J. Chem. Eng. Data **1995,** *40,* 493–495

Solubility of Carbon Dioxide in Methyldiethanolamine + Methanol + Water

Amr Henni and Alan E. Mather*

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

The solubility of CO_2 in a mixed nonaqueous solvent of methyldiethanolamine (MDEA) and methanol has been measured at 40 °C. The results are compared with the solubility of CO_2 in pure methanol. The solubility of CO_2 has also been obtained at 40 and 100 °C in an aqueous mixed solvent consisting of methanol (40 mass %), MDEA (40 mass %), and water (20 mass %) at partial pressures of the acid gas up to 7.04 MPa. The solubility results are compared with the nonaqueous mixed solvent results and previously reported data for aqueous methyldiethanolamine.

Introduction

Aqueous solutions of methyldiethanolamine (MDEA) are attractive solvents for the selective removal of H_2S from process streams containing CO_2 and hydrocarbons. MDEA is a tertiary amine and is more selective for H_2S than conventional amines such as monoethanolamine (MEA) and diethanolamine (DEA).

Methanol is widely used as a physical solvent for the removal of CO_2 from gas streams. Enhancement of the solubility of CO_2 in aqueous monoethanolamine by the presence of methanol was observed at high partial pressures (Banasiak, 1981). The solubility was 25% higher in a MEA + methanol mixture than in an aqueous MEA solution of equivalent concentration. Mixed solvents (chemical and physical) are expected to have a higher capacity for the acid gases over a wide range of partial pressures than the physical or chemical solvent alone.

The present work provides solubilities of CO_2 in a nonaqueous mixture of MDEA (50 mass %) and methanol (50 mass %) and solubilities of CO_2 in a mixture of MDEA, methanol, and water at temperature and pressure conditions of industrial interest.

Experimental Section

The apparatus used in this work is similar to that employed by Jou et al. (1982). The windowed equilibrium cell was placed in a constant-temperature bath. The temperature was controlled by a Hallikainen Thermotrol to within ±0.1 °C. A 250 cm^3 tubular reservoir was mounted at the top of the cell to increase the volume of the vapor phase. The pressure in the cell was measured by a 0–12000 kPa Heise gauge with an accuracy of ±0.1% of full scale. The temperature was measured by a calibrated iron–constantan thermocouple.

The cell was heated and evacuated; then the solvent was fed into the cell by gravity. Carbon dioxide was added to an amount determined by the pressure. Nitrogen was used to keep the pressure above 200 kPa. Standard techniques were used to keep the solvent (MDEA + methanol) water-free. Samples of the mixed solvent were injected into the gas chromatograph, but no water was detected. The vapor phase was recirculated through the bottom of the cell by a magnetic pump for about 8 h. The pump was then stopped and a sample of the liquid (less than 2 g) was withdrawn into a 50 cm^3 sample bomb containing about 10 g of 50 mass % aqueous diglycolamine (DGA). Care was taken to have enough DGA to absorb all of the carbon dioxide present.

A 1 μL sample was injected in a gas chromatograph (Hewlett-Packard 5710A) containing a column 3 m long and of 6.35 mm o.d., packed with Chromosorb 104. The column temperature was 120 °C and programmed to reach 250 °C after the appearance of the carbon dioxide peak. The vapor sample was sent directly to the gas chromatograph. The column used for the gas phase analysis was 3 m long and packed with Porapak S. The column temperature was 70 °C when nitrogen was present and was programmed to reach 250 °C.

Anhydrous methanol with a purity of 99+ mass % (water <0.005 mass %) was used in the nonaqueous solvent, and methanol with a purity of 99.9 mass % was used in the aqueous mixture. Methanol and MDEA (99 mass % pure) were purchased from Aldrich Chemical Co. (Milwaukee, WI). The carbon dioxide (99.9 mol % pure) and nitrogen (UHP) were supplied by Linde (Edmonton, AB). The partial pressure of water over the aqueous mixed MDEA was calculated from Raoult's law. The concentration of the MDEA + methanol system was monitored by titration using hydrochloric acid (0.1 mol·dm^{-3}). Methyl red was used as an indicator.

Results and Discussion

The solubility of CO_2 in a mixed solvent comprised of 50 mass % MDEA (chemical) and 50 mass % methanol (physical) was measured at 40 °C. The experimental data are presented in Table 1.

The solubility of CO_2 is compared with that in pure methanol (Henni, 1994) and is shown in Figure 1. At low acid gas partial pressures the solubility of CO_2 is higher in the mixed solvent than in pure methanol. The trend is reversed at higher partial pressures of CO_2.

The solubility of CO_2 in a mixture of methanol (40 mass %), MDEA (40 mass %), and water (20 mass %) was measured at 40 and 100 °C. The results are presented in Table 2. Comparisons between the solubility of CO_2 at 40 and 100 °C in this aqueous mixture, in the nonaqueous mixed MDEA, and in aqueous MDEA solutions (48.7 and 30 mass %) are shown in Figures 2 and 3. Two solubility points were measured at 120 °C to check the converging trend of the data at 40 and 100 °C.

Carbon dioxide appears to be more soluble in aqueous MDEA than in the aqueous mixed MDEA at 40 and 100 °C at low partial pressures. According to Sen et al. (1992),

---

* Author to whom correspondence should be addressed (email mather@chopin.eche.ualberta.ca).

0021-9568/95/1740-0493$09.00/0

Table 1. Solubility of CO_2 (1) at 40 °C in Methanol (2) (50 Mass %) + MDEA (50 Mass %)

P_1[a]/kPa	x_1[b]	x_2[b]
313	0.059	0.757
565	0.075	0.787
1161	0.118	0.744
1911	0.151	0.706
2596	0.172	0.694
3496	0.195	0.657
4417	0.221	0.651
5813	0.246	0.613
7392	0.275	0.577

[a] P_i = partial pressure. [b] x_i = mole fraction.

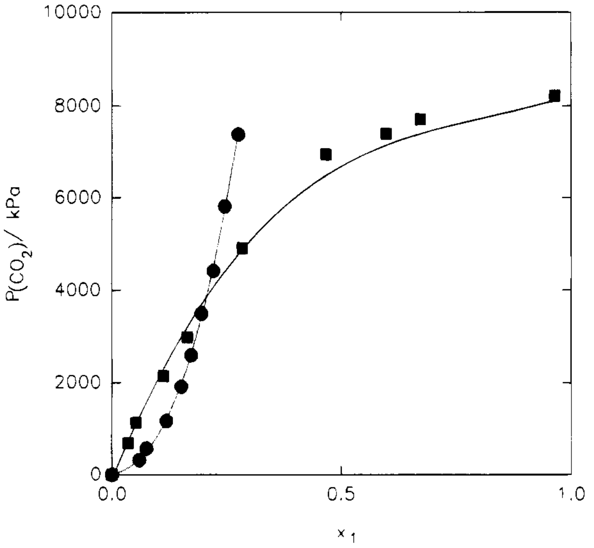

Figure 1. Effect of addition of MDEA on the mole fraction solubility of CO_2 (1) in methanol at 40 °C: (●) MDEA (50 mass %) + methanol (50 mass %); (■) methanol, Henni (1994); (—) PR correlation.

Table 2. Solubility of CO_2 (1) in MDEA (40 Mass %) + Methanol (40 Mass %) + H_2O (20 Mass %) at 40 and 100 °C

P_1/kPa	α (mol of CO_2/mol of MDEA)	P_1/kPa	α (mol of CO_2/mol of MDEA)
		40 °C	
3	0.040	537	0.991
12	0.029	726	1.205
33	0.128	1012	1.240
47.3	0.203	2046	1.310
110.4	0.259	3052	1.565
157	0.421	4618	1.630
305	0.732	5447	2.078
438	0.920		
		100 °C	
48	0.010	1973	0.776
78.6	0.014	2314	1.057
110.6	0.019	3866	1.458
123.8	0.021	5367	1.734
552.8	0.368	7044	1.752
1641.2	0.568		
		120 °C	
5464	1.239	7731	1.723

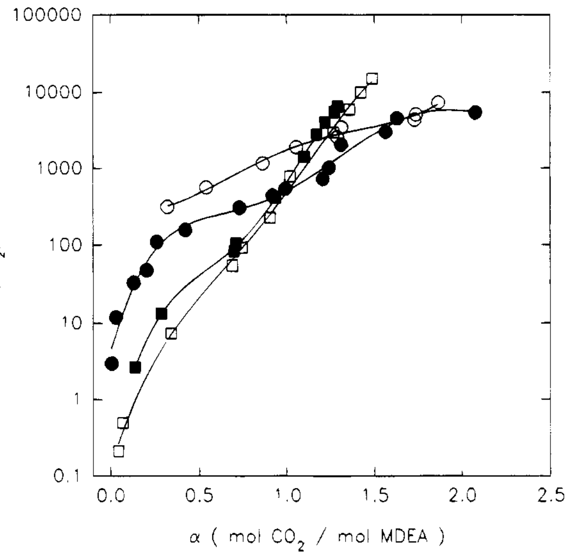

Figure 2. Solubility of CO_2 in mixed MDEA solvents at 40 °C: (●) MDEA (40 mass %) + methanol (40 mass %) + water (20 mass %); (○) MDEA (50 mass %) + methanol (50 mass %); (■) MDEA (48.7 mass %) + water (51.3 mass %), Jou et al. (1982); (□) MDEA (30 mass %) + water (70 mass %), Jou et al. (1994).

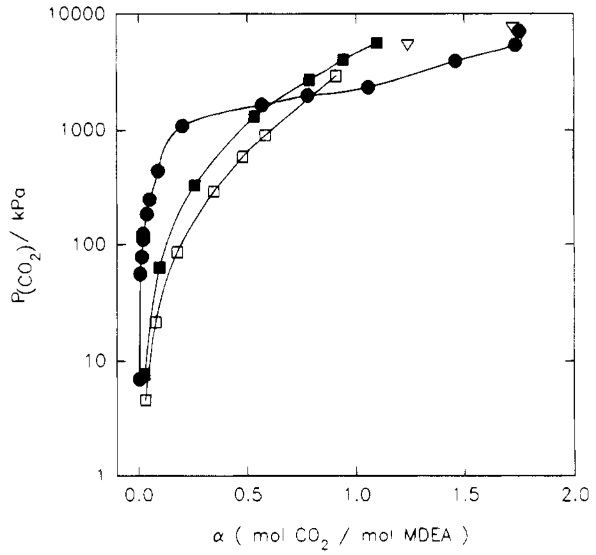

Figure 3. Solubility of CO_2 in mixed MDEA solvents at 100 °C: (●) MDEA (40 mass %) + methanol (40 mass %) + water (20 mass %); (■) MDEA (48.7 mass %) + water (51.3 mass %), Jou et al. (1982); (□) MDEA (30 mass %) + water (70 mass %), Jou et al. (1994); (▽) MDEA (40 mass %) + methanol (40 mass %) + water (20 mass %), 120 °C.

the formation of ions is favored in solvents of high dielectric constants. The dielectric constants of pure methanol and water at 40 °C are 29.8 and 73.1, respectively. Figure 2 also shows that at higher partial pressures of CO_2 the solubility in the mixed nonaqueous solvent becomes larger than in the aqueous MDEA. The difference in the solubility of CO_2 in the aqueous mixed MDEA and nonaqueous mixed MDEA is considerably reduced. Figures 2 and 3 also show that at higher partial pressures (loading >1 mol of CO_2/mol of MDEA) the solubility in the aqueous mixed MDEA with methanol as a solvent becomes significantly greater than in the aqueous amine.

The enhancement of the solubility in the aqueous mixed MDEA can be explained by the absorbing power of the physical solvent (methanol) at loadings where chemical reaction is complete.

The nonaqueous solubility data were correlated using the Peng–Robinson (PR) equation of state (Peng and Robinson, 1976). The optimum interaction parameter, δ_{12}, in the mixing rule of the equation of state for CO_2 (1) + methanol (2) with a value of 0.0685 was taken from Henni (1994). The critical pressure (P_c) and critical temperature (T_c) for MDEA were estimated using the correlation of Lydersen (Reid et al., 1987). The acentric factor (ω) was obtained from Lee–Kesler correlation (Reid et al., 1987). The calculated parameters for pure MDEA and those of metha-

Table 3. Pure Component Parameters for the Peng–Robinson Equation of State

compd	T_c/K	P_c/kPa	ω
CO_2[a]	304.2	7381	0.225
MDEA[b]	680.7	4053	1.125
methanol[c]	512.6	8096	0.565

[a] Angus et al. (1976). [b] Estimated in this work. [c] Daubert and Danner (1991).

nol are presented in Table 3. The parameters for pure CO_2 were published by Angus et al. (1976) and those for pure methanol by Daubert and Danner (1991). The remaining interaction parameters in the mixing rule of the equation of state were obtained by minimizing the error in the predicted bubble point pressure.

The following objective function was used:

$$f(\delta_{12}) = \left(\sum \frac{|P_{\mathrm{exptl}} - P_{\mathrm{calcd}}|}{P_{\mathrm{exptl}}}\right) / (\mathrm{NP}) \qquad (1)$$

P_{exptl} is the experimental bubble point pressure, P_{calcd} is the calculated bubble point pressure, and NP is the number of data points. A value of 43.1% for the objective function was obtained with values of the interaction parameters δ_{13} of -0.25 and δ_{32} of -0.5. The data could not be well correlated by the PR equation of state even though the PR equation could correlate very well the data for the CO_2 + methanol mixture.

Rivas and Prausnitz (1979) assumed that complexes are formed when CO_2 was absorbed in a nonaqueous mixed solvent composed of either MEA or DEA. Sada et al. (1989) maintained that a chemical reaction occurs when CO_2 is absorbed in a mixture of triethanolamine (a tertiary amine) and methanol. This statement contradicts the finding of Versteeg and van Swaaij (1988). They concluded that no chemical reaction occurs when CO_2 is absorbed in a solution of MDEA and ethanol. The absorption is purely a physical one.

Literature Cited

Angus, S.; Armstrong, B.; de Reuck, K. M. *International Thermodynamic Tables of the Fluid State, Vol. 3, Carbon Dioxide*; Pergamon Press: Oxford, U.K., 1976.

Banasiak, J. Solubility of Carbon Dioxide in Methanol-Monoethanolamine Mixtures. *Gaz, Woda Tech. Sanit.* **1981**, *55*, 196–199.

Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*; Hemisphere: Washington, DC, 1991.

Henni, A. M.Sc. thesis, University of Alberta, Edmonton, AB, Canada, 1994.

Jou, F.-Y.; Mather, A. E.; Otto, F. D. Solubility of H_2S and CO_2 in Aqueous MDEA Solutions. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 539–544.

Jou, F.-Y.; Mather, A. E.; Otto, F. D. Vapor-Liquid Equilibrium of Carbon Dioxide in Aqueous Mixtures of Monoethanolamine and Methyldiethanolamine. *Ind. Eng. Chem. Res.* **1994**, *33*, 2002–2005.

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

Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*; 4th ed.; McGraw-Hill: New York, 1987.

Rivas, O. R.; Prausnitz, J. M. Sweetening of Sour Natural Gases by Mixed-Solvent Absorption: Solubility of Ethane, Carbon Dioxide, and Hydrogen Sulfide in Mixtures of Physical and Chemical Solvents. *AIChE J.* **1979**, *25*, 975–984.

Sada, E.; Kumazawa, H.; Ikehara, Y.; Han, Z. Q. Chemical Kinetics of the Reaction of Carbon Dioxide with Triethanolamine in Non-Aqueous Solvents. *Chem. Eng. J.* **1989**, *40*, 7–12.

Sen, B.; Roy, R. N.; Gibbons, J. J.; Johnson, D. A.; Adcock, L. H. Computational Techniques of Ionic Processes in Water-Organic Mixed Solvents. *Adv. Chem. Ser.* **1979**, *No. 177*, 215–248.

Versteeg, G. F.; van Swaaij, W. P. M. On the Kinetics Between CO_2 and Alkanolamines Both in Aqueous and Non-Aqueous Solutions. Part 2: Tertiary Amines. *Chem. Eng. Sci.* **1988**, *43*, 587–591.

Received for review September 8, 1994. Accepted December 28, 1994.[⊗] This work was supported by the Natural Sciences and Engineering Research Council of Canada.

JE9401878

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1995.