Solubility of Methanethiol and Ethanethiol in a Diethanolamine Solution in the Presence of Acid Gases

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The solubility of methanethiol and ethanethiol in an aqueous solution of 35 mass % diethanolamine was measured at 40 °C and 70 °C. Measurements were made in the absence of acid gases, H_2S and CO_2, with individual acid gases present, and with mixtures of acid gases present. The total pressure of the experiments was 6890 kPa, which was maintained by methane. The partial pressures of the thiols ranged from 0.1 to 15.8 kPa.

Introduction

Natural gas often contains the acid gases, CO_2 and H_2S, as well as traces of sulfur compounds such as COS and thiols (mercaptans). The acid gases are usually removed by absorption in an aqueous alkanolamine solution where the reaction of the weak acid gases with the weak base forms a compound, which decomposes at higher temperatures. However, the thiols are much weaker acids than H_2S, and they do not react with the alkanolamine. This work was undertaken to determine the solubility of methanethiol (MSH) and ethanethiol (EtSH) in an aqueous solution of diethanolamine, in the presence and absence of acid gases.

Experimental Section

The experimental apparatus and procedure were described in our previous paper,[1] and only the salient features will be repeated here. The equilibrium cell is mounted in an air bath. A magnetic pump is used to circulate the vapor phase and bubble it through the liquid phase. The temperature of the contents of the cell was measured by a calibrated iron−constantan thermocouple, and the pressure in the cell was measured by digital Heise gauges. These gauges had an accuracy of 0.1% of full scale by comparison with a dead-weight gauge. The thermocouple had an accuracy of ±0.1% by comparison with a platinum resistance thermometer. The apparatus was checked by determination of the critical point and vapor pressure of propane, carbon dioxide, and hydrogen sulfide. Differences of 0.1 °C and 0.1% in vapor pressure were found.

The diethanolamine (DEA) solution was prepared gravimetrically using distilled water and DEA with a purity of 99+% obtained from Fisher. Methanethiol (MSH) with a purity of 99.5% was obtained from Aldrich; ethanethiol with a purity of 97% was also obtained from Aldrich. Methane with a purity of 99.97%, carbon dioxide with a purity of 99.99%, and hydrogen sulfide with a purity of 99.6% were obtained from Linde. About 100 cm^3 of the aqueous solution was fed into the evacuated equilibrium cell at room temperature. The solution was purged with methane to remove air, and MSH and/or EtSH were added in an amount monitored by the pressure. Methane was then added to bring the total pressure to 6890 kPa, and circulation of the vapor phase was continued for about 8 h. A sample of the gas phase was then taken in a 1 mL sampling loop and injected into a chromatograph for analysis. A 2 m column of Haye Sep Q, 80/100 mesh, packed in 3.175 mm SS tubing was used. A sample of the liquid phase was taken for analysis using a Pressure-Lok syringe. About 4 μL was injected into a chromatograph containing a 30 m × 0.53 μm i.d. × 3 nm capillary column coated with HP Innowax. Temperature programming was necessary to elute the water and DEA. As noted in our previous paper,[1] the uncertainty in the determination of the thiols is 5−7% in the absence of acid gases; in the presence of acid gases, the uncertainty increases to 10−15%. Hydrogen sulfide, MSH, and EtSH are toxic, flammable, and irritating materials. MSH and EtSH have an overpowering offensive odor, and they are used as odorants for natural gas and liquefied petroleum gas. Small quantities of these materials were used in this work, and the contents of the cell were disposed of by injection into a gas flame, the products of which were vented outside of the building.

Results

All measurements were made at a total pressure of 6890 kPa, which was maintained by methane. Data for the solubility of MSH in a 35 mass % DEA solution at 40 °C and 70 °C are presented in Tables 1 and 2, respectively. Data for the solubility of EtSH in a 35 mass % DEA solution in the presence and absence of acid gases at 40 °C are given in Table 3, while data for the same system at 70 °C are given in Table 4. Table 5 presents the results of experiments with mixtures of MSH and EtSH in various

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Table 1. Data of MSH in a Solution of 35 mass % DEA at 6890 kPa and 40 °C[a]

P_{tot}	p_{CH_4}	m_{CH_4}	x_{CH_4}	H_{CH_4}	p_{CO_2}	α_{CO_2}	p_{H_2S}	α_{H_2S}	p_{MSH}	m_{MSH}	x_{MSH}	H_{MSH}
kPa	kPa	mmol kg^{-1}		MPa	kPa		kPa		kPa	mmol kg^{-1}		MPa
6890	6880	71.4	1.81×10^{-3}	3424					0.105	0.832	2.11×10^{-5}	6.0
6890	6879	66.4	1.68×10^{-3}	3637					1.06	6.93	1.75×10^{-4}	6.0
6890	6874	68.0	1.72×10^{-3}	3540					6.12	25.3	6.13×10^{-4}	6.0
6890	6857	25.6	6.19×10^{-4}	9829	22.2	0.602			0.601	0.755	1.82×10^{-5}	19.8
6890	6859	31.0	7.48×10^{-4}	8135	16.6	0.574			4.77	3.44	8.32×10^{-5}	34.3
6890	6858	27.2	6.60×10^{-4}	9217	12.2	0.562			9.38	7.54	1.83×10^{-4}	30.7
6890	6867	45.4	1.09×10^{-3}	5589			12.3	0.533	1.20	3.49	8.40×10^{-5}	8.6
6890	6847	39.1	9.38×10^{-4}	6476			23.7	0.667	8.89	16.5	3.95×10^{-4}	13.5
6890	6865	33.6	8.07×10^{-4}	7550	3.00	0.361	11.6	0.314	0.82	1.93	4.62×10^{-5}	10.6
6890	6861	31.1	7.47×10^{-4}	6697	2.45	0.358	9.84	0.291	6.39	11.7	2.82×10^{-4}	13.6

[a] p_{H_2O} = 10 kPa at 40 °C.

Table 2. Data of MSH in a Solution of 35 mass % DEA at 6890 kPa and 70 °C[a]

P_{tot}	p_{CH_4}	m_{CH_4}	x_{CH_4}	H_{CH_4}	p_{CO_2}	α_{CO_2}[b]	p_{H_2S}	α_{H_2S}[c]	p_{MSH}	m_{MSH}	x_{MSH}	H_{MSH}
kPa	kPa	mmol kg^{-1}		MPa	kPa		kPa		kPa	mmol kg^{-1}		MPa
6890	6860	64.9	1.64×10^{-3}	3840					0.307	0.687	1.74×10^{-5}	16.8
6890	6857	61.3	1.55×10^{-3}	4061					2.79	5.68	1.44×10^{-4}	16.8
6890	6848	70.3	1.78×10^{-3}	3537					12.5	18.7	4.74×10^{-4}	16.8
6890	6770	36.2	6.36×10^{-4}	9776	87.9	0.563			0.978	0.570	1.38×10^{-5}	48.1
6890	6787	29.0	7.03×10^{-4}	8982	62.5	0.524			10.7	5.41	1.31×10^{-4}	55.4
6890	6779	29.5	7.15×10^{-4}	8710	75.9	0.541			4.73	2.47	5.98×10^{-5}	53.6
6890	6810	50.0	1.21×10^{-3}	5173			46.3	0.495	2.47	2.81	6.84×10^{-5}	24.5
6890	6768	36.8	8.86×10^{-4}	7020			79.7	0.613	12.6	12.7	3.07×10^{-4}	27.7

[a] p_{H_2O} = 30 kPa at 70 °C. [b] α_{CO_2} = mol CO_2/mol DEA. [c] α_{H_2S} = mol H_2S/mol DEA.

Table 3. Data of EtSH in a Solution of 35 mass % DEA at 6890 kPa and 40 °C

P_{tot}	p_{CH_4}	m_{CH_4}	x_{CH_4}	H_{CH_4}	p_{CO_2}	α_{CO_2}[b]	p_{H_2S}	α_{H_2S}[c]	p_{EtSH}	m_{EtSH}	x_{EtSH}	H_{EtSH}
kPa	kPa	mmol kg^{-1}		MPa	kPa		kPa		kPa	mmol kg^{-1}		MPa
6890	6872	66.4	1.63×10^{-3}	3619					8.26	18.5	4.69×10^{-4}	9.0
6890	6877	61.0	1.55×10^{-3}	3947					2.79	9.27	2.35×10^{-4}	9.0
6890	6880	64.5	1.63×10^{-3}	3734					0.268	1.11	2.81×10^{-5}	9.0
6890	6544	30.2	7.13×10^{-4}	8141	318	0.876			8.25	2.53	5.96×10^{-5}	69.8
6890	6860	38.6	9.30×10^{-4}	6543	18.0	0.572			2.23	1.39	3.35×10^{-5}	34.3
6890	6755	41.5	9.89×10^{-4}	5992	124	0.769			0.844	0.372	8.85×10^{-6}	48.8
6890	6864	46.2	1.14×10^{-3}	6088			3.42	0.362	12.8	8.60	2.11×10^{-4}	31.1
6890	6839	40.3	9.63×10^{-4}	6066			34.0	0.729	7.00	4.39	1.05×10^{-4}	34.2
6890	6867	40.4	9.73×10^{-4}	6092			10.6	0.505	1.22	1.62	3.90×10^{-5}	16.1
6890	6872	28.7	6.92×10^{-4}	6094	1.70	0.341	6.50	0.261	1.18	1.21	2.93×10^{-5}	20.8

[a] p_{H_2O} = (10 ± 2) kPa. [b] α_{CO_2} = mol CO_2/mol DEA. [c] α_{H_2S} = mol H_2S/mol DEA.

Table 4. Data of EtSH in a Solution of 35 mass % DEA at 6890 kPa and 70 °C[a]

P_{tot}	p_{CH_4}	m_{CH_4}	x_{CH_4}	H_{CH_4}	p_{CO_2}	α_{CO_2}[b]	p_{H_2S}	α_{H_2S}[c]	p_{EtSH}	m_{EtSH}	x_{EtSH}	H_{EtSH}
kPa	kPa	mmol kg^{-1}		MPa	kPa		kPa		kPa	mmol kg^{-1}		MPa
6890	6848	71.8	1.82×10^{-3}	3455					12.2	11.1	2.81×10^{-4}	23.6
6890	6854	62.6	1.59×10^{-3}	3960					6.07	6.02	1.53×10^{-4}	23.6
6890	6859	62.7	1.59×10^{-3}	3969					1.16	1.48	3.74×10^{-5}	23.6
6890	6860	70.4	1.78×10^{-3}	3537					0.200	0.205	6.19×10^{-6}	23.6
6890	6783	35.2	8.52×10^{-4}	7313	69.7	0.547			7.27	1.88	4.54×10^{-5}	95.4
6890	6780	33.5	8.11×10^{-4}	7681	77.5	0.552			2.60	0.732	1.77×10^{-5}	88.9
6890	6829	51.9	1.28×10^{-3}	4906			16.3	0.35	14.5	6.22	1.53×10^{-4}	57.2
6890	6732	44.8	1.07×10^{-3}	5779			112	0.67	15.8	5.85	1.40×10^{-4}	67.8
6890	6823	36.1	8.74×10^{-4}	7166			35.2	0.46	2.04	1.20	2.91×10^{-5}	42.4
6890	6819	28.8	5.04×10^{-4}	12431	16.5	0.321	22.1	0.24	2.42	1.19	2.88×10^{-5}	50.8

[a] p_{H_2O} = (30 ± 2) kPa. [b] α_{CO_2} = mol CO_2/mol DEA. [c] α_{H_2S} = mol CO_2/mol DEA.

amine solutions at 40 °C and 70 °C, in the absence of acid gases.

Discussion of Results

A re-examination of the data previously published for MSH and EtSH in a 50 mass % MDEA solution[1,2] led to the conclusion that the solubility of both thiols at the low levels investigated is independent of the type of amine and is a function only of the partial pressure at a given temperature when acid gases are absent. This fact is not surprising as the 35 mass % DEA solution is 3.5 M and the 50 mass % MDEA solution is 4.4 M, which is close enough so that no significant change in the solubility can be observed. Another observation of the data in Table 5 indicates that the presence of one thiol has no effect on the solubility of the other thiol. Proof of these two observa-

Table 5. Data of MSH + EtSH in Amine Solutions at 6890 kPa[a]

P_{tot} / kPa	p_{CH_4} / kPa	m_{CH_4} / mmol kg^{-1}	x_{CH_4}	H_{CH_4} / MPa	p_{MSH} / kPa	m_{MSH} / mmol kg^{-1}	x_{MSH}	p_{EtSH} / kPa	m_{EtSH} / mmol kg^{-1}	x_{EtSH}
50 mass % MDEA; $t = 40$ °C										
6890	6879	69.1	2.16×10^{-3}	2830	0.561	1.35	4.23×10^{-5}	0.576	0.709	2.21×10^{-5}
50 mass % MDEA; $t = 70$ °C										
6890	6859	78.7	2.46×10^{-3}	2563	0.684	1.00	3.13×10^{-5}	0.456	0.400	1.24×10^{-5}
10 mass % DEA + 40 mass % MDEA; $t = 40$ °C										
6890	6877	73.9	2.34×10^{-3}	2653	1.42	6.36	1.98×10^{-4}	1.85	4.28	1.33×10^{-4}
10 mass % DEA + 40 mass % MDEA; $t = 70$ °C										
6890	6854	69.6	2.17×10^{-3}	2903	2.76	4.88	1.52×10^{-4}	2.94	3.28	9.17×10^{-5}
35 mass % DEA; $t = 40$ °C										
6890	6878	68.9	1.75×10^{-3}	3611	0.778	4.21	1.07×10^{-4}	0.745	1.96	4.97×10^{-5}
35 mass % DEA; $t = 70$ °C										
6890	6857	59.7	1.61×10^{-3}	3914	1.76	3.07	7.77×10^{-5}	1.31	1.14	2.88×10^{-5}

[a] $p_{H_2O} = 10$ kPa at 40 °C and $p_{H_2O} = 30$ kPa at 70 °C. $p_{CO_2} = 0$ and $p_{H_2S} = 0$.

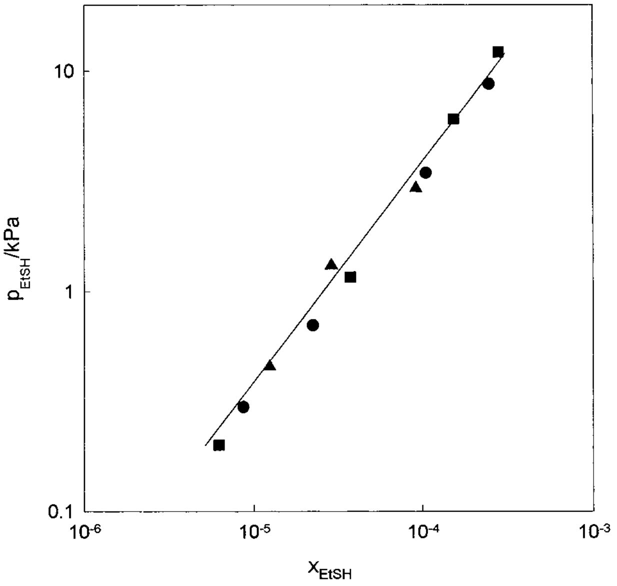

Figure 1. Partial pressure of EtSH versus mole fraction of EtSH in the liquid phase at 70 °C: ●, 50 mass % MDEA; ■, 35 mass % DEA; ▲, mixed thiols.

Table 6. Henry's Constants for MSH and EtSH in Amine Solutions at 6890 kPa

		(p_i/x_i)/MPa	$\hat{\varphi}_i$	H_i/MPa
MSH	40 °C	10.0 ± 0.1	0.600	6.0 ± 0.1
	70 °C	24.8 ± 0.1	0.679	16.8 ± 0.1
EtSH	40 °C	17.5 ± 0.7	0.515	9.0 ± 0.7
	70 °C	39.0 ± 1.3	0.606	23.6 ± 1.3

tions is provided in Figure 1, where the partial pressure of EtSH at 70 °C is plotted versus the mole fraction of EtSH in the liquid phase on logarithmic coordinates. The data fall on a straight line with a slope of unity, independent of the type of amine in the solution or the presence of MSH. Similar plots were obtained for EtSH at 40 °C and for MSH at 40 °C and 70 °C. The data were fit by least squares, and the resulting values of the coefficient with its standard deviation are reported in Table 6, together with values of the Henry's constants.

The Henry's constants were obtained by application of the equation $H_i = \hat{\varphi}_i y_i P/x_i$. The fugacity coefficients were calculated using the Peng−Robinson[3] equation of state. As noted previously,[1] the fugacity coefficients are sensitive only to the binary interaction parameter of methane with the thiol. This observation is a result of the large concentration of methane in the system. A value of 0.16 was used for the binary interaction parameter of both methane−MSH and methane−EtSH.

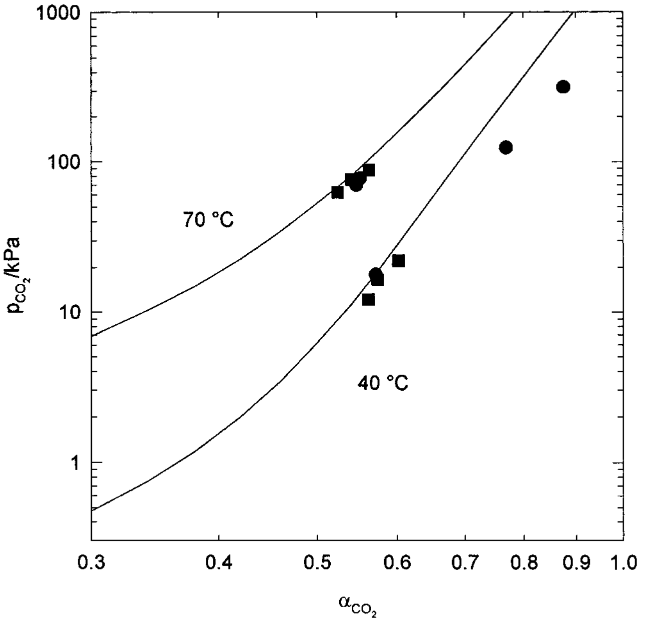

Figure 2. Partial pressure of CO_2 versus CO_2 loading in a 35 mass % DEA solution: ■, MSH; ●, EtSH; —, AMSIM correlation.

The presence of the acid gases affects the solubility of the thiols. With increased loading of the acid gases, the solubility of the thiols is decreased. This is manifested in the increase in the values of the Henry's constants of the thiols, as shown in Tables 1−4. It seems that the effect is more pronounced with carbon dioxide and is a function of the total amount of the acid gas(es) present. In our previous paper,[1] there did not seem to be a difference between the effects of carbon dioxide and hydrogen sulfide on the thiol solubility.

Although there is a large body of experimental solubility data for the acid gases in DEA solutions, there are no data for a 35 mass % solution at 40 °C and 70 °C. Hence, the AMSIM[4] correlation was used to calculate the solubility of CO_2 in the 35 mass % solution for comparison with the data from Tables 1−4. The results are shown in Figure 2, and the agreement is good, except at the highest CO_2 loadings.

Literature Cited

(1) Jou, F.-Y.; Mather, A. E.; Schmidt, K. A. G.; Ng, H.-J. Vapor-Liquid Equilibria in the System Ethanethiol + Methyldiethanolamine + Water in the Presence of Acid Gases. *J. Chem. Eng. Data* **1999**, *44*, 833−835.

(2) Jou, F.-Y.; Mather, A. E.; Ng, H.-J. Effect of CO_2 and H_2S on the solubility of methanethiol in an aqueous methyldiethanolamine solution. *Fluid Phase Equilib.* **1999**, *158−160*, 933−938.

(3) Peng, D.-Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−*64*.

(4) AMSIM v7.0, DBR Group of Companies, 9419−20th Avenue, Edmonton, AB, 2000.

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