown in Fig. 1. The cell was constructed for a “static-analytic” method with liquid and vapor samplings at constant temperature and pressure. It was custom built by Sanchez Technologies for Statoil. The apparatus is a modified version of the one used by Addicks [17] for high pressure VLE measurements for the  $CO_2$ – $CH_4$ –MDEA– $H_2O$  system. The central part of the apparatus is a variable volume cell consisting of two cylindrical compartments connected through a cylindrical sapphire window. Both compartments are equipped with pistons which make it possible to vary the cell volume. A stirrer is fitted inside the lower piston to ensure mixing in the liquid phase. There is hydraulic oil on the back side of the pistons. The maximum volume is 450 cm<sup>3</sup>, and the cell can be operated up to 70,000 kPa and in the temperature range of –50 to 200 °C. The cell is placed inside an air bath to keep the temperature inside the cell constant. The air bath temperature has a maximum temperature variation within  $\pm 0.5$  °C. The temperature in the cell is measured with a platinum resistance thermometer with an accuracy of  $\pm 0.1$  °C, which is placed within the wall of the cell. Each piston is driven by the pressure difference between the hydraulic oil and the “process”. The pressure in the hydraulic oil is controlled during an experiment. The pressure on the process side is slightly lower than the pressure in the hydraulic oil due to the friction between the piston and the cell wall. The pressure is measured with a high-pressure sensor up to 100,000 kPa, and its accuracy is  $\pm 0.1\%$  of full scale. All the measuring devices are connected to a PC to store measurements and to control the operation of the cell. In order to avoid leaking between the hydraulic oil and the process side, there are two sets of O-rings on each piston. During operation, the

**Table 1**  
VLE data for  $H_2S$ –MDEA– $H_2O$  and  $H_2S$ – $CH_4$ –MDEA– $H_2O$  systems.

MDEA concentration (wt%)	$T$ (°C)	$P_{H_2S}$ (kPa)	Loading (mol $H_2S$ /mol MDEA)	Methane presence	Reference	Number of experiments
11.8, 23.4, 48.9	25, 40, 70, 100, 120	0.0012–5890	0.001–3.220	–	Jou et al. [5]	153
11.8, 19.9	25, 37.8, 65.6, 115.6	13.23–1536.60	0.180–2.1700	–	Maddox et al. [6]	49
23.4	40	52–1600	0.130–1.725	–	Macgregor and Mather [7]	27
35, 50	40, 100	0.0018–313	0.0040–1.077	–	Jou et al. [8]	50
30	40, 60, 80, 100	1.498–445.7	0.082–0.902	–	Li and Shen [9]	43
18.7, 32.2	40, 60, 100, 120, 140	165.2–4895.9 <sup>a</sup>	0.480–1.934	–	Kuranov et al. [10]	71
23, 50	40, 70, 100, 120	0.0033–3673	0.0020–1.74	–	Huang and Ng [11]	42
11.8, 23.6	25, 40	0.023–1.61	0.01–0.26	–	Lemoine et al. [12]	29
48.8	40, 81, 122	147.9–2783	0.15–1.42	–	Kamps et al. [13]	26
46.7	40, 100	6.21–1040	0.03–1.1	–	Sidi-Boumedine et al. [14]	27
35, 50	10, 25, 40	0.141–18.98	0.023–0.575	–	Ter Maat et al. [15], Huttenhuis et al. [4]	37
50	50	3–278	0.096–0.889	–	Dicko et al. [16]	5

<sup>a</sup> Bubble pressure is measured ( $P_{H_2S}$  + solvent vapor pressure).

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