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Vapor−Liquid Equilibria in the System Ethanethiol + Methyldiethanolamine + Water in the Presence of Acid Gases

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This investigation was carried out to determine the solubility of ethanethiol in a methyldiethanolamine (MDEA) solution. 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. Experiments with an aqueous solution of 50 mass % MDEA were carried out at 40 and 70 °C. The total pressure for most of the experiments was 6890 kPa, which was maintained by methane. Partial pressures of ethanethiol ranged from 0.2 to 15 kPa.

Introduction

The treatment of natural gas to remove non-hydrocarbon impurities such as H_2S, CO_2, COS, and thiols (mercaptans) is usually accomplished by absorption of the non-hydrocarbons in an aqueous solution of an alkanolamine. There is little or no reaction between thiols and alkanolamines; hence, the amount removed is small. This work was undertaken to determine the vapor−liquid equilibria of ethanethiol and an aqueous methyldiethanolamine (MDEA) solution, in the presence and absence of H_2S and CO_2.

Experimental Section

The equilibrium cell consisted of a Jerguson liquid level gauge. It was mounted in an insulated air bath, equipped with a heater as well as a refrigeration unit. A magnetic pump was used to circulate the gas phase and bubble it through the liquid phase. The total volume of the apparatus was about 250 cm^3. A heated vapor sampling line led from the top of the gauge to a sampling valve located outside of the air bath. All sampling lines and tubing were Teflon-lined 316 stainless steel of 3.175 mm o.d. and 1.78 mm i.d. The temperature of the cell contents 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 °C by comparison with a platinum resistance thermometer. The apparatus was checked by measurements of the vapor pressure and critical point of propane, carbon dioxide, and hydrogen sulfide. Differences of 0.1 °C and 0.1% in vapor pressure were found.

The MDEA solution was prepared gravimetrically using distilled water and MDEA with a purity of 99+% obtained from Aldrich. The ethanethiol (EtSH) was also obtained from Aldrich and had a purity of 97%. 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 introduced into the evacuated cell at room temperature. The apparatus was then purged with methane for a short time to remove air. The EtSH was added in an amount monitored by the pressure. The methane was added to bring the total pressure to 6890 kPa, and circulation of the gas phase was continued for about 8 h. Then a sample of the gas phase was taken in a 1 mL sampling loop and injected into a chromatograph for analysis. A 2 m × 3.175 mm column packed with 80/100 mesh Haye Sep Q 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 and temperature programming was used to elute the MDEA.

Note that hydrogen sulfide and EtSH are flammable, toxic, irritating materials. EtSH has an overpowering offensive odor, and for this reason is used as an odorant for natural gas and liquefied petroleum gas. In this work small quantities of these materials were used and the contents of the cell were disposed of by injection into a natural gas burner which was vented outside the building.

Results and Discussion

Data were obtained for the solubility of EtSH in a 50 mass % solution of MDEA at 40 and 70 °C, under a total pressure of 6890 kPa. The total pressure was maintained at this level by the addition of methane as a diluent. The concentration of EtSH ranged from 1 to 100 ppm by mass in the gas phase. Data were obtained in the absence of any acid gas, in the presence of CO_2, in the presence of H_2S, and in the presence of H_2S and CO_2. Acid gas loading, defined as moles of acid gas/mole MDEA, ranged from 0 to 1.06. The data are presented in Tables 1 and 2 for 40 and 70 °C, respectively. In previous work with methanethiol (*1*), the solubility of methanethiol in water was measured to test the apparatus and sampling techniques. Agreement with the data of Kilner et al. (*2*) within 2−5% was found. In Tables 1 and 2 the data obtained in the absence of the acid gases indicate that the uncertainty is from 5 to 7%.

An attempt was made to estimate the Henry's constant of EtSH from

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Table 1. Data of EtSH in a Solution of 50 Mass Percent MDEA at 40 °C

P_{tot}/ kPa	p_{CH_4}/ kPa	m_{CH_4}/ mmol kg^{-1}	x_{CH_4}	H_{CH_4}/ MPa	p_{CO_2}/ kPa	α_{CO_2}	p_{H_2S}/ kPa	α_{H_2S}	p_{EtSH}/ kPa	m_{EtSH}/ mmol kg^{-1}	x_{EtSH}	H_{EtSH}/ MPa
6890	6870	73.5	2.30×10^{-3}	2650	–	–	–	–	10.2	17.6	5.49×10^{-4}	9.6
6890	6880	74.2	2.30×10^{-3}	2654	–	–	–	–	2.48	4.36	1.31×10^{-4}	9.8
6890	6880	73.3	2.29×10^{-3}	2665	–	–	–	–	0.612	0.994	3.11×10^{-5}	10.2
6890	6880	72.6	2.27×10^{-3}	2689	–	–	–	–	0.195	0.381	1.19×10^{-5}	8.5
6890	6860	49.9	1.47×10^{-3}	4140	–	–	23.3	0.461	0.75	0.83	2.44×10^{-5}	15.8
6890	6850	48.0	1.41×10^{-3}	4310	–	–	27.0	0.495	6.80	7.23	2.12×10^{-4}	16.5
6890	6870	64.4	1.98×10^{-3}	3078	2.94	0.112	–	–	3.51	4.78	1.47×10^{-4}	12.3
6890	6875	59.7	1.84×10^{-3}	3315	4.51	0.160	–	–	0.708	1.06	3.25×10^{-5}	11.2
6890	6875	51.6	1.58×10^{-3}	3860	5.40	0.170	–	–	0.178	0.257	7.85×10^{-6}	11.7
6890	6840	51.6	1.52×10^{-3}	3992	36.4	0.471	–	–	3.36	2.96	8.72×10^{-5}	19.8
6890	6550	23.7	6.63×10^{-4}	8767	321.0	0.897	–	–	6.76	3.72	1.04×10^{-4}	32.9
6890	6870	52.2	1.59×10^{-3}	3833	3.88	0.0912	3.40	0.123	6.10	8.95	2.72×10^{-4}	11.5
6890	6860	37.2	1.11×10^{-3}	5483	11.0	0.151	8.93	0.193	1.87	2.41	7.20×10^{-5}	13.4
6890	6790	40.8	1.17×10^{-3}	5149	40.8	0.259	39.2	0.404	11.0	9.01	2.59×10^{-4}	21.7
6890	6810	41.0	1.19×10^{-3}	5077	48.3	0.364	18.4	0.221	2.65	2.50	7.24×10^{-5}	18.8
6890	6010	24.7	6.80×10^{-4}	7855	437.0	0.430	431	0.615	3.83	1.89	5.20×10^{-5}	35.6
6890	6150	16.7	4.61×10^{-4}	11849	541.0	0.720	180	0.313	11.1	5.05	1.39×10^{-4}	39.2
6890	5530	24.9	6.82×10^{-4}	7224	853.0	0.599	487	0.465	9.86	4.20	1.15×10^{-4}	40.2

[a] $p_{H_2O} = (10 \pm 2)$ kPa. α_{CO_2} = mol of CO_2/mol of MDEA. α_{H_2S} = mol of H_2S/mol of MDEA.

Table 2. Data of EtSH in a Solution of 50 Mass Percent MDEA at 70 °C

P_{tot}/ kPa	p_{CH_4}/ kPa	m_{CH_4}/ mmol kg^{-1}	x_{CH_4}	H_{CH_4}/ MPa	p_{CO_2}/ kPa	α_{CO_2}	p_{H_2S}/ kPa	α_{H_2S}	p_{EtSH}/ kPa	m_{EtSH}/ mmol kg^{-1}	x_{EtSH}	H_{EtSH}/ MPa
6890	6850	79.8	2.49×10^{-3}	2528	–	–	–	–	8.75	7.94	2.48×10^{-4}	21.4
6890	6860	82.6	2.58×10^{-3}	2443	–	–	–	–	3.45	3.36	1.05×10^{-4}	19.9
6890	6860	80.1	2.50×10^{-3}	2521	–	–	–	–	0.705	0.718	2.24×10^{-5}	19.1
6890	6860	79.5	2.49×10^{-3}	2531	–	–	–	–	0.298	0.277	8.66×10^{-6}	20.9
6890	6750	56.6	1.66×10^{-3}	3736	–	–	112	0.521	0.90	0.48	1.41×10^{-5}	38.4
6890	6750	56.5	1.66×10^{-3}	3736	–	–	99.6	0.484	7.75	4.33	1.27×10^{-4}	36.7
6890	6750	45.9	1.38×10^{-3}	4494	111	0.297	–	–	1.29	0.535	1.61×10^{-5}	48.4
6890	6225	25.0	7.18×10^{-4}	7972	631	0.673	–	–	3.77	1.17	3.36×10^{-5}	66.3
6890	5355	–	–	–	1500	0.873	–	–	4.38	1.19	3.34×10^{-5}	74.8
6890	6720	47.9	1.43×10^{-3}	4318	98.1	0.185	41.1	0.196	4.16	2.30	6.84×10^{-5}	36.6
6890	6710	45.9	1.36×10^{-3}	4533	123	0.289	20.2	0.127	8.44	4.86	1.45×10^{-4}	35.0
6890	6590	43.2	1.25×10^{-3}	4844	158	0.225	101	0.370	12.9	6.62	1.92×10^{-4}	40.1
6890	6625	38.2	1.12×10^{-3}	5435	182	0.270	49.1	0.195	4.13	2.02	5.96×10^{-5}	41.6
6890	5800	33.3	9.37×10^{-4}	5698	855	0.557	192	0.309	14.8	5.37	1.51×10^{-4}	56.5

[a] $p_{H_2O} = (30 \pm 2)$ kPa. α_{CO_2} = mole CO_2/mole MDEA. α_{H_2S} = mole H_2S/mole MDEA.

$$H = \hat{\varphi}_i y_i P / x_i$$

Fugacity coefficients were calculated using the Peng–Robinson (*3*) equation of state.

The fugacity coefficient of ethanethiol was sensitive only to the binary interaction parameter for methane–ethanethiol. This is not surprising, because the concentration of methane is large. Although Vostretsov et al. (*4*) assert that data were obtained for methane–ethanethiol, none are reported in the paper. A value of 0.16 for the binary interaction parameter of methane–ethanethiol was used, the same value used for methane-methanethiol in our previous work (*1*). The fugacity coefficients for EtSH were about 0.51 at 40 °C, compared with 0.42 when a binary interaction parameter of zero was used.

The solubility of EtSH in water was also measured by Kilner et al. (*2*) at 50 and 80 °C. The data for the solubility of EtSH in a 50 mass % MDEA solution indicate that the solubility is about three times that in water at the same temperature and pressure. The addition of acid gas (either H_2S and CO_2) causes a reduction in the solubility of EtSH as the acid gas reacts with the MDEA. This effect is shown in Figure 1 where the Henry's constant for EtSH is plotted versus the acid gas loading. The small amount of EtSH does not affect the solubility of the acid gases in the MDEA solution, and the data for H_2S and CO_2 are in good agreement with published values (*5*, *6*).

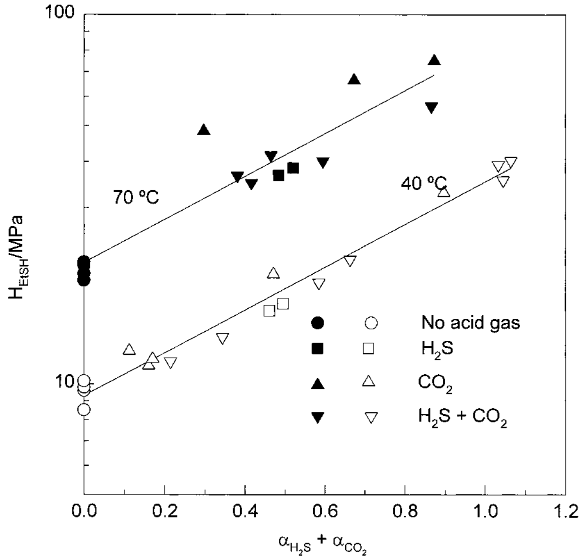

Figure 1. Effect of acid gas loading on the Henry's constant of ethanethiol.

Literature Cited

(1) 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 Equilibria* **1999**, *158–160*, 933–938.
(2) Kilner, J.; McBain, S. E.; Roffey, M. G. (Vapour+liquid) equilibria of (methanethiol or ethanethiol or propan-1-thiol or butan-1-thiol

+ n-hexane or n-decane or toluene or water) for mole fractions x = 0 to 0.2 of thiol at temperatures between 323 and 373 K. *J. Chem. Thermodynam.* **1990**, *22*, 203−210.
(3) Peng, D.-Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.
(4) Vostretsov, M. N.; Stepanenko, V. V.; Adzhiev, A. Yu.; Skorokhodova, T. I. Phase Equilibrium of Mercaptan-Hydrocarbon Mixtures. *Russ. J. Appl. Chem.* **1989**, *62*, 2551−2555.
(5) Jou, F.-Y.; Mather, A. E.; Otto, F. D. Solubility of H_2S and CO_2 in Aqueous Methyldiethanolamine Solutions. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 539−544.
(6) Huang, S. H.; Ng, H.-J. Solubility of H_2S and CO_2 in Alkanolamines. Gas Processors Association Research Report RR-155, 1998.

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