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Solubility of Carbon Dioxide in Propylene Carbonate at Elevated Pressures and Higher than Ambient Temperatures

Phillip D. Mantor,[†] **Osmar Abib, Jr.,**[‡] **Kyoo Y. Song, and Riki Kobayashi***

Chemical Engineering Department, Rice University, Houston, Texas 77001

Solubility data of carbon dioxide in propylene carbonate at pressures ranging from 13.6 to 68 atm (200–1000 psia) and at temperatures from 26.7 to 104.4 °C (80–220 °F) are presented. The Krichevsky–Kasarnovsky solubility equation, which has been known to work well with a very dilute system, also predicted solubility well at substantial finite concentrations, in excellent agreement with the experimental data to an average accuracy of 1.09% with a maximum deviation of 2.7%. The Henry's law constants obtained from the current data through extremely low pressure extrapolation showed good agreement with literature values and were used in the prediction of solubility of carbon dioxide. Values of the constants are 81.7 atm at 80 °F, 103.5 atm at 100 °F, 159.4 atm at 160 °F, and 227.8 atm at 220 °F. An attempt has been made to predict the solubility of carbon dioxide in propylene carbonate by using the Krichevsky–Ilinskaya (K–I) equation, which contains a liquid-phase activity coefficient. However, the equation did not improve the predictions.

Introduction

Application of propylene carbonate at elevated pressures and at higher than ambient temperatures as a carbon dioxide absorbing agent is common practice in the sweetening process of natural gas. The absorbing agent may perform a rather important role in the treatment of carbon dioxide rich gas for the enhanced oil recovery process. However, the solubility data for carbon dioxide in propylene carbonate at possible design conditions are very limited.

This study was conducted to determine the solubility of gaseous carbon dioxide in propylene carbonate at 80 °F and of supercritical carbon dioxide in the same solvent at temperatures of 100, 160, and 220 °F and to provide a correlation of the data.

Experimental Section

Apparatus. The experimental equipment, consisting of an equilibrium cell, a pressure maintenance arrangement, and an analytical train, is, in principle, the same as the design described by Kobayashi (*3*). Figure 1 shows a schematic diagram of the experimental apparatus.

The equilibrium apparatus consisting of a high-pressure windowed cell rated to hold pressures up to 10 000 psia was mounted in a constant-temperature air bath. The gas charge line was connected to the top of the cell, and the liquid sampling line was drawn from the bottom of the cell. Constant temperature was maintained within ±0.1 °F in the bath by electrical heating coils installed in the circulated air. The temperature of the cell was measured by a thermocouple connected to a Leeds and Northrup precision portable potentiometer. Cell pressure was measured by a calibrated 2000-psi Heise gauge with 2-psi subdivisions.

A gas cylinder, a gas reservoir, and a mercury displacement pump were used for the pressure maintenance scheme, and also to charge the cell with gas at pressures greater than that in the gas cylinder.

The analytical train consists of a buret used as a flash chamber for the liquid phase, a drying tube to remove foreign matter from the flash gas, a manometer to measure the sample pressure, and a flask of predetermined volume into which the flash gas expanded. A three-way stopcock at the top of the flask was used to evacuate the system. The tubing connections were made with India rubber tubing impregnated with paraffin wax.

Reagents. Carbon dioxide of a purity of 99.6 mol % was purchased from the Spencer Chemical Co. The propylene carbonate was obtained from the Jefferson Chemical Co. with a minimum purity of 99 wt %. The densities of the carbon dioxide and the propylene carbonate at 25 °C and 1 atm were 0.001 808 and 1.190 g/cm^3, respectively, as given in ref *4* and *5*.

Procedure. The cell was charged initially with propylene carbonate. The cell was agitated while it was charged with carbon dioxide. After a period when there was no further pressure drop with time, the cylinder valve was closed and the system further agitated for at least 1 h at constant temperature. The system was allowed to sit for at least 2 h at the same constant temperature before sampling.

The sampling tube was flushed with about 5 cm^3 of the equilibrium liquid in the cell into a beaker. Then, the tube was connected to the analytical train. The analytical train was evacuated and allowed to sit for 5 min to check for any leak. The valve on the sampling tube was opened to allow liquid sample to pass into the buret. When about 10 cm^3 of flush liquid was collected in the buret, the valve was closed. The

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[†] Present address: Hamilton International Oil Co., Denver, CO 80202.
[‡] Present address: Arco Oil and Gas Co., Dallas, TX 75221.

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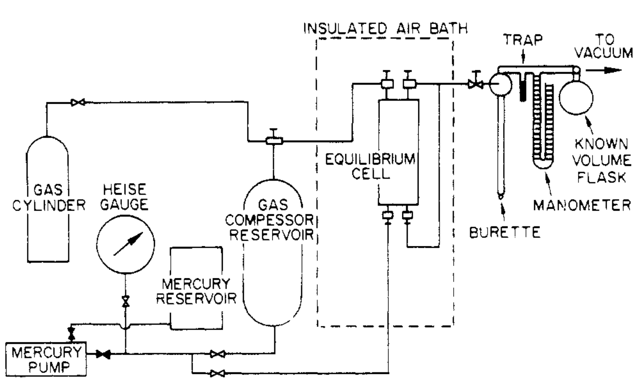

Figure 1. Schematic diagram of the experimental apparatus.

Table I. Experimental and Predicted Solubility of Carbon Dioxide in Propylene Carbonate

T, °C/°F	P, atm/psia	solubility[a]	mole fraction exptl	mole fraction predicted	deviations,[b] %
26.7/80	54.8/805	405.9	0.588	0.579	1.53
	54.5/799	387.7	0.577	0.569	1.39
	53.5/787	376.5	0.570	0.565	0.88
	43.6/641	268.5	0.486	0.485	0.21
	31.9/469	159.3	0.359	0.357	0.56
	19.4/285	85.8	0.232	0.231	0.43
37.8/100	59.7/877	278.8	0.495	0.488	1.41
	53.9/793	235.7	0.454	0.488	1.32
	43.7/642	171.7	0.377	0.376	0.27
	33.3/489	121.3	0.299	0.297	0.67
	22.8/335	76.1	0.211	0.210	0.47
71.1/160	68.1/1001	153.9	0.352	0.346	1.70
	60.2/885	133.6	0.320	0.314	1.88
	48.8/717	98.0	0.257	0.250	2.72
	29.0/573	77.9	0.215	0.214	0.47
	29.6/435	58.4	0.171	0.171	0.0
104.4/220	60.9/895	82.9	0.226	0.220	2.66
	46.6/685	63.2	0.182	0.178	2.20
	21.2/311	28.1	0.090	0.090	0.0
					av = 1.09

[a] Volume of gas/volume of liquid, at 25 °C and 1 atm.
[b] 100(exptl – predicted)/exptl.

volume of liquid and the cell pressure were recorded. The equilibrium temperature was maintained constant as more data were taken at decreasing pressures with agitation and settling allowed at each new equilibrium pressure.

To determine the gaseous composition, we connected the sampling tube to the top of the cell, and the mercury pump to the bottom of the cell. The cell was filled with liquid and gas and brought to equilibrium. The sampling valve was opened to allow the gas sample to flow into a series of two absorption chambers (not shown in the diagram) containing distilled water to absorb propylene carbonate.

The gas from the second chamber was expanded to a flask of predetermined volume. In the course of sampling, the cell pressure was maintained constant by injecting mercury into the bottom of the cell. The manometer and barometric pressure gave the gas pressure. The amount of propylene carbonate dissolved in the absorption chamber was determined by a titrimetric method developed by Jefferson Chemical Co. (*8*). Each measurement required approximately 45 min. The analysis showed that the composition of propylene was always less than 0.001 mole fraction.

Experimental Results

The experimental solubility data for carbon dioxide in propylene carbonate at 80, 100, 160, and 220 °F and at various pressures up to 1000 psia are given in Table I. Under the conditions at which the data are presented, carbon dioxide was in the gaseous or supercritical state.

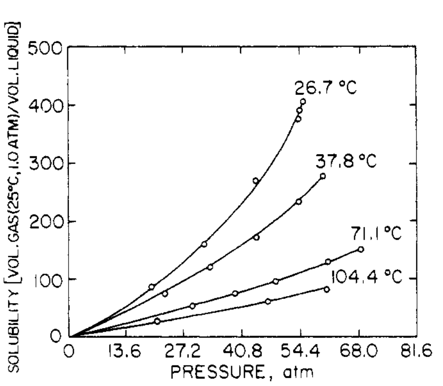

Figure 2. Isothermal solubility of carbon dioxide in propylene carbonate vs. pressure.

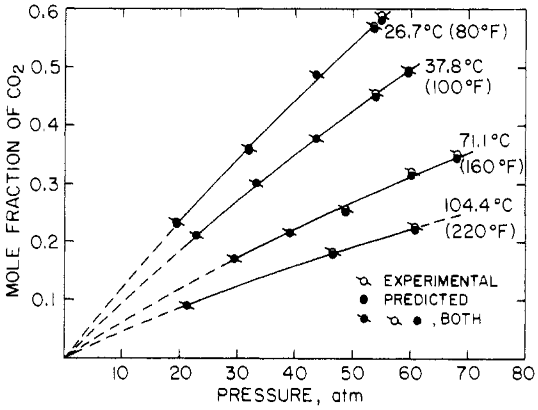

Figure 3. Mole fraction of carbon dioxide in propylene carbonate vs. pressure.

The solubility and the liquid-phase composition of carbon dioxide in propylene carbonate vs. pressure are shown in Figures 2 and 3, respectively.

Discussion

General Information. The carbon dioxide was supercritical at all experimental temperatures studied except for the 80 °F isotherm. The solubility of carbon dioxide in propylene carbonate is moderately high, ranging up to 58.8 mol % CO_2 in the liquid phase at 80 °F and 805 psia. At higher temperatures and lower pressures the solubility drops significantly to a low value of 9 mol % CO_2 in the liquid phase at 220 °F and 311 psia.

Correlation with the Krichevsky-Kasarnovsky Equation. The experimental data were used to derive the constants for the Krichevsky-Kasarnovsky solubility equation (*2*):

$$\log (f^\circ_{v_1}/x_1) = \log K_1 + \bar{V}_1(P - P_2)/(2.303RT)$$

where $f^\circ_{v_1}$ = the fugacity of pure carbon dioxide in the vapor, x_1 = the mole fraction of carbon dioxide in the liquid, K_1 = the Henry's law constant, $\bar{V}_1$ = the partial molar volume of carbon dioxide in the liquid, P = the system pressure, P_2 = the pure propylene carbonate vapor pressure (usually negligible), R = the gas constant, and T = the absolute temperature of the system.

The plot of values of log $(f^\circ_{v_1}/x_1)$ vs. $(P - P_2)/(2.303RT)$ showed high linearity, indicating constant values for the intercept and the slope at various temperatures. The intercept at P_2, when the vapor pressure of propylene carbonate is negligibly low, is equal to the Henry's law constant. The slopes (equal to $\bar{V}_1$) were negative, probably the results of interstitial solubility plus strong attraction effects, leading to system volume contraction due to the dissolution of carbon dioxide. (Obviously,

Table II. Henry's Law Constants and Partial Molar Volumes of Carbon Dioxide in Propylene Carbonate

T, °C/°F	Henry's law constant, atm	partial molar vol, cm^3/(g-mol)
25/77	81.13, 82.80[c]	
26.7/80	81.7	−0.067 86
37.8/100	101.7	−0.047 62
40/104	103.5, 116.5,[a] 112.7[b]	
50/122	120.8, 123.1[c]	
70/158	166.0[b]	
71.1/160	159.4	−0.010 00
75/167	169.8	
100/212	222.3, 220.6,[c] 265,[a] 257.3[b]	
104.4/220	227.8	0.022 73

[a] Reference 1. [b] Reference 7. [c] Reference 6.

precise $P-V-T$ measurements are in order.)

The values obtained for log K_1 and $\bar{V}_1$, when used in the Krichevsky-Kasarnovsky equation to predict the carbon dioxide concentration in the liquid phase, showed excellent agreement with the experimental results, as shown in Table I. The Krichevsky-Kasarnovsky equation, known to apply well to infinitely dilute systems, has been proved to predict accurately the solubility of carbon dioxide in propylene carbonate with an average deviation of 1.09% and a maximum deviation of 2.7% as shown in Table I. Figure 3 shows the comparison of experimental measurements with the predictions.

The Henry's law constants, determined from the high-pressure data by extrapolating to solvent vapor pressure which is negligibly low, show good agreement with literature values. They are given in Table II.

An attempt to predict the carbon dioxide solubility in propylene carbonate has been made by using the Krichevsky-Ilinskaya equation (*9*). In the use of this equation, the deviations between the experimental data and the prediction obtained from the Krichevsky-Kasarnovsky equation were determined. The calculated deviations were utilized to fit the constant for a two-suffix Margules equation at a constant temperature for different pressures. The average value of the constant for that temperature was substituted into the Krichevsky-Ilinskaya equation to predict carbon dioxide mole fraction using the same values of Henry's law constant and partial molar volume for the temperature and pressure. The calculations showed that the extra parameters of the K-I equation did not improve the predictions and gave rather scattered values on the carbon dioxide solubility in propylene carbonate.

From the current study, we concluded that the Krichevsky-Kasarnovsky equation is the preferred equation to predict carbon dioxide solubility in propylene carbonate.

Glossary

f	fugacity, atm
K	Henry's law constant, atm
P	pressure, atm
R	gas constant
T	temperature, K
$\bar{V}$	partial molar volume, cm^3/(g-mol)
x	mole fraction in liquid phase

Subscripts

1	component 1, carbon dioxide
2	component 2, propylene carbonate
v_1	vapor state of component 1

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