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Solubility of Carbon Dioxide in Monoethanolamine + Ethylene Glycol + Water and Monoethanolamine + Poly(ethylene glycol) + Water

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The solubility of carbon dioxide in monoethanolamine (MEA) + ethylene glycol (EG) + water and monoethanolamine (MEA) + poly(ethylene glycol) (PEG) + water has been measured at 313.2 K and at partial pressure ranges of carbon dioxide up to 2500 kPa. The concentrations of aqueous mixtures are 15.3 mass % MEA + 15.3 mass % EG, 15.3 mass % MEA + 42.3 mass % EG, 15.3 mass % MEA + 15.3 mass % PEG, and 15.3 mass % MEA + 42.3 mass % PEG. In each case, the solubility was represented as functions of partial pressures of carbon dioxide.

Introduction

Alkanolamine aqueous solutions have been extensively used for the removal of acid gases in gas mixtures. Particularly, the removal of carbon dioxide by using chemical absorbents has been of great interest, since it was found that the global warming effect is primarily due to excessive discharge of carbon dioxide and methane. Aqueous monoethanolamine (MEA) solutions are the most frequently used chemical absorbents because of high reactivity to such chemicals as carbon dioxide. However, it is known that these solutions can also react with unrelated materials such as reactor vessels, tubing lines, and several process compartments. For this reason, the highly MEA-concentrated aqueous solutions should be avoided for the carbon dioxide removal process.

The use of mixed solutions of chemical and physical absorbents may have the potential advantage of solving this problem. Several studies on the removal of acid gases by using aqueous alkanolamine solutions mixed with physical absorbents have been recently reported in the literature (Roberts and Mather, 1988; Woertz, 1972; Henni and Mather, 1995; Oyevaar et al., 1989). In this study, we provide measurements on the solubility of carbon dioxide in aqueous MEA solutions mixed with ethylene glycol (EG) and poly(ethylene glycol) (PEG) as physical absorbents.

Experimental Section

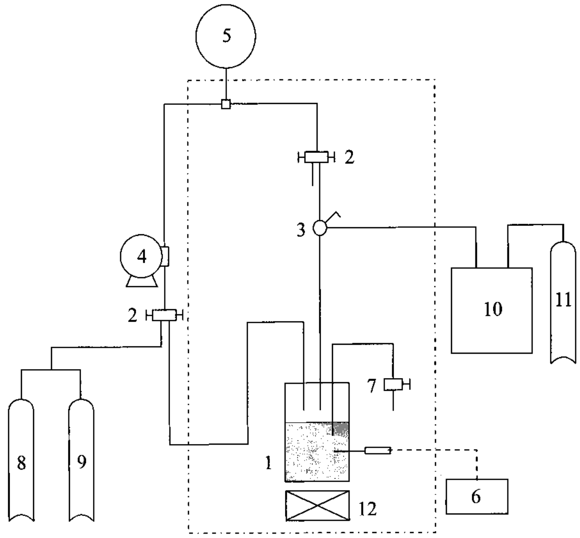

Figure 1. Schematic diagram of the experimental apparatus used in this work: (1) equilibrium cell; (2) three-way valve; (3) vapor sampling valve; (4) high-pressure pump; (5) pressure gauge; (6) thermometer; (7) liquid sampling valve; (8) carbon dioxide cylinder; (9) nitrogen cylinder; (10) gas chromatograph; (11) helium cylinder; (12) magnet.

Apparatus and Procedure. A schematic diagram of the equilibrium apparatus used in this study is shown in Figure 1. The main part of the apparatus consists of an equilibrium cell and a sampling compartment. The equilibrium cell is made of 316 stainless steel and has an internal volume of about 200 cm^3. The pressure in the equilibrium cell can be measured by a Heise gauge (CM 118324, (0 to 500) psi range). The measurement accuracy of this gauge is ±0.1% of the gauge range. The temperature in the equilibrium cell was measured by a K-type thermocouple with a digital thermometer (Cole-Parmer, 8535-26) of which the resolution is ±0.1 K. The vapor phase in the cell is recirculated to obtain a rapid equilibration and to transport the vapor samples into a sampling valve by using a high-pressure metering pump (Milton Roy, 2396-31). The vapor sampling valve (Rheodyne, 7410) has a loop of about 500 mL. Most components of the equilibrium apparatus are contained in an air bath controlled to ±0.1 K by a PID temperature controller. A gas chromatograph (Hewlett-Packard, 5890A) is connected to this sampling valve on-line. The gas chromatograph uses a thermal conductivity detector (TCD) and a 6 ft by $^1/_8$ in. diameter column packed with Porapak Q for analysis of the vapor samples. The conditions of gas chromatography for sample analysis are a carrier gas flow rate of 20 mL/min, a column

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Table 1. Solubility of Carbon Dioxide in 15.3 Mass % MEA Aqueous Solution at 313.2 K

P/kPa	α/(mol of CO_2/mol of MEA)	P/kPa	α/(mol of CO_2/mol of MEA)
3.1	0.490	94.0	0.686
5.2	0.500	247	0.753
10.0	0.525	456	0.802
28.0	0.572	1255	0.953
61.6	0.619	2359	1.061

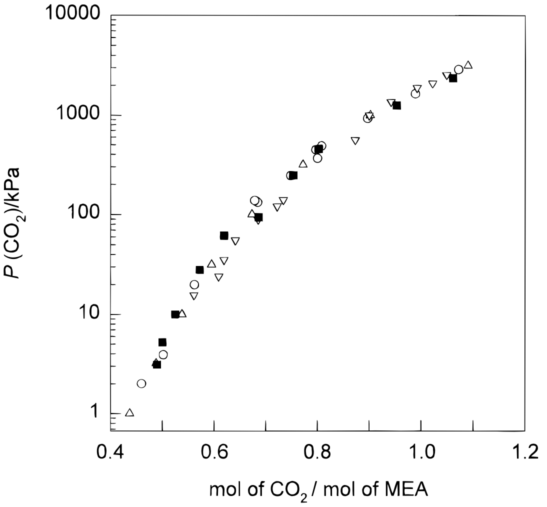

Figure 2. Solubility of carbon dioxide in 15.3 mass % MEA aqueous solution at 313.2 K: (■) this work; (▽) Shen and Li (1992); (○) Lee et al. (1974); (△) Lee et al. (1976).

Table 2. Solubility of Carbon Dioxide in 15.3 Mass % Aqueous MEA Solutions Mixed with EG and PEG

P/kPa	α/(mol of CO_2/mol of MEA)	P/kPa	α/(mol of CO_2/mol of MEA)
MEA 15.3 mass % + EG 15.3 mass %		MEA 15.3 mass % + EG 42.3 mass %	
4.2	0.510	10.7	0.540
9.4	0.530	27.3	0.555
21.1	0.555	83.3	0.605
140	0.663	223	0.669
341	0.767	707	0.784
1176	0.935	1524	0.881
2513	1.014	2379	0.939
MEA 15.3 mass % + PEG 15.3 mass %		MEA 15.3 mass % + PEG 42.3 mass %	
3.1	0.474	3.1	0.453
12.0	0.536	7.2	0.472
34.2	0.581	25.3	0.536
91.8	0.643	67.7	0.584
279	0.737	203	0.636
683	0.830	654	0.744
1207	0.901	1247	0.828
		1866	0.875
		2270	0.924

temperature of 50 °C, and a detector temperature of 120 °C.

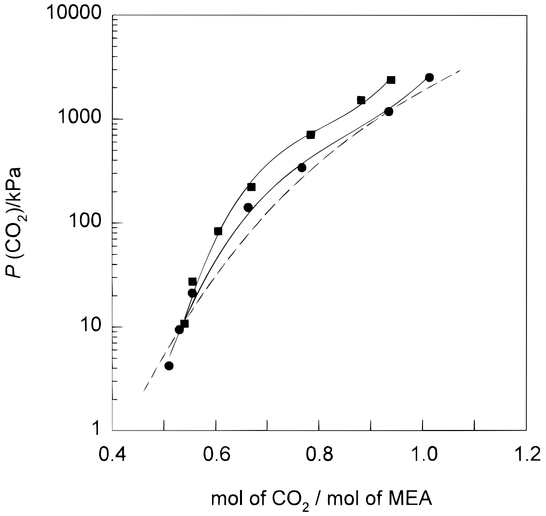

Figure 3. Solubility of carbon dioxide in MEA + EG + water system at 313.2 K: (●) 15.3 mass % MEA + 15.3 mass % EG; (■) 15.3 mass % MEA + 42.3 mass % EG; (- - -) 15.3 mass % MEA aqueous solution (Shen and Li, 1992; Lee et al., 1974; Lee et al., 1976).

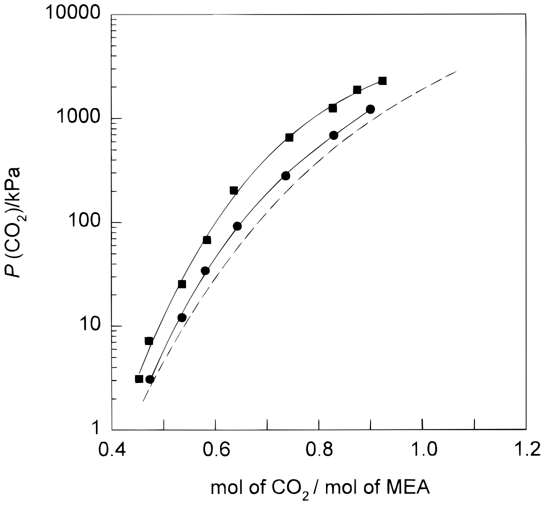

Figure 4. Solubility of carbon dioxide in MEA + PEG + water system at 313.2 K: (●) 15.3 mass % MEA + 15.3 mass % PEG; (■) 15.3 mass % MEA + 42.3 mass % PEG; (- - -) 15.3 mass % MEA aqueous solution (Shen and Li, 1992; Lee et al., 1974; Lee et al., 1976).

The experiment begins by charging the equilibrium cell in a condition of evacuation with a mixture of liquid. Approximately 150 mL of the aqueous mixtures is fed to the equilibrium cell. After the cell is slightly pressurized by nitrogen or carbon dioxide, it is slowly heated to the experimental temperature. For the experiments at carbon dioxide partial pressures lower than atmospheric pressure, only a minute amount of carbon dioxide should be carefully added to the cell. In this case, more rapid equilibration could be attained by stirring a magnetic spin bar with an external magnet. When the system pressure and vapor compositions did not change during 4 h, the condition was considered to be an equilibrium point. In general, 24 h was consumed to reach an equilibrium condition.

Once an equilibrium condition was reached, the liquid samples in the cell were withdrawn and analyzed at least two times to measure the carbon dioxide loading in the aqueous absorbents. The analysis of liquid samples was carried out by the titration method (Shen and Li, 1992). The partial pressure of carbon dioxide was calculated from available information on the system total pressure, the vapor phase compositions, and the partial pressure of water at the specified temperature. The partial pressure of water was obtained by using Raoult's law. It is also reasonable to assume that the other liquid solvents are nonvolatile and thus do not affect the partial pressure of carbon dioxide.

Materials. The solvents and absorbents used in this study were obtained from Sigma-Aldrich Chemical Co. with a minimum purity of 99 mol % and were used without further purification. A PEG of molecular weight 400 was used. All solutions were prepared with distilled water. The carbon dioxide and nitrogen gases provided were of a commercial grade with a purity of 99.5 mol %.

Results and Discussion

To establish the validity of the equilibrium apparatus and procedure used in this work, the solubility measurements of carbon dioxide in 15.3 mass % MEA aqueous solution at 313.2 K were carried out at partial pressures of carbon dioxide ranging from 3.0 to 2360 kPa and compared with available data in the literature (Lee et al., 1976; Shen and Li, 1992). The experimental results are presented in Table 1 and depicted in Figure 2. As shown in Figure 2, both results were found to be in good agreement over the entire pressure range considered in this study.

The solubilities of carbon dioxide in aqueous MEA + EG solutions were measured at two different compositions of 15.3 mass % MEA + 15.3 mass % EG and 15.3 mass % MEA + 42.3 mass % EG, carbon dioxide partial pressures up to 2520 kPa, and 313.2 K. In addition, the solubility of carbon dioxide in aqueous solutions of 15.3 mass % MEA + 15.3 mass % PEG and 15.3 mass % MEA + 42.3 mass % PEG were also measured at 313.2 K and carbon dioxide partial pressures up to 2270 kPa. The overall results are summarized in Table 2 and plotted in Figures 3 and 4. The solubility of carbon dioxide increases with an increase in the carbon dioxide partial pressures and at a fixed carbon dioxide partial pressure gradually decreases at higher EG and PEG mass fractions. It is interesting to note here that, at carbon dioxide partial pressures lower than 10 kPa, the solubility of carbon dioxide in MEA + EG aqueous solutions was slightly higher than its solubility in aqueous MEA solution.

Unfortunately, because of the limitations of our experimental apparatus, the solubility at very low partial pressures of carbon dioxide could not be obtained. Moreover, at EG and PEG concentrations higher than 42.3 mass % the solution mixtures become too viscous to produce reliable equilibrium solubility data.

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