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Solubility of Methane in an Aqueous Methyldiethanolamine Solution (Mass Fraction 50 %)

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The solubility of methane in an aqueous methyldiethanolamine solution (mass fraction 50 %) has been measured at temperatures in the range (298 to 423) K at pressures up to 20 MPa. Salting-in ratios, Henry's constants, and Setchenow coefficients have been obtained from the results.

Introduction

Methyldiethanolamine (MDEA) solutions are widely used for the removal of the acid gases, H_2S and CO_2, from gas streams. In aqueous solution, it forms a weak base ($pK_a = 8.5$) which reacts with the weak acids. It is normally employed as an aqueous solution with a mass fraction of (30 to 50) %. The solubility of methane in an MDEA solution of mass fraction 34.7 % was measured earlier.[1] To cover the range of applications, knowledge of the solubility in a more concentrated solution is needed. For this reason, the present work was done.

Experimental Section

The apparatus and experimental technique that were used are similar to those described by Jou et al.[2] The equilibrium cell was mounted in an air bath. 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, (0 to 10, 0 to 35) MPa. The uncertainty in the pressures was ± 0.1 % of full scale by comparison with a deadweight gauge. The experimental uncertainty in the temperature was ± 0.1 K by comparison with a platinum resistance thermometer. The methane was UHP grade (99.99 %) and was obtained from Praxair. The methyldiethanolamine (MDEA, CAS No. 105-59-9) was obtained from Aldrich and had a purity of 99.3 %. The water used was distilled. The amine solution was made up to 50 % mass fraction at laboratory conditions. Prior to the introduction of the fluids, the cell was evacuated. About 120 cm^3 of the MDEA solution was drawn into the cell. The methane was added to the cell by the cylinder pressure or by means of a spindle press. The circulation pump was started, and the vapor bubbled through the solvent for at least 4 h to ensure that equilibrium was reached. At high pressures, a sample of the liquid phase, (2 to 20) g, depending on the solubility, was withdrawn from the cell into a 50 cm^3 sample bomb that had previously been evacuated and weighed. The bomb contained a magnetic stirring bar to help in degassing the sample. The sample bomb was reweighed to determine the mass of the sample and then attached to a vacuum rack. The rack consisted of 6.35 mm o.d. stainless steel tubing connected to a calibrated Digigauge (range (0 to 1.0) MPa) and a 50 cm^3 buret. The rack was evacuated, and the gas was allowed to evolve from the sample bomb into the buret, which was maintained at the local atmospheric pressure and room temperature. The moles collected were calculated from the $P-V-T$ data, assuming ideal gas behavior. A correction was made for the residual methane left in the sample at atmospheric pressure by injection of an aliquot into a gas chromatograph. At low pressures, a 2 μL sample of liquid was taken from the liquid sample outlet and injected directly into the gas chromatograph. The uncertainty in the liquid phase analyses is estimated to be ± 3 %.

Table 1. Solubility of Methane (2) in Methyldiethanolamine (1) and Water (3); $w_1 = 50$ %

T/K					
298.15		313.15		343.15	
P/MPa	$x_2 \cdot 10^3$	*P*/MPa	$x_2 \cdot 10^3$	*P*/MPa	$x_2 \cdot 10^3$
20.0	4.62	20.0	5.10	19.0	5.29
15.0	3.88	15.0	4.15	15.0	4.62
10.0	2.97	10.0	3.00	10.0	3.21
6.00	1.94	6.00	1.96	6.00	2.11
3.00	1.09	3.00	1.10	3.00	1.16
1.00	0.383	1.00	0.398	1.00	0.42
0.30	0.108[a]	0.30	0.115[a]	0.30	0.104[a]
0.1043	0.0377[a]	0.17	0.0664[a]	0.126	0.0394[a]
		0.117	0.0443[a]		

T/K			
373.15		423.15	
P/MPa	$x_2 \cdot 10^3$	*P*/MPa	$x_2 \cdot 10^3$
19.0	6.54	18.0	8.62
15.0	5.48	14.0	7.18
10.0	3.89	10.32	5.81
6.00	2.52	6.89	3.91
3.00	1.32	3.00	1.69
1.00	0.443	1.30	0.598
0.40	0.137[a]	0.70	0.191[a]
0.1893	0.0448[a]	0.522	0.072[a]

[a] By gas chromatography.

Results and Discussion

The solubility of methane in a mass fraction of 50 % aqueous solution of methyldiethanolamine in water was measured at the temperatures of (298.15, 313.15, 343.15, 373.15, and 423.15) K at pressures up to 20.0 MPa. The experimental data are presented in Table 1.

The data were correlated using the model of Carroll and Mather.[3] The model used in this work is identical to that

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Table 2. Salting-In Ratios and Setchenow Coefficients for Methane (2) in a Solution of Methyldiethanolamine (1) and Water (3)

	amine concentration				
T/K	w_1	c_1/mol·L^{-1}	salting-in ratio	Setchenow coefficient	ref
298.15	50.0	4.39	1.64 ± 0.09	0.113 ± 0.013	this work
298.15	34.7	3.00	1.46 ± 0.07	0.126 ± 0.016	1
313.15	50.0	4.39	2.10 ± 0.08	0.169 ± 0.009	this work
313.15	34.7	3.00	1.52 ± 0.03	0.139 ± 0.006	1
343.15	50.0	4.39	2.68 ± 0.11	0.225 ± 0.010	this work
343.15	34.7	3.00	1.84 ± 0.04	0.203 ± 0.007	1
348.15	34.7	3.00	1.98 ± 0.07	0.228 ± 0.011	1
373.15	50.0	4.39	3.21 ± 0.10	0.266 ± 0.007	this work
373.15	34.7	3.00	2.17 ± 0.07	0.258 ± 0.011	1
403.15	34.7	3.00	2.42 ± 0.21	0.295 ± 0.029	1
423.15	50.0	4.39	3.70 ± 0.20	0.298 ± 0.012	this work[a]

[a] Excluding the gas chromatography data.

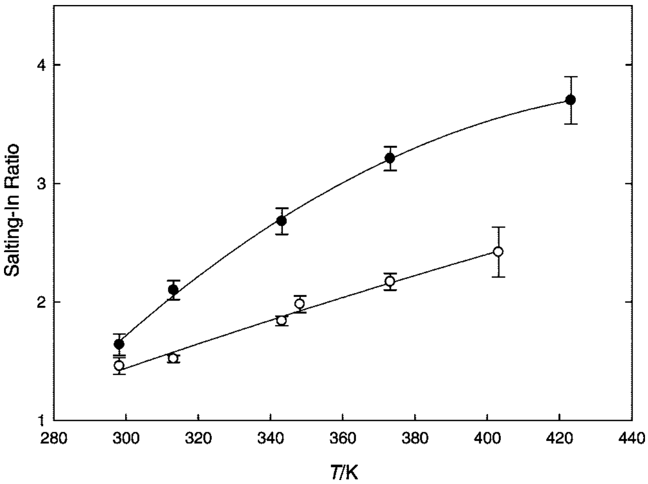

Figure 1. Salting-in ratios for methane in MDEA (1) and water (3): ●, w_1 = 50 %; ○, w_1 = 34.7 %.

Table 3. Henry's Constants for Methane

	H_{21}/MPa MDEA[6]	H_{23}/MPa water[5]			
T/K	$w_1 = 1$	$w_1 = 0$	H_{2m}/MPa $w_1 = 34.7$ %[1]	H_{2m}/MPa $w_1 = 50$ %	α_{13}
298.15	158.7	4081	2870	2446	1.15
313.15	161.3	5094	3231	2481	2.49
343.15	168.7	6373	3398	2354	4.82
348.15	168.8	6475	3365	2311	5.16
373.15	166.5	6556	3036	2044	6.68
403.15	160.9	5980	2462	1683	8.07
423.15	158.3[a]	5387	2071[a]	1456	8.74

[a] Extrapolated.

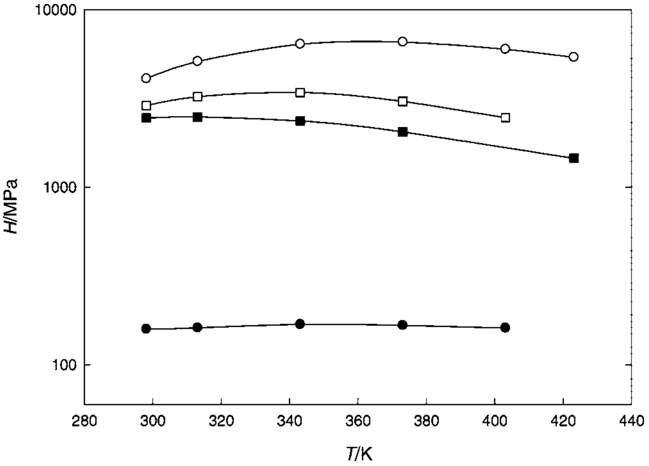

Figure 2. Temperature dependence of the Henry constants of methane in: ●, MDEA;[6] ○, water;[5] □, w_1 = 34.7 % MDEA solution;[1] ■, w_1 = 50 % MDEA solution.

presented in that paper, and the required parameters were taken from that work. The model uses a combined Henry's law–Raoult's law method for the aqueous phase and the Peng–Robinson[4] equation of state for the vapor phase. Salting-in ratios, defined as the mole fraction solubility in the amine solution divided by the mole fraction solubility in pure water, were determined from the new data of this work. Because there are no experimental data for the solubility of methane in water at the exact conditions of the data presented in this work, the model of Carroll and Mather was used to calculate the solubilities. The average relative uncertainty of the prediction is 7.2 %. With the measured values for the 50 % solution and the calculated solubilities for pure water, the methane salting-in ratios were calculated. The salting-in ratios are presented in Table 2 and Figure 1. They were calculated point by point. The values given in the table are the mean value for a given temperature, and the stated ranges are the standard deviations. The following polynomial was fit to the salting-in ratios

$$S = -13.959 + 7.790 \cdot 10^{-2}(T/\mathrm{K}) - 8.547 \cdot 10^{-5}(T/\mathrm{K})^2 \tag{1}$$

This correlation reproduces the experimental solubility data with an overall average deviation of 3.8 %, about the same as the experimental uncertainty.

To correlate the effect of concentration of the amine solution, the Setchenow equation can be used

$$\ln S = kc_a \tag{2}$$

where k is the Setchenow coefficient, which is assumed to be independent of the alkanolamine concentration. c_a is the concentration of the amine, in molarity. Values of the Setchenow coefficient for both the 34.7 % mass fraction amine solution and the 50 % mass fraction amine solution are given in Table 2. The average Setchenow coefficients at a given temperature, based on eq 1 and the salting-in correlation of the 34.7 % solution[1] were used to obtain the following correlation

$$k = -1.3880 + 7.563 \cdot 10^{-3}(T/\mathrm{K}) - 8.416 \cdot 10^{-6}(T/\mathrm{K})^2 \tag{3}$$

The salting-in ratios can be used to obtain the Henry constant from

$$S = H_w / H_a \tag{4}$$

where H_w is the Henry constant of methane in water and H_a is the Henry constant of methane in the aqueous alkanolamine solution.

Values of the Henry constant, determined from eqs 1 and 4, are given in Table 3 and are plotted in Figure 2 for comparison with data for the Henry constant of methane in water,[5] in an aqueous solution of w_1 = 34.7 % MDEA[1] and in pure MDEA.[6] The Setchenow coefficient correlation, eq 3, reproduces the Henry constants with an overall average deviation of 2.9 % for the w_1 = 34.7 % solution and 1.8 % for the w_1 = 50 % solution over the entire temperature range.

O'Connell and Prausnitz[7] have derived a relationship between the Henry constant in a mixed solvent and the Henry constant in the individual solvents. A simple relationship for the excess Gibbs energy, a one-parameter Margules equation, was used. This equation is suitable for nonpolar solutions as shown by Prausnitz et al.[8] For a binary mixed solvent, the expression is

$$\ln H_{2\mathrm{m}} = x_1 \ln H_{21} + x_3 \ln H_{23} - \alpha_{13} x_1 x_3 \qquad (5)$$

where $H_{2\mathrm{m}}$ is the Henry constant of methane in a mixture of MDEA and water; H_{21} is the Henry constant of methane in MDEA; H_{23} is the Henry constant of methane in water; x_1 is the mole fraction of MDEA in the mixed solvent; x_3 is the mole fraction of water in the mixed solvent; and α_{13} is a parameter related to the deviation of the two solvents from an ideal mixture. Two sets of values for $H_{2\mathrm{m}}$ are available, and hence an optimum value of α_{13} at each temperature was obtained. They are presented in Table 3. The values differ from those published previously.[6]

The α_{13} values were regressed to obtain the following correlation

$$\alpha_{13} = -49.716 + 2.480 \cdot 10^{-1}(T/\mathrm{K}) - 2.596 \cdot 10^{-4}(T/\mathrm{K})^2 \qquad (6)$$

The calculated results at each temperature are presented in Table 3. This correlation reproduces the Henry constants with an overall average deviation of 4.7 % for the $w_1 = 34.7$ % solution and 6.5 % for the $w_1 = 50$ % solution over the entire temperature range.

The values are positive, which indicates that the solute-free mixture exhibits positive deviations from Raoult's law. However, Xu et al.,[9] who measured the boiling points of MDEA + water mixtures, found that the data were in good agreement with Raoult's law. The reason for this discrepancy probably lies in the simple relation for the excess Gibbs energy used in the derivation of eq 5. Mixtures of MDEA and water contain both polar and hydrogen-bonded molecules, and the equation is more suitable for nonpolar mixtures.[7]

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