J. Chem. Eng. Data **2006,** *51,* 1429−1430

Solubility of Methane in Methyldiethanolamine

Fang-Yuan Jou and Alan E. Mather*

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 2G6, Canada

The solubility of methane in methyldiethanolamine has been measured at temperatures in the range (298 to 403) K at pressures up to 20.3 MPa. Henry's constants have been obtained from the results.

Introduction

Methyldiethanolamine (MDEA) is widely used for the removal of the acid gases, H_2S and CO_2, from gas streams. It is normally employed as an aqueous solution of 3 to 5 mol·L^{-1}. The solubility of methane in a 3 mol·L^{-1} solution was measured earlier.[1] To model the solubility in aqueous solutions, a knowledge of the solubility in the pure alkanolamine 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 Registry No. 105-59-9) was obtained from Aldrich and had a purity of 99.3 %. Before the start of the experiments, the MDEA was distilled under vacuum to remove water and amine impurities. The final sample had a mass fraction purity of 99.8 %, the balance being water. Prior to the introduction of the fluids, the cell was evacuated. About 120 cm^3 of MDEA 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 At high pressures, a sample of the liquid phase, (2 to 20) g depending on the solubility, was withdrawn from the cell into a 50 cm^3 sample bomb that had previously been evacuated and weighed.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 %.

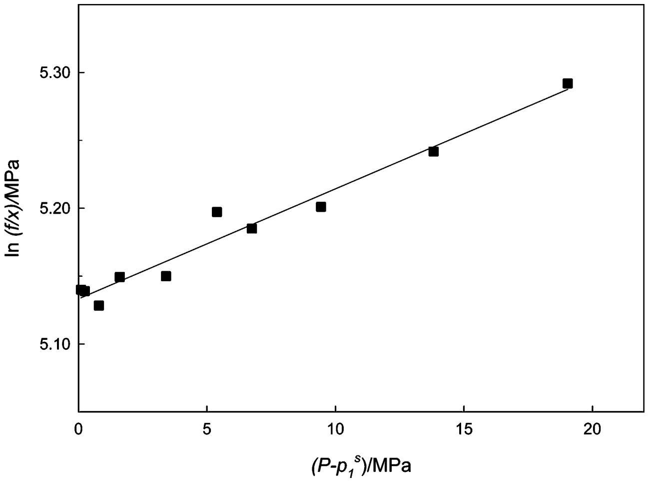

Figure 1. Krichevsky−Kasarnovsky plot for 343.15 K.

Results and Discussion

The solubility of methane in methyldiethanolamine was measured at the temperatures of (298.15, 313.15, 343.15, 373.15, and 403.15) K at pressures up to 20.3 MPa. The experimental data are presented in Table 1. The experimental data were modeled by the Krichevsky−Kasarnovsky[3] equation:

$$\ln(\hat{f}_2/x_2) = \ln H_{21} + \frac{\bar{v}_2^{\infty}(P - P_1^{s})}{RT} \qquad (1)$$

Here $\hat{f}_2$ is the fugacity of methane, x_2 is the mole fraction methane in the liquid phase, H_{21} is the Henry's constant, $\bar{v}_2^{\infty}$ is the partial molar volume of methane at infinite dilution, P is the total pressure, P_1^{s} is the vapor pressure of the solvent (MDEA), R is the gas constant, and T is the absolute temperature. The fugacity of the methane was calculated by the Peng−Robinson[4] equation of state. The vapor pressure of MDEA was taken from DIPPR,[5] and the maximum value was 1.75 kPa at 403.15 K. A typical plot is shown in Figure 1. The data are well-represented by a straight line, and the intercept on the ordinate is ln H_{21}. The slopes of the plots were all similar, and the value of $\bar{v}_2^{\infty}$ is 25.2 ± 2.5 cm^3 mol^{-1}. However, as Gibbs

---

* To whom correspondence should be addressed. E-mail alan.mather@ualberta.ca.

10.1021/je060118g CCC: $33.50

Table 1. Solubility of Methane (2) in Methyldiethanolamine (1)

$T = 298.15$ K		$T = 313.15$ K		$T = 343.15$ K		$T = 373.15$ K		$T = 403.15$ K	
P/MPa	$x_2 \cdot 10^3$	P/MPa	$x_2 \cdot 10^3$	P/MPa	$x_2 \cdot 10^3$	P/MPa	$x_2 \cdot 10^3$	P/MPa	$x_2 \cdot 10^3$
20.30	74.35	19.46	74.77	19.04	79.71	18.60	83.77	17.65	85.92
16.06	65.28	16.00	67.54	13.82	63.09	14.93	71.81	14.29	73.85
12.00	54.26	11.72	54.74	9.44	46.73	10.49	53.51	10.25	54.16
7.19	36.40	7.08	35.59	6.75	34.90	7.40	39.68	6.35	35.28
5.25	27.85	5.10	27.64	5.39	27.98	4.39	24.56	4.71	27.71
3.26	18.69	3.50	19.99	3.41	19.01	2.64	15.35	2.78	16.62
1.72	10.39	1.574	9.210	1.61	9.197	0.940	5.497	0.534	3.275[a]
0.631	3.879	0.484	2.997[a]	0.800	4.716	0.770	4.623	0.190	1.179[a]
0.175	1.089[a]	0.126	0.7674[a]	0.246	1.446[a]	0.230	1.356[a]		
0.118	0.7348[a]			0.100	0.588_2[a]	0.147	0.8719[a]		

[a] By gas chromatography.

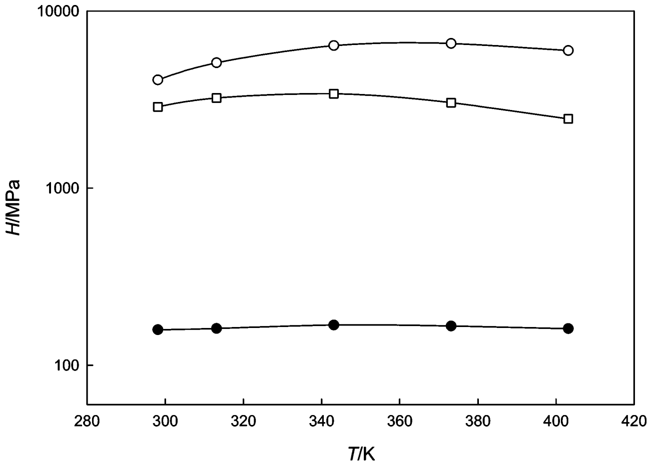

Figure 2. Temperature dependence of the Henry's constants of methane in ●, MDEA; ○, water;[7] □, 3 mol·L^{-1} MDEA solution.[1]

Table 2. Henry's Constants for Methane

T/K	H_{21}/MPa MDEA	H_{23}/MPa water[7]	H_{2m}/MPa 3 mol·L^{-1} MDEA[1]	α_{13}
298.15	158.7	4081	2874	1.6
313.15	161.3	5096	3225	2.9
343.15	168.7	6376	3409	5.2
373.15	166.5	6557	3035	7.3
403.15	160.9	5980	2461	9.1

and Van Ness[6] have shown, it is not always true that the slope on the Krichevsky−Kasarnovsky plot is equal to $\bar{v}_2^{\infty}/RT$. Values of the Henry's constant are given in Table 2 and are plotted in Figure 2 for comparison with data for the Henry's constant of methane in water[7] and in an aqueous solution of 3 mol·L^{-1} MDEA.[1]

O'Connell and Prausnitz[8] have shown the relationship between the Henry's constant in a mixed solvent and the Henry's constant in the individual solvents. For a binary mixed solvent the expression is

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

where H_{2m} is the Henry's constant of methane in a mixture of MDEA and water, H_{21} is the Henry's constant of methane in MDEA, H_{23} is the Henry's 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. Values of α_{13} are presented in Table 2. They 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 2. Mixtures of MDEA and water contain both polar and hydrogen-bonded molecules, and the excess Gibbs energy for this mixture is unlikely to follow a one-parameter Margules equation.

Literature Cited

(1) Jou, F.-Y.; Carroll, J. J.; Mather, A. E.; Otto, F. D. Solubility of methane and ethane in aqueous solutions of methyldiethanolamine, *J. Chem. Eng. Data* **1998**, *43*, 781−784.
(2) Jou, F.-Y.; Deshmukh, R. D.; Otto, F. D.; Mather, A. E. Vapor−liquid equilibria for acid gases and lower alkanes in triethylene glycol. *Fluid Phase Equilib.* **1987**, *36*, 121−140.
(3) Krichevsky, I. R.; Kasarnovsky, J. S. Thermodynamical calculations of solubilities of nitrogen and hydrogen in water as high pressures. *J. Am. Chem. Soc.* **1935**, *57*, 2168−2171.
(4) Peng, D.-Y.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.
(5) *DIPPR*, Public Version 1.2.0, Diadem, 2000.
(6) Gibbs, R. E.; Van Ness, H. C. Solubility of gases in liquids in relation to the partial molar volumes of the solute: carbon dioxide−water. *Ind. Eng. Chem. Fundam.* **1971**, *10*, 312−315.
(7) Crovetto, R.; Fernández-Prini, R.; Japas, M. L. Solubilities of inert gases and methane in H_2O and in D_2O in the temperature range of 300 to 600 K. *J. Chem. Phys.* **1982**, *76*, 1077−1086.
(8) O'Connell, J. P.; Prausnitz, J. M. Thermodynamics of gas solubility in mixed solvents. *Ind. Eng. Chem. Fundam.* **1964**, *3*, 347−351.
(9) Xu, S.; Qing, S.; Zhen, Z.; Zhang, C.; Carroll, J. J. Vapor pressure measurements of aqueous *N*-methyldiethanolamine solutions. *Fluid Phase Equilib.* **1991**, *67*, 197−201.

Received for review March 13, 2006. Accepted April 12, 2006. The authors are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this research.

JE060118G