Solubility of Methane and Ethane in Aqueous Solutions of Methyldiethanolamine

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Data are presented for the solubility of methane and of ethane in a 3 kmol/m³ (34.7 mass %) solution of methyldiethanolamine. Temperatures in this study ranged from 25 to 130 °C and pressures to 13 MPa. The data were incorporated into a rigorous thermodynamic model that has been applied to other similar systems. The model is a combined Raoult's law−Henry's law approach. The solubilities in the alkanolamine solution are correlated in terms of the salting-in ratio, the ratio of the mole fraction solubility in the amine solution to that in pure water.

Introduction

Aqueous solutions of alkanolamines are commonly used in the hydrocarbon-processing industry to remove acid gases (carbon dioxide and hydrogen sulfide) from raw hydrocarbon streams. One of the amines used in this process is methyldiethanolamine (MDEA). MDEA has an advantage over other amines; it is capable of selectively separating hydrogen sulfide from a stream containing carbon dioxide. Because of this, MDEA is becoming more popular in the natural gas industry.

This paper is a part of an ongoing project to provide experimental data useful for the design of plants for the hydrocarbon-processing industry. Previously, data were published for the solubility of propane in MDEA (Carroll et al., 1992) and butane (Jou et al., 1996) in MDEA. This paper completes the homologous series from methane to butane.

In addition, it is shown in this paper that there is a trend that as the alkane increases in size, so does the salting-in ratio. The salting-in ratio is a measure of the increase in the solubility, expressed in mole fraction, due to the presence of the amine in the aqueous phase.

Experimental Work

The experimental procedure and apparatus are well-established and will only be reviewed here briefly. The apparatus consisted of an equilibrium cell equipped with large windows such that the contents of the cell are easily visible. The contents of the cell are mixed using a magnetic piston pump, which is similar to the one devised by Ruska et al. (1970). The cell and the pump are housed in a temperature-controlled air bath.

The pressure of the contents of the apparatus was measured using two digital Bourdon tube pressure gauges. The gauges were calibrated against a dead weight gauge and were found to be accurate to within 0.1% of full scale. The temperature was measured using a thermocouple. A port was drilled through the cell wall, and the tip of the

thermocouple was placed in the aqueous liquid phase. The thermocouple was calibrated against a platinum resistance thermometer and was found to be accurate to within ±0.1 °C over the range of temperatures studied in this work.

The MDEA was obtained from Aldrich and had a stated purity of 99%. It was used without further purification. The water used was distilled. The amine solution was made up to be 3 kmol/m³ (34.7 mass %) at laboratory conditions. The methane and ethane were obtained from Matheson and were used as received. A sample of each of the hydrocarbons was injected into a gas chromatograph, and in both cases no significant impurities were detected.

Results

The solubilities of methane in the 3 kmol/m³ solution of MDEA as a function of temperature and pressure are given in Table 1, and those for ethane are in Table 2.

The data were correlated using the model of Carroll and Mather (1997a). The model used in this work is identical to that presented in that paper, and most of the required parameters (Henry's constants, vapor pressure of water, partial molar volumes, etc.) were taken from that work. The model uses a combined Henry's law−Raoult's law method for the aqueous phase and the Peng and Robinson (1976) equation of state for the nonaqueous phases. Salting-in ratios, defined as the mole fraction solubility in the amine solution divided by the mole fraction solubility in pure water, were derived from the new data from this work. Because there are no experimental data for the solubilities of these hydrocarbons at the exact conditions of the data presented in this work, the model of Carroll and Mather (1997a) was used to calculate the solubilities. Then using these calculated solubilities for pure water and the measured solubilities for the amine solutions, the salting-in ratios were calculated.

The salting-in ratios for methane in the 3 kmol/m³ MDEA solution are summarized in Table 3, and those for ethane are in Table 4. The salting-in ratios were calculated point by point. The values given in the table are the mean for a given temperature, and the stated ranges are the standard deviations.

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Table 1. Mole Fraction Solubility, *x*, and Molal Solubility, *m*, of Methane in a 3 kmol/m³ Aqueous Solution of Methyldiethanolamine

t/°C	P/MPa	1000x	m/(mol CH$_4$/ 100 kg solvent)
25.0	13.21	3.02	11.9
	11.21	2.74	10.87
	9.07	2.33	9.14
	7.11	2.00	7.83
	5.22	1.50	5.87
	3.17	0.920	3.61
	1.18	0.436	1.71
	0.337	0.117	0.460
	0.095	0.0418	0.131
40.0	12.78	2.64	10.4
	10.55	2.29	9.01
	8.82	2.02	7.93
	7.02	1.67	6.56
	5.12	1.29	5.04
	3.35	0.899	3.52
	0.931	0.258	1.01
	0.253	0.075	0.296
70.0	11.21	2.44	9.48
	8.03	1.84	7.22
	6.37	1.51	5.91
	4.44	1.13	4.45
	2.47	0.677	2.65
	0.862	0.239	0.935
	0.244	0.062	0.245
75.0	13.11	2.88	11.3
	11.30	2.57	10.1
	9.38	2.23	8.75
	7.29	1.79	7.02
	5.22	1.38	5.42
	2.52	0.738	2.89
	0.848	0.239	0.936
	0.244	0.067	0.264
100.0	11.14	2.86	11.2
	8.64	2.23	8.76
	5.95	1.70	6.67
	3.05	0.918	3.60
	1.000	0.299	1.17
	0.319	0.074	0.291
130.0	10.99	3.26	12.8
	8.91	2.85	11.2
	6.71	2.17	8.53
	3.42	1.17	4.60
	1.047	0.329	1.29
	0.470	0.088	0.346

Table 2. Mole Fraction Solubility, *x*, and Molal Solubility, *m*, of Ethane in a 3 kmol/m³ Aqueous Solution of Methyldiethanolamine

t/°C	P/MPa	1000x	m/(mol CH$_4$/ 100 kg solvent)
25.0	4.24	1.57	6.15
	3.30	1.35	5.31
	2.19	1.01	3.95
	0.821	0.464	1.82
	0.281	0.168	0.656
	0.096	0.0535	0.210
40.0	8.60	2.02	7.93
	5.77	1.64	6.42
	5.39	1.74	6.81
	4.12	1.60	6.26
	3.22	1.23	4.83
	1.88	0.854	3.35
	0.732	0.392	1.54
	0.232	0.123	0.482
70.0	13.31	2.34	9.18
	9.66	2.07	7.90
	7.03	2.02	7.75
	5.71	1.73	6.79
	4.01	1.45	5.70
	2.82	1.08	4.24
	1.77	0.720	2.82
	0.696	0.288	1.13
	0.258	0.114	0.446
75.0	13.51	2.20	8.63
	10.68	2.05	8.04
	8.53	2.00	7.84
	6.52	1.78	7.00
	5.26	1.59	6.23
	2.56	0.944	3.70
	0.947	0.370	1.45
	0.217	0.0723	0.284
100.0	13.01	3.02	11.9
	9.60	2.65	10.4
	6.57	2.28	8.88
	4.74	1.77	6.93
	3.53	1.36	5.35
	1.94	0.806	3.16
	0.749	0.335	1.31
	0.324	0.118	0.464
130.0	11.40	3.52	13.8
	8.08	2.86	11.3
	5.02	2.16	8.49
	3.20	1.49	5.84
	1.430	0.598	2.35
	0.539	0.0150	0.590

For methane the following polynomial was fit to the calculated salting-in ratios

$$S_{\text{C1-MDEA}} = -2.420 + 1532 \times 10^{-2}(T/\text{K}) - 8.165 \times 10^{-6}(T/\text{K})^2 \quad (1)$$

and for ethane

$$S_{\text{C2-MDEA}} = -15.747 + 8.993 \times 10^{-2}(T/\text{K}) - 1.028 \times 10^{-4}(T/\text{K})^2 \quad (2)$$

where S is the salting-in ratio and the subscript on the S indicates the amine−alkane pair and T is the temperature.

In our previous work (Carroll and Mather, 1997a), a linear correlation was presented for the salting-in ratio for propane in 3 kmol/m³ MDEA. In light of this work, the correlation was revised to be quadratic in temperature. The new correlation is

$$S_{\text{C3-MDEA}} = -15.766 + 8.799 \times 10^{-2}(T/\text{K}) - 0.922 \times 10^{-4}(T/\text{K})^2 \quad (3)$$

where S is the salting-in ratio and T is the temperature.

Previously, data were taken for the phase equilibria in the system butane + 3 kmol/m³ MDEA (Jou et al., 1996). Because of a discrepancy in the system butane + water, these data were not incorporated into the model of Carroll and Mather (1997a). It was demonstrated by Carroll and Mather (1997b) that there is serious disagreement among the various experimental investigations of this system. The difficulties with the binary system butane + water have been partially resolved (Carroll and Mather, 1997b). Table 5 summarizes the salting-in coefficients for this system butane + 3 kmol/m³ MDEA. These values were correlated with the following quadratic in the absolute temperature:

$$S_{\text{C}_4\text{-MDEA}} = -15.851 + 9.714 \times 10^{-2}(T/\text{K}) - 1.129 \times 10^{-4}(T/\text{K})^2 \quad (4)$$

Despite the problems with the binary system butane + water, the correlation of Carroll and Mather (1997a) with the above salting-in ratios and other parameters from Carroll and Mather (1997b) represents an excellent fit of the experimental data.

Table 3. Salting-in Ratios for Methane in 3 kmol/m³ MDEA

t/°C	number of points	salting-in ratio from data	salting-in ratio from eq 1
25.0	9	1.46 ± 0.07	1.42
40.0	8	1.52 ± 0.03	1.58
70.0	7	1.84 ± 0.04	1.87
75.0	8	1.98 ± 0.07	1.92
100.0	6	2.17 ± 0.07	2.16
130.0	6	2.42 ± 0.21	2.43

Table 4. Salting-in Ratios for Ethane in 3 kmol/m³ MDEA

t/°C	number of points	salting-in ratio from data	salting-in ratio from eq 2
25.0	9	1.87 ± 0.05	1.93
40.0	8	2.46 ± 0.13	2.33
70.0	7	3.07 ± 0.12	3.01
75.0	8	2.89 ± 0.09	3.10
100.0	6	3.62 ± 0.15	3.50
130.0	6	3.78 ± 0.25	3.80

Table 5. Salting-in Ratios for Butane in 3 kmol/m³ MDEA

t/°C	number of points	salting-in ratio from data	salting-in ratio from eq 4
25.0	14	3.10 ± 0.02	3.08
50.0	11	3.72 ± 0.07	3.75
75.0	13	4.28 ± 0.18	4.28
100.0	10	4.72 ± 0.18	4.68
125.0	11	4.93 ± 0.18	4.93
150.0	9	5.04 ± 0.21	5.08

There is a similarity between the correlations for ethane, propane, and butane (i.e., the coefficients of the regressed equations are very similar). On the other hand, the correlation for methane is more nearly linear, and its coefficients are significantly different. However, there is a clear trend. As the size of the alkane increases, so does the salting-in ratio. This can be seen in Figure 1 where the salting-in ratios for four alkanes are plotted.

Unfortunately, this trend does not appear to be highly correlated. For example, as the temperature increases the difference between the salting-in ratios for methane and ethane increases significantly. On the other hand, the difference between the salting-in ratios for propane and butane decreases with increasing temperature. The difference is so small that they are approximately equal at 150 °C.

At this time, only data for a 3 kmol/m³ MDEA solution have been measured and correlated. To use this correlation for other concentrations, the Setchenow equation can be used

$$\ln S_{ia} = k_{ia} C_a \tag{5}$$

where k_{ia} is a Setchenow coefficient and is assumed to be concentration-independent. In this equation the amine concentration, C_a, must be in molarity, kmol/m³.

Figure 2 shows the solubility of methane in the MDEA solution for five temperatures (the 70 °C isotherm was omitted for clarity). The model predictions were performed using eq 1 for the salting-in ratios. At low pressure the solubility is a fairly weak function of the temperature. At high pressure the solubility goes through a minimum. This makes the plot a little difficult to interpret.

Figure 3 shows the solubility of ethane in the MDEA solution. The model predictions were performed using the salting-in ratios from eq 2. As with the methane solubility, at low pressure the solubility of ethane is a weak function
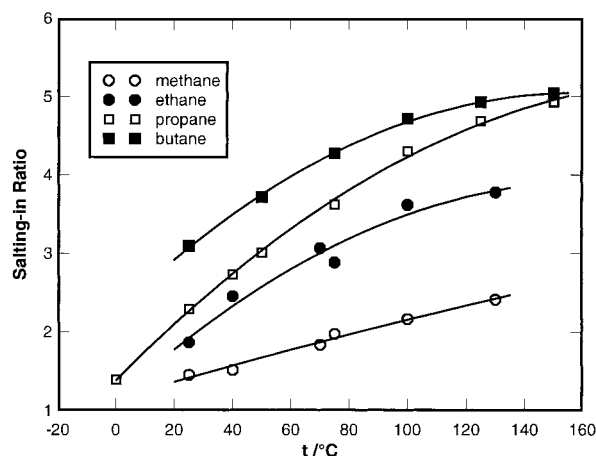
Figure 1. Salting-in ratios for methane, ethane, propane, and butane in a 3 kmol/m³ aqueous solution of methyldiethanolamine.
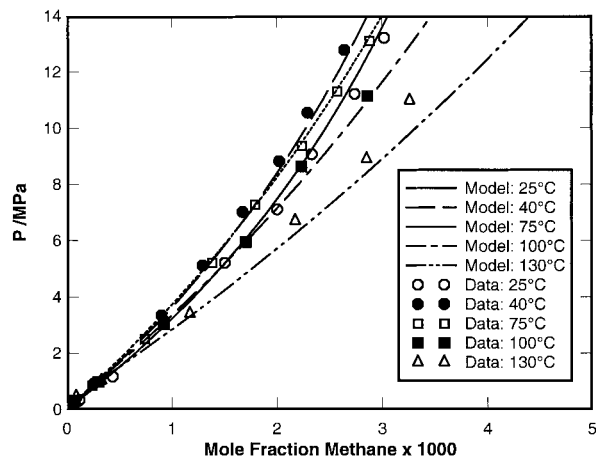
Figure 2. Solubility of methane in a 3 kmol/m³ aqueous solution of methyldiethanolamine as a function of pressure and temperature.
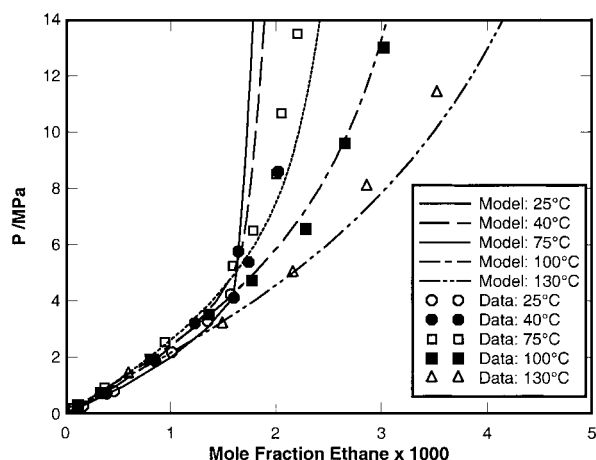
Figure 3. Solubility of ethane in a 3 kmol/m³ aqueous solution of methyldiethanolamine as a function of pressure and temperature.

of the temperature. A significant difference in solubilities of ethane and methane exists because at low temperature ethane liquefies. The 25 °C isotherm shows a cusp at 4.2 MPa, which is a three-phase point. At pressures above the three-phase pressure, the equilibrium is between two liquids (LLE). Although no data were measured for the liquid−liquid equilibrium, this portion of the curve is shown. The model has been successfully applied to LLE

for both propane and butane. The 40 °C isotherm does not exhibit LLE, since this temperature is greater than the critical temperature (i.e., ethane does not liquefy). However, in the critical region, the fluid becomes dense and has a behavior similar to a liquid at high pressure. That is, the solubility is less sensitive to the pressure than it would be for a gas.

Conclusions

New data are presented for the solubility of methane and ethane in an aqueous solution of MDEA. Such data should be useful in the design of plants for stripping acid gas components from hydrocarbons.

The data were incorporated into the model of Carroll and Mather (1997a). It is demonstrated that as the size of the alkane increases, so does the salting-in ratio.

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