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Solubilities of Carbon Dioxide in Aqueous Mixtures of Diethanolamine and 2-Amino-2-methyl-1-Propanol

Dong-Joo Seo and Won-Hi Hong*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusung-dong Yusung-gu Taejeon, 301-701, Korea

The gas solubility of CO_2 has been measured in aqueous mixtures of diethanaolamine and 2-amino-2-methyl-1-propanol at (40, 60, and 80) °C and in the pressure range (10 to 300) kPa. The concentrations of the amine mixtures were 6 mass % diethanolamine (DEA) + 24 mass % 2-amino-2-methyl-1-propanol (AMP), 12 mass % DEA + 18 mass % AMP, and 18 mass % DEA + 12 mass % AMP. The solubilities show a systematic change as the composition of the aqueous mixtures varies.

Introduction

Absorption of acid gases such as CO_2 and H_2S with a suitable solvent is an important industrial process. Monoethanolamine (MEA) and diethanolamine (DEA) solutions are the most widely used solvents for the acid gas absorption process. Aqueous MEA solutions have properties of high reactivity, low solvent cost, ease of reclamation, and low absorption of hydrocarbons (Issacs et al., 1980). A complete review of the literature of the ethanolamines for acid gas removal is given by Kohl and Reisenfield (1985). The solubility of amines mainly depends on carbamate stability. Primary and secondary amines form stable carbamates and have a CO_2 loading limitation of 0.5 mol of CO_2/mol of amine when carbamate formation is the only reaction (Satori and Savage, 1983). Tertiary amines such as *N*-methyldiethanolamine (MDEA) have a higher loading capacity (about 1.0 mol of CO_2/mol of amine) and lower enthalpy of reaction. Aqueous MDEA solutions were found to be the attractive solution for a lower regeneration energy. However, a slow reaction with CO_2 limits the use of MDEA. Sterically hindered alkanolamines have been proposed lately as gas treating solvents (Satori and Savage, 1983). 2-Amino-2-methyl-1-propanol (AMP) is the hindered form of MEA. The bulky group attached to the tertiary carbon atom of AMP inhibits the formation of stable carbamate ion. Therefore, AMP takes a CO_2 loading up to 1.0 mol of CO_2/mol of amine. The solubility of CO_2 in aqueous AMP solution has been reported (Roberts and Mather, 1988, Teng and Mather, 1989). AMP has a higher reaction rate constant than MDEA (Yih et al., 1988).

Recently it has been shown that a solution of two or more amines improves the absorption rate and reduces the solvent regeneration energy (Chakaravarty et al., 1985). Solutions containing a mixture of amines have the combined properties of the constituent amines. Aqueous mixtures of MEA or DEA + MDEA (Austgen et al., 1991) and MEA + AMP (Li and Chang, 1994) have been reported. DEA has a lower enthalpy of reaction than MEA. Stewart and Lanning (1994) reported that MEA is much more volatile than DEA and MDEA. The solubility of CO_2 in aqueous DEA solutions has been reported at low partial pressure (Lal *et al.*, 1985) and high partial pressure (Lee *at al.*, 1972). However, the solubility of CO_2 in aqueous mixtures of DEA + AMP has not been reported. In this study the solubilities of CO_2 in aqueous mixtures of DEA and AMP were determined at (40 to 80) °C over a partial pressure range of (10 to 300) kPa.

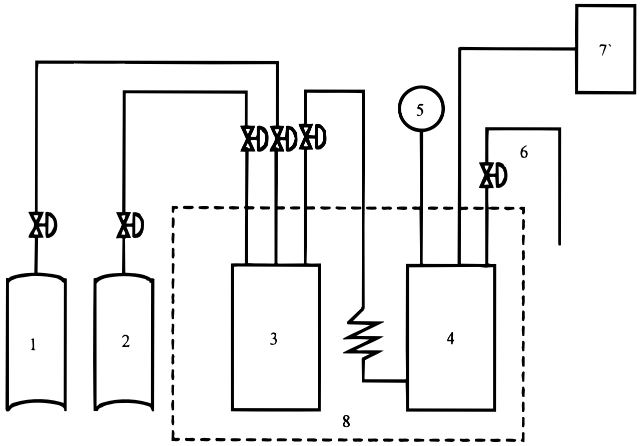

Figure 1. Experimental apparatus: (1) CO_2 cylinder, (2) N_2 cylinder, (3) saturation bottle, (4) equilibrium cell, (5) pressure gauge, (6) liquid sample outlet, (7) GC, (8) water bath.

Experimental Section

The solubilities of DEA + AMP aqueous solution were measured in a stainless steel equilibrium cell. DEA is from Aldrich (reagent grade) with 99% purity, and AMP is from Janssen Chemica with 99% purity. The amines were used without further purification. The blended alkanolamines were prepared with distilled water. The total volume of the cell was about 400 cm^3. Figure 1 shows a schematic diagram of the apparatus. The system temperature was controlled by a thermostat water bath. Temperature was controlled within ±0.1 °C of the set point temperature. The pressure of the system was measured by a Heise gauge [(0 to 100) psig]. The accuracy of the gauge was ±0.1% of the full-scale span. Prior to the introduction of the fluids, the apparatus was brought to the desired temperature and purged with N_2 to remove traces of O_2. Approximately 100 cm^3 of the solvent was fed into the equilibrium cell. Then CO_2 was added to the cell. N_2 was used to measure the CO_2 partial pressure range below the atmospheric pressure. The gas circulation pump was started, and the vapor was recirculated though the solvent. Additional CO_2 was added until the desired partial pressure had been obtained. The equilibrium was assumed to have been reached when both the system pressure and the gas concentration did not vary for 2 h. At equilibrium, the liquid sample was

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* To whom correspondence should be addressed. E-mail: whhong@hanbit.kaist.ac.kr.

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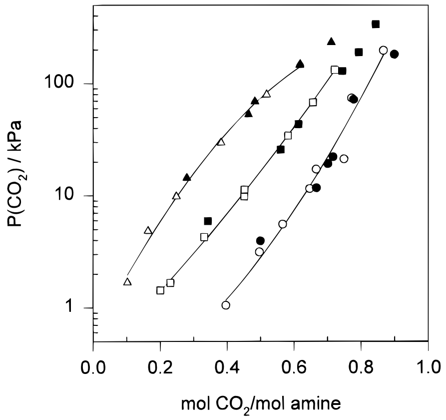

Figure 2. Comparison of CO_2 solubility data in 30 mass % AMP solution at (40, 60, and 80) °C of this study and previous reports: Li and Chang (1994): ○, 40 °C; □, 60 °C; △, 80 °C. This study: ●, 40 °C; ■, 60 °C; ▲, 80 °C. Lines are smoothed values of Li and Chang (1994).

Table 1. Solubilities of CO_2 in DEA + AMP Aqueous Solutions at (40, 60, and 80) °C[a]

$t = 40$ °C		$t = 60$ °C		$t = 80$ °C	
P/kPa	α	P/kPa	α	P/kPa	α
mass % DEA/mass % AMP = 0/30					
3.94	0.500	5.9	0.342	14.4	0.279
11.7	0.667	25.7	0.560	53.2	0.464
19.2	0.701	43.3	0.613	69.0	0.483
22.2	0.717	129.7	0.744	149.2	0.618
72.0	0.778	190.6	0.793	231.9	0.711
182.4	0.899	336.6	0.843		
mass % DEA/mass % AMP = 6/24					
1.61	0.372	3.00	0.262	87.2	0.533
15.3	0.614	38.2	0.619	207.8	0.658
32.0	0.686	75.7	0.681	269.9	0.717
89.5	0.774	171.0	0.766		
		243.5	0.810		
mass % DEA/mass % AMP = 12/18					
11.0	0.554	17.6	0.516	17.1	0.329
21.2	0.587	27.0	0.522	43.0	0.441
37.3	0.630	40.7	0.544	59.8	0.473
138.0	0.774	80.5	0.608	107.8	0.531
241.0	0.821	136.6	0.659	163.0	0.570
		226.2	0.720	328.5	0.635
		364.9	0.764	345.7	0.633
mass % DEA/mass % AMP = 18/12					
3.8	0.439	27.0	0.503	14.1	0.343
5.5	0.479	132.3	0.632	32.7	0.416
14.3	0.562	184.8	0.677	56.5	0.466
50.1	0.640	233.1	0.686	105.8	0.539
158.7	0.748	357.3	0.712	172.8	0.598
mass % DEA/mass % AMP = 30/0					
9.3	0.487	4.85	0.407	11.6	0.404
22.8	0.548	28.9	0.509	31.2	0.454
49.9	0.603	75.5	0.557	51.0	0.470
100.3	0.634	181.4	0.637	58.5	0.491
280.5	0.727	239.8	0.668	160.9	0.543
		357.3	0.691		

[a] CO_2 loading α = mol of CO_2/total mol of amine.

withdrawn from the equilibrium cell. An excess amount of 1.0 N NaOH solution was added to the liquid sample, converting dissolved CO_2 into the nonvolatile ionic species. Then an excess amount of $BaCl_2$ solution was added to the solution. Absorbed CO_2 precipitates as $BaCO_3$. The excess NaOH was titrated with 0.5 N HCl solution using phenolphthalein as the indicator. After this titration, using Methyl Orange as the indicator, HCl was added to measure the amount of $BaCO_3$. The titration method is similar to that of Li and Chang (1994). The CO_2 partial pressure was measured with an HP5890 gas chromatograph. Rault's law was used to determine the partial pressure of water.

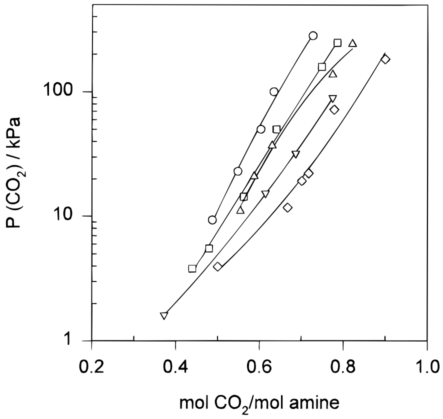

Figure 3. Solubility of CO_2 in various DEA + AMP aqueous solutions at 40 °C. DEA mass %/AMP mass %: ○, 30/0; □, 18/12; △, 12/18; ▽, 6/24 ; ◇, 0/30.

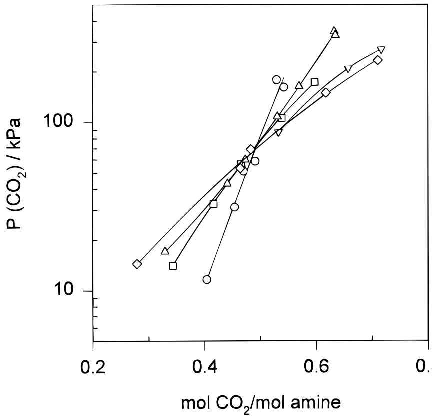

Figure 4. Solubility of CO_2 in various DEA + AMP aqueous solutions at 80 °C. DEA mass %/AMP mass % : ○, 30/0; □, 18/12; △, 12/18; ▽, 6/24; ◇, 0/30.

Results and Discussion

The solubilities of CO_2 in aqueous 30 mass % AMP solution from this study agree well with those of Li and Chang (1994). Comparison of the experimental data with previously reported solubility in 30 mass % AMP solution is graphically shown in Figure 2. Table 1 shows the CO_2 solubility data in aqueous mixtures of DEA and AMP at (40, 60, and 80) °C. The experimental error was estimated to be ±2−3% of the CO_2 loadings. The solubilities of CO_2 in 30 mass % AMP, 6 mass % DEA + 24 mass % AMP, 12 mass % DEA + 18 mass % AMP, 18 mass % DEA + 12 mass % AMP, and 30 mass % DEA aqueous solutions at (40, 60, and 80) °C were presented graphically. The total amine concentration was maintained at 30 mass %. As the temperature increased, the solubilities of CO_2 decreased. Figures 3 and 4 show the solubilities of CO_2 at 40 and 80 °C in various concentrations of aqueous amine solutions. As shown in Figures 3 and 4 the solubilities vary systematically with varying concentration of amines. A cross-point of the solubility curve occurred in Figure 4. Li and Shen (1992) reported a similar cross-point with MEA + MDEA aqueous solution.

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