Solubility of Carbon Dioxide in Aqueous Solutions of 2-Amino-2-methyl-1,3-propanediol

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The equilibrium solubility of carbon dioxide in aqueous solutions of 2-amino-2-methyl-1,3-propanediol (AMPD) has been measured at (30, 40, and 60) °C and the partial pressure of carbon dioxide ranging from (0.5 to 3065) kPa. The concentrations of the aqueous solutions were (10 and 30) mass % AMPD. The tendency of the solubility of carbon dioxide in 30 mass % AMPD aqueous solution at 40 °C was found to be similar to that in 30 mass % *N*-methyldiethanolamine aqueous solution.

Introduction

The absorption technology of acid gases such as CO_2, H_2S, and COS with aqueous solutions of alkanolamine has been widely used in the chemical industries to purify gas mixtures. Particularly the separation of CO_2 from the flue gas produced by burning fossil fuel has been of great interest owing to the global warming caused by the increase in the concentration of CO_2 in the atmosphere. Therefore the separation of CO_2 by absorption with chemical absorbents such as alkanolamines has been considered as a challenging method. Industrially important chemical absorbents are alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA), and di-2-propanolamine (DIPA). MEA aqueous solutions are the most frequently used alkanolamine absorbents owing to their high reactivity with CO_2, low solvent cost, and ease of reclamation (Isaacs et al., 1980). It is also known, however, that MEA aqueous solutions are corrosive and require high regeneration energy. MDEA aqueous solutions are better than MEA or DEA solutions in that they have the properties of high loading capacity (mol of CO_2/mol of amine) up to 1.0, less regeneration energy, and high resistance to thermal and chemical degradation. However, the slow reactivity with CO_2 of MDEA solutions limits their use. Recently, sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) and 2-piperidineethanol (PE) have been proposed as new CO_2 absorbents because of their advantages in loading capacity, absorption rate, and regeneration energy (Satori and Savage, 1983; Yih and Shen, 1988). Because of the hindrance of the bulky group attached to the tertiary carbon atom, unstable carbamate ions are formed in the reaction of the AMP solutions with CO_2 resulting in the theoretical loading capacity up to 1.0. A number of research papers related to the solubility of CO_2 in AMP aqueous solutions and blended amine solutions containing AMP have been published (Li and Chang, 1994; Seo and Hong, 1996; Tontiwachwuthikul et al., 1991).

In this study 2-amino-2-methyl-1,3-propanediol (AMPD) aqueous solutions have been studied to ascertain if it is an effective CO_2 absorbent. The solubility of CO_2 in AMPD aqueous solutions has not been reported in the literature.

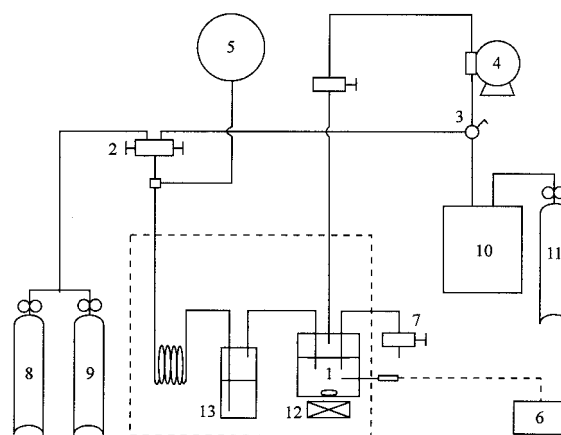* To whom correspondence should be addressed. Email: jhyoon@kepri.re.kr.

Figure 1. Schematic diagram of the experimental setup: (1) equilibrium cell; (2) three-way valve; (3) vapor sampling valve; (4) circulation 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; (13) saturation tank.

Table 1. Solubility of CO_2 in 30 mass % MDEA Aqueous Solution at 40 °C

P/kPa	α^a	P/kPa	α^a
1.02	0.128	118	0.827
2.84	0.214	170	0.904
6.39	0.324	308	0.976
11.5	0.416	549	1.010
13.6	0.452	1169	1.074
25.6	0.586	1916	1.129

^{a} mol of CO_2/mol of MDEA.

The equilibrium solubility of CO_2 in (10 and 30) mass % AMPD aqueous solutions was measured at (30, 40, and 60) °C and over the CO_2 partial pressure range of (0.5−3065) kPa.

Experimental Section

A schematic diagram of the experimental setup used in this study is shown in Figure 1. The equilibrium solubility of CO_2 in alkanolamine aqueous solutions was measured by using an equilibrium cell made of 316 stainless steel. The equilibrium cell with an internal volume of about 450
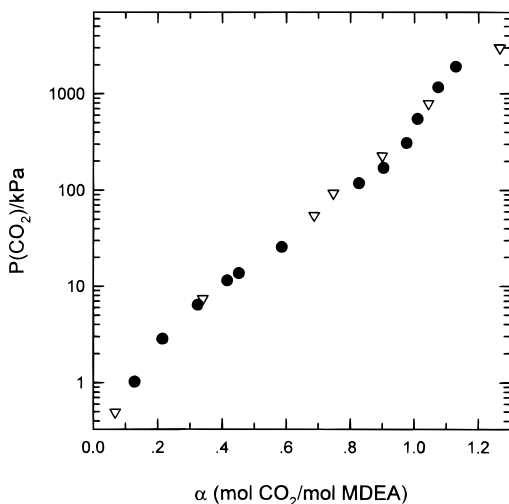
Figure 2. Solubility of CO_2 in 30 mass % MDEA aqueous solution at 40 °C: (●) this work; (▽) Jou et al. (1994).

Table 2. Solubility of CO_2 in AMPD Aqueous Solutions

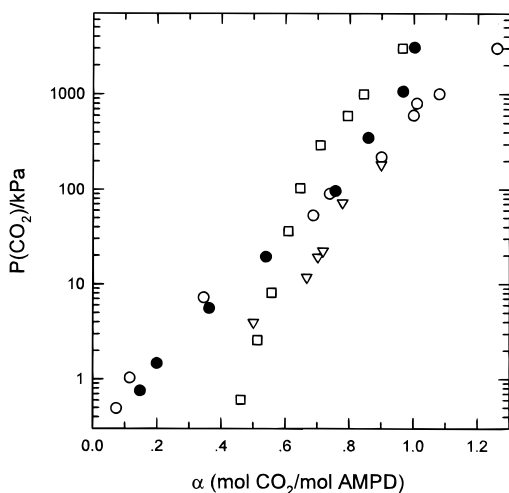| 10 mass %		30 mass %					
40 °C		30 °C		40 °C		60 °C	
P/kPa	α^a	P/kPa	α^a	P/kPa	α^a	P/kPa	α^a
1.04	0.293	0.60	0.196	0.75	0.147	2.06	0.115
7.37	0.523	1.72	0.317	1.47	0.199	6.59	0.206
65.5	0.844	5.59	0.492	5.57	0.362	18.9	0.313
314	0.945	23.8	0.669	19.3	0.540	78.0	0.538
927	1.069	97.3	0.823	96.2	0.756	277	0.732
2991	1.156	389	0.920	349	0.859	807	0.865
		1065	0.987	1064	0.964	2894	0.962
		2911	1.017	3064	1.002		

^{a} mol of CO_2/mol of AMPD.

Figure 3. Solubility of CO_2 in 30 mass % alkanolamine aqueous solution at 40 °C: (●) AMPD (this work); (□) MEA (Jou et al., 1995); (○) MDEA (Jou et al., 1994); (▽) AMP (Seo and Hong, 1996).

mL was mounted in a water bath kept at ±0.1 °C of the set point temperature by a refrigerator/heater (Jeio Tech, RBC-20). The temperature in the equilibrium cell was measured by a K-type thermocouple with a digital thermometer (OMEGA, MDSS41-TC) of which the resolution is ±0.1 °C. The system pressure was measured by a bourdon tube type of pressure gauge (Heise, CMM-123928) with an accuracy of ±0.1% of the full-scale span [(0 to 5170) kPa]. The composition of the vapor phase was determined by a gas chromatograph (Hewlett-Packard, 5890 Series II Plus). The gas chromatograph includes a thermal conduc-
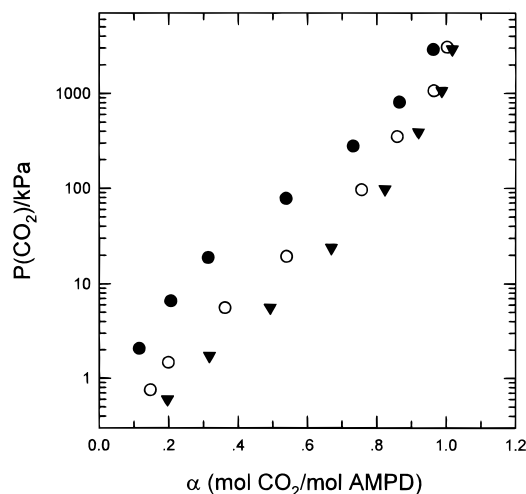

Figure 4. Effect of temperature on the equilibrium solubility of CO_2 in 30 mass % AMPD aqueous solutions: (▼) 30 °C; (○) 40 °C; (●) 60 °C.
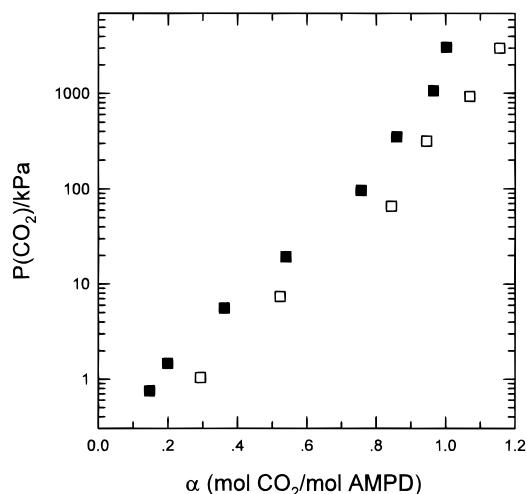

Figure 5. Effect of concentration on the equilibrium solubility of CO_2 in AMPD aqueous solutions at 40 °C: (□) 10 mass %; (■) 30 mass %.

tivity detector (TCD) and a 6 ft by $^1/_8$ in. diameter column packed with Porapak Q. The analysis conditions of the gas chromatograph for the vapor sample was a TCD temperature of 200 °C, a column temperature of 50 °C, and a carrier gas flow rate of 20 mL/min. The vapor sample was analyzed four times at each equilibrium point. The average of the individual compositions was considered as the equilibrium composition. The reproducibility of the vapor mole fraction was generally within ±0.001.

Initially, the apparatus was purged with N_2 to remove remaining air and heated to the desired temperature. Then CO_2 was carefully introduced into the equilibrium cell. For rapid equilibration, aqueous alkanolamine solutions in the equilibrium cell were stirred with a magnetic spin bar with an external magnet. For the experiment at the partial pressures of CO_2 under atmospheric pressure, the vapor phase was recirculated at the rate of 60–70 mL/min by a peristaltic pump (MasterFlex, 7553-75) until the desired equilibrium partial pressure of CO_2 was obtained. When the system pressure and vapor compositions are not changed during 3 h, the system is considered to be in equilibrium. It generally takes (8–10) h to reach equilibrium. For the experiment at the partial pressures of CO_2 over atmospheric pressure, the system was fully charged with CO_2 and the vapor phase was checked with the gas

chromatograph to confirm that the system did not contain N_2. Then, the recirculation compartment including the pump and gas chromatography was disconnected by two valves. Additional CO_2 was introduced into the equilibrium cell to obtain the desired equilibrium partial pressure of CO_2. When the system pressure is not changed during 3 h, the system is considered to be in equilibrium. It generally takes (6−8) h to reach equilibrium. At equilibrium, about 20 mL of liquid sample was withdrawn at least twice from the equilibrium cell and the loading of CO_2 in the aqueous absorbents was obtained by analyzing the sample by the titration method (Li and Chang, 1994). The experimental error in the loading of CO_2 is estimated to be $\pm 3\%$. The partial pressure of CO_2 was corrected for water vapor pressure at the equilibrium temperature.

Alkanolamine aqueous solutions were prepared from deionized water, 99+% MDEA from Acros Organics, and 99+% AMPD from Sigma. CO_2 and N_2 with a purity of 99.99% were supplied from the commercial cylinders.

Results and Discussion

To verify the applicability of the experimental setup and the procedure used in this study, the solubility of CO_2 in 30 mass % MDEA aqueous solutions at 40 °C was measured at the partial pressure of CO_2 ranging from 0.02 to 2000 kPa and compared with the previously reported data in the literature (Jou et al., 1994). The experimental results are presented in Table 1 and depicted in Figure 2. All data points are fitted to a polynomial equation by the least-squares method. The determined equation is as follows

$$\ln(P/\text{kPa}) = -2.626 + 33.43\alpha - 127.9\alpha^2 + 318.7\alpha^3 - 433.2\alpha^4 + 297.5\alpha^5 - 79.72\alpha^6$$

where P is the partial pressure of CO_2 and α is the loading capacity (mol of CO_2/mol of amine). The average and maximum percent absolute deviations between the calculated and experimental partial pressures of CO_2 obtained in this work are 7.9 and 19.5, respectively. The average and maximum percent absolute deviations between the calculated and experimental partial pressures of CO_2 obtained by Jou et al. (1994) are 17.8 and 47.3, respectively.

As shown in Figure 2, both results are found to be in good agreement over the entire pressure range considered in this study.

The solubility of CO_2 in AMPD aqueous solutions at various conditions (temperature, 30, 40, and 60 °C; concentration, 10 and 30 mass %; CO_2 partial pressure, 0.5−3070 kPa) is presented in Table 2 and plotted in Figures 3−5. In Figure 3, the solubility of CO_2 in 30 mass % AMPD aqueous solutions at 40 °C was compared with the solubility of CO_2 in 30 mass % MEA, MDEA, and AMP aqueous solutions at the same temperature of 40 °C (Jou et al., 1994, 1995; Seo and Hong, 1996). The tendency of the solubility of CO_2 in AMPD aqueous solution was found to be similar to that in MDEA solution. The temperature effect on the solubility of CO_2 in AMPD aqueous solutions is shown in Figure 4. Solubility decreases with the increase in temperature. Figure 5 shows the effect of AMPD concentrations on the solubility of CO_2 at 40 °C. It is found that the solubility of CO_2 in 10 mass % AMPD aqueous solution is higher than that in 30 mass % AMPD aqueous solution.

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