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Solubilities of Carbon Dioxide in Aqueous Potassium Carbonate Solutions Mixed with Physical Solvents

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The solubilities of carbon dioxide in aqueous potassium carbonate (K_2CO_3) solutions mixed with physical solvents were measured at 298.2 and 323.2 K with a CO_2 partial-pressure range of 5 kPa to 2 MPa. 1,2-propanediol and propylene carbonate were selected as physical solvents. The aqueous solutions treated in this study were 5 mass% K_2CO_3–15 mass% 1,2-propanediol, 5 mass% K_2CO_3–30 mass% 1,2-propanediol, 5 mass% K_2CO_3–7.5 mass% propylene carbonate, and 5 mass% K_2CO_3–15 mass% propylene carbonate. The experimental solubility results were presented by the mole ratio of CO_2 and K_2CO_3 contained in the liquid mixture. The addition of 1,2-propanediol to 5 mass% K_2CO_3 solution lowered the solubility of CO_2 at constant temperature and pressure conditions within the CO_2 partial-pressure range of 5 kPa to 2 MPa. In the case of propylene carbonate, the addition of propylene carbonate increased the experimental solubilities in the region of low CO_2 partial pressures and decreased as the CO_2 partial pressure was increased above atmospheric. The solubilities of CO_2 decreased with increasing temperature in the range of 298.2 to 323.2 K.

KEY WORDS: absorption; aqueous solutions; carbon dioxide; potassium carbonate; solubility.

1. INTRODUCTION

The removal of acidic gases such as CO_2, H_2S, and COS from gas streams is a very important operation for petrochemical, oil refineries, ammonia manufacture, coal gasification, and natural gas purification plants [1]. The common techniques for the bulk removal of carbon dioxide are based on

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chemical and/or physical absorption [2]. In physical absorption, the solubilities of gases in absorbent solutions are proportional to the partial pressures of the solubilized gases in the feed. The magnitude of the heat of absorption in physical absorption is lower than that in chemical absorption. The physical absorption process can be more advantageous in the high partial-pressure region where the treated gas removal at low partial pressure is not required. On the other hand, chemical absorption is the coupling reaction between chemical absorbent and treated gas, and the resulting solubilities are mainly governed by the stoichiometric relations. Since the capacity is not highly sensitive to the gas partial pressure, it is preferable for the case where the removal to high purity is required.

Aqueous alkanolamine and potassium carbonate solutions are known to be typical chemical absorbents used for the removal of acidic gases. The use of blended alkanolamine solutions can have a combination of the merits of amines such as higher loading capacity and faster reaction rate [3]. In addition, mixed solutions of amines and physical absorbents such as sulfolane [4, 5], propylene carbonate, *N*-methylpyrrolidone [6], and methanol [7] can improve gas solubility at high-pressure conditions and save the energy requirements in the regeneration step. In particular, aqueous potassium carbonate solutions are commonly used in hot carbonate processes for bulk CO_2 removal because of their low cost, large capacity, ease of handling, and relative ease of regeneration [1]. Although several studies have been reported in the literature [8–10] for solubilities of acidic gases in K_2CO_3 solutions, they are mainly focused on the relatively high concentration range of K_2CO_3 at high temperature conditions. In our previous study [11], solubilities of CO_2 in aqueous K_2CO_3 solutions at low concentrations of K_2CO_3 and moderate temperatures were measured.

On the other hand, the present study covers the solubilities of CO_2 in aqueous K_2CO_3 solutions and K_2CO_3 solutions mixed with 1,2-propanediol and propylene carbonate at 298.2 and 333.2 K which were measured in the CO_2 partial-pressure range of 5 kPa to 2 MPa. The objective of this study is to measure the equilibrium solubilities of CO_2 at various combinations of the liquid absorbents and to investigate the effect of the physical absorbents on the solubilities by comparing with the results when only K_2CO_3 is used.

2. EXPERIMENTAL

2.1. Apparatus and Procedure

The equipment and procedure used for the solubility measurements are the same as for our previous investigation [11]. The main apparatus consists of an equilibrium cell, sampling compartment, and gas chromatograph. The equilibrium cell is made of 316 stainless steel with an internal volume of about 400 cm^3. A vapor sampling valve (Rheodyne, 7410) with a loop of about 500 μl was connected to the gas chromatograph (Young In, M600D) equipped with a thermal-conductivity detector (TCD) for the on-line measurement of the vapor sample. The column is 1.83 m length by 0.0032 m diameter and packed with Porapak Q. Most components of the apparatus are contained in a water bath except the gas circulation lines. To keep the temperature uniform in the apparatus, the lines exposed to room temperature were enclosed by heating coils.

To begin an experiment, an aqueous solution of about 250 ml was added to the equilibrium cell, and all the lines were purged with nitrogen to remove oxygen in the apparatus. After filling the compartments of apparatus with nitrogen, the system pressure was increased up to 2.5 MPa at the experimental temperature for the leak test. Next, carbon dioxide was introduced into the cell to obtain the desired partial pressure. For easy sampling of the liquid phase, nitrogen was used to maintain the system pressure above atmospheric pressure when the partial pressure of CO_2 is below atmospheric. Equilibrium was assumed when the system pressure and vapor-phase composition remained stable for, at least, 10 hours. It takes more than 24 hours to reach complete equilibrium. The analysis of the liquid samples was carried out by the titration method similar to that of Shen and Li [3]. The amount of water in the vapor phase was determined by Raoult's law. The partial pressure of CO_2 was directly calculated from the total system pressure, vapor-phase composition, and the partial pressure of water. Potassium carbonate, 1,2-propanediol, and propylene carbonate were assumed to be nonvolatile with negligible effect on the partial pressure of CO_2.

2.2. Materials

Potassium carbonate, 1,2-propanediol, and propylene carbonate were purchased from Sigma-Aldrich Chemical Co. Potassium carbonate was in anhydrous form with a minimum purity of 99.5 mol%. Water distilled in the laboratory was used. The carbon dioxide and nitrogen gases were of commercial grade with a minimum purity of 99.5 mol%.

3. RESULTS AND DISCUSSION

Since the reliability of the equilibrium apparatus and experimental procedure has already been verified in our previous study [11], test measurements were not performed. In the present work, the solubilities of

CO_2 in 5 mass% K_2CO_3–15 mass% 1,2-propanediol and 5 mass% K_2CO_3–30 mass% 1,2-propanediol aqueous solutions were measured at 298.2 and 323.2 K. The results are shown in Table I and plotted in Figs. 1 and 2 along with the solubilities in a 5 mass% K_2CO_3 aqueous solution. The CO_2 solubilities were represented by the loading, i.e., the mol of CO_2 absorbed per mol of K_2CO_3. As shown in Figs. 1 and 2, the CO_2 solubility increases with the partial pressure of CO_2 and decreases with the solution temperature. The CO_2 loading decreased gradually with an increase in the amount of 1,2-propanediol at constant temperature and pressure. The

Table I. Measured Solubility of Carbon Dioxide in Aqueous K_2CO_3–1,2-Propanediol Solutions

Mixture	T (K)	P_{CO_2} (kPa)	loading (mol of CO_2/mol of K_2CO_3)
5 mass% K_2CO_3–15 mass% 1,2-propanediol	298.2	6.16	0.774
		12.70	0.840
		29.97	0.810
		31.02	0.881
		133.0	1.049
		420.4	1.163
		854.0	1.424
		1283	1.579
	323.2	6.50	0.694
		19.51	0.782
		41.90	0.825
		42.11	0.832
		131.8	0.944
		472.3	1.053
		1180	1.285
5 mass% K_2CO_3–30 mass% 1,2-propanediol	298.2	6.31	0.730
		17.36	0.765
		45.61	0.849
		129.0	0.920
		428.1	1.075
		1053	1.313
		1346	1.442
	323.2	3.19	0.585
		20.25	0.708
		47.15	0.815
		127.6	0.888
		470.9	1.011
		1306	1.203

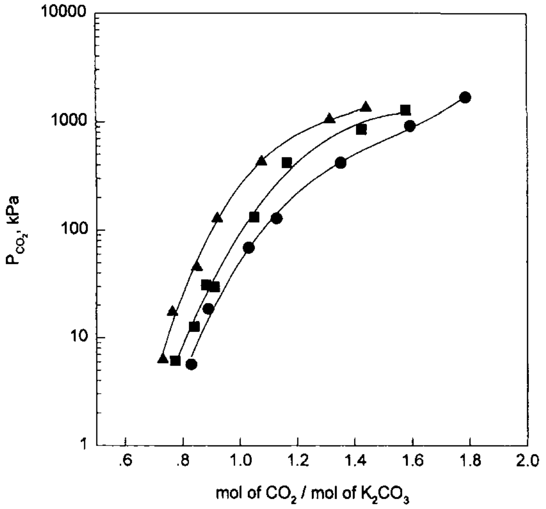

Fig. 1. Solubilities of carbon dioxide in aqueous 5 mass% K_2CO_3–1,2-propanediol solutions at 298.2 K: (●) 5 mass% K_2CO_3; (■) 5 mass% K_2CO_3–15 mass% 1,2-propanediol; (▲) 5 mass% K_2CO_3–30 mass% 1,2-propanediol.

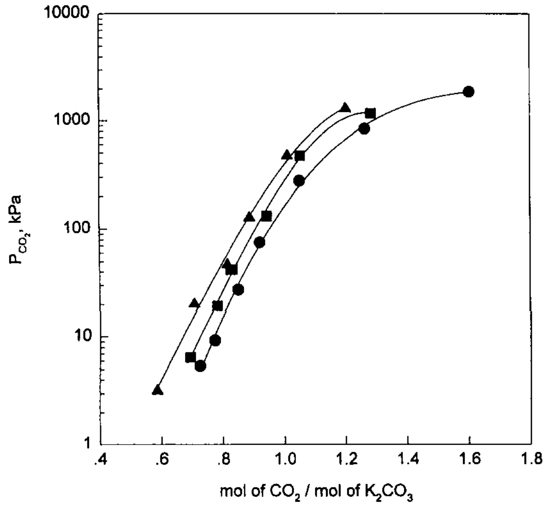

Fig. 2. Solubilities of carbon dioxide in aqueous 5 mass% K_2CO_3–1,2-propanediol solutions at 323.2 K: (●) 5 mass% K_2CO_3; (■) 5 mass% K_2CO_3–15 mass% 1,2-propanediol; (▲) 5 mass% K_2CO_3–30 mass% 1,2-propanediol.

solubility of CO_2 in 5 mass% K_2CO_3–7.5 mass% propylene carbonate and 5 mass% K_2CO_3–15 mass% propylene carbonate aqueous solutions was also measured at 298.2 and 323.2 K in order to examine the absorption efficiency of propylene carbonate. These data are reported in Table II and graphically compared with the results for a 5 mass% K_2CO_3 aqueous solution in Figs. 3 and 4. The CO_2 solubilities increase as the mass% of propylene carbonate increases below atmospheric pressure (100 kPa) at 298.2 and 323.2 K, while, above 100 kPa, the CO_2 solubilities decrease with

Table II. Measured Solubility of Carbon Dioxide in Aqueous K_2CO_3–Propylene Carbonate Solutions

Mixture	T (K)	P_{CO_2} (kPa)	loading (mol of CO_2/mol of K_2CO_3)
5 mass% K_2CO_3–7.5 mass% propylene carbonate	298.2	7.57	0.881
		31.24	0.979
		87.36	1.097
		31.02	0.881
		325.4	1.244
		759.5	1.388
		1627	1.651
	323.2	5.41	0.747
		16.22	0.845
		55.98	0.936
		153.4	1.017
		670.4	1.178
		1544	1.326
5 mass% K_2CO_3–15 mass% propylene carbonate	298.2	6.61	0.928
		13.38	0.971
		38.98	1.076
		418.3	1.202
		430.7	1.225
		1002	1.370
		1031	1.403
		1609	1.640
		2000	1.800
	323.2	6.38	0.783
		13.36	0.874
		50.00	0.971
		192.3	1.027
		760.3	1.153
		1008	1.223
		1838	1.358

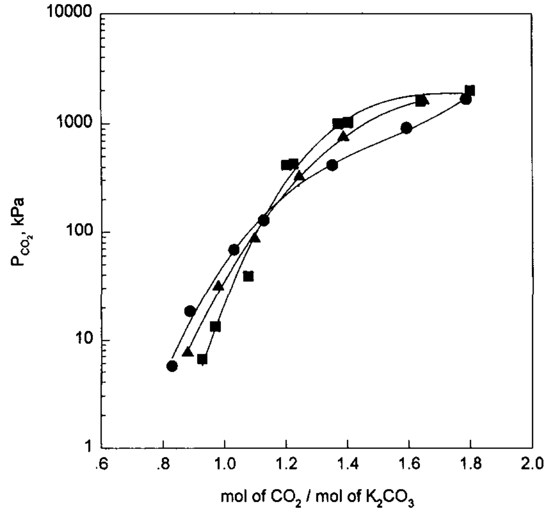

Fig. 3. Solubilities of carbon dioxide in aqueous 5 mass% K_2CO_3–propylene carbonate solutions at 298.2 K: (●) 5 mass% K_2CO_3; (▲) 5 mass% K_2CO_3–7.5 mass% propylene carbonate; (■) 5 mass% K_2CO_3–15 mass% propylene carbonate.

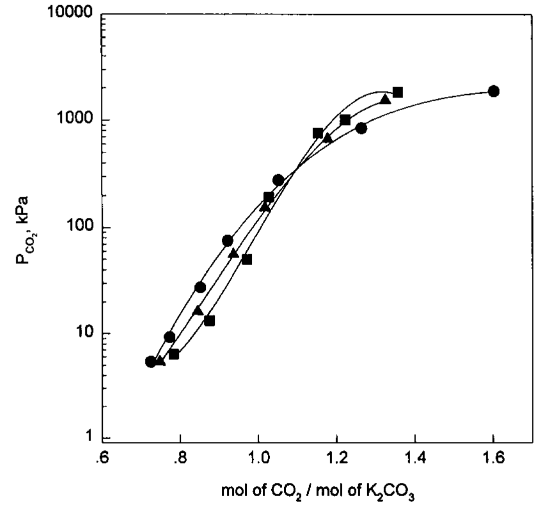

Fig. 4. Solubilities of carbon dioxide in aqueous 5 mass% K_2CO_3–propylene carbonate solutions at 323.2 K: (●) 5 mass% K_2CO_3; (▲) 5 mass% K_2CO_3–7.5 mass% propylene carbonate; (■) 5 mass% K_2CO_3–15 mass% propylene carbonate.

an increase in the propylene carbonate mass%. Due to a solubility limit, the experiment could not be extended to higher concentrations of propylene carbonate.

4. CONCLUSION

The equilibrium solubilities of CO_2 in aqueous K_2CO_3–1,2-propanediol and K_2CO_3–propylene carbonate solutions were measured at 298.2 and 323.2 K. The loadings of CO_2 decrease with increasing temperature from 298.2 to 323.2 K. The addition of 1,2-propanediol to 5 mass% K_2CO_3 solution lowers the solubility of CO_2 at a constant temperature and pressure within the CO_2 partial-pressure range of 5 kPa to 2 MPa. The CO_2 solubility increases with the mass% of propylene carbonate below 100 kPa, while it decreases above 100 kPa at constant temperature and pressure.

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