

Vapor–Liquid Equilibrium in the Carbon Dioxide–Propylene Carbonate System at High Pressures

Laurie L. Williams, Eric M. Mas, and James B. Rubin*

Los Alamos National Laboratory, MS E574, Los Alamos, New Mexico 87545

Vapor–liquid equilibrium data (P , T , x , y) for the binary mixture of carbon dioxide + propylene carbonate were measured on four isotherms from 298.15 K to 373.15 K and at pressures ranging from 41.4 to 206.8 bar (600–3000 psi). Comparisons are made between experimental results and calculations of the Soave–Redlich–Kwong (SRK) cubic equation of state with three interaction parameters. The experimental data of other ester compounds are also modeled with the SRK equation, and the interaction parameters are presented.

Introduction

Carbon dioxide is a prospective solvent for supercritical fluid separation applications. Because of its nontoxicity and low critical temperature, it is currently used for extracting natural materials, mainly in the food and pharmaceutical industries. Utilization of CO_2 in applications involving polar, acidic, or basic materials may require the addition of miscible cosolvents. The concept of adding cosolvents, also known as modifiers or entrainers, is an increasingly common technique for manipulating the polarity or acid–base characteristics of supercritical CO_2 .

Propylene carbonate (CAS registry no. 108-32-7) is a cyclic ester that has been used as a supercritical CO_2 modifier in research applications at the Los Alamos National Laboratory. For the optimal design of a supercritical solvent mixture system, knowledge of the phase behavior in the critical region is necessary. Existing vapor–liquid equilibrium (VLE) data for mixtures of carbon dioxide with propylene carbonate at high pressure are limited, and no data are available for the CO_2 -rich vapor phase.

Phase behavior, especially vapor–liquid equilibria, is important in the design, development, and operation of supercritical fluid separation processes. This paper presents carbon dioxide + propylene carbonate vapor–liquid equilibrium data at pressures higher than those previously reported in the literature and includes both the vapor- and liquid-phase data. Modeling of the experimental data was carried out using the Soave–Redlich–Kwong (SRK) cubic equation of state.

Experimental Section

Apparatus. The experimental apparatus used for the vapor–liquid equilibrium measurements is shown in Figure 1. The apparatus consists of a 725 cm³ stainless steel cell equipped with vapor and liquid sampling lines and a pressure measurement line. The cell was placed inside a constant temperature liquid bath. The pressure was measured with a 3D Instruments precision pressure gauge with an estimated accuracy of $\pm 0.25\%$. A calibrated platinum resistance thermometer was placed into a thermowell in the cell for temperature measurement. The platinum

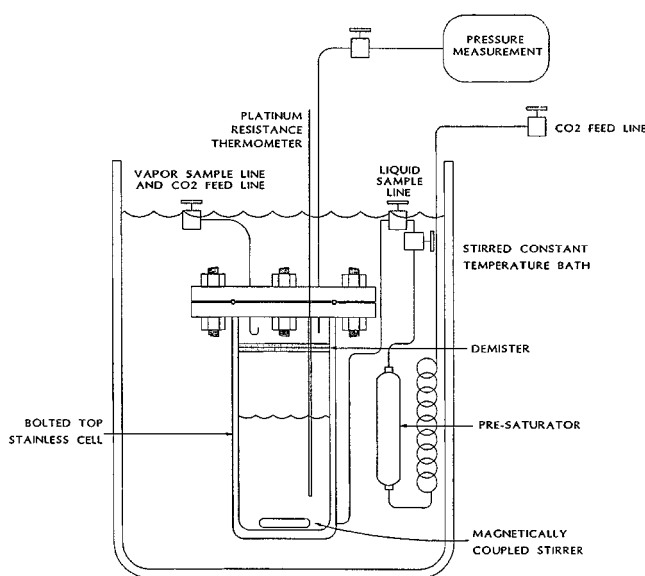


Figure 1. Bolted-top PT_{xy} apparatus.

thermometer was calibrated using ice and steam points and was referenced to a NIST traceable standard resistance thermometer. Temperatures were measured with an accuracy of ± 0.025 °C.

Procedure. A run was initiated by evacuating the equilibrium cell and then purging it with instrument grade CO_2 . The cell was again evacuated and purged with CO_2 . This procedure was repeated a third time, and the cell was charged with a known amount of liquid propylene carbonate. The bath was controlled at the run temperature, and the cell contents were allowed to reach thermal equilibrium. CO_2 was then added to the cell with a positive displacement syringe pump until the desired equilibrium system pressure was reached.

After achieving equilibrium at the appropriate temperature and pressure, several vapor samples were withdrawn into weighed, evacuated receiving cylinders. Samples ranging in size from 10 to 80 g were taken depending on the amount of propylene carbonate in the samples. CO_2 was added through the liquid line into the cell in order to maintain the system pressure to within ± 0.34 bar (5 psi)

* To whom correspondence should be addressed. E-mail: jbr@lanl.gov.

of the desired value while sampling the vapor. The added CO₂ entered the equilibrium cell at approximately the same concentration as that of the vapor that was being removed from the cell. This CO₂ was then bubbled through the saturated liquid in the cell before entering the vapor space. A similar procedure was used to sample the liquid phase.

The sample cylinders (connected to the liquid or vapor sample lines in Figure 1) were placed in ice water, and the CO₂ in the samples was slowly vented from the cylinders. The CO₂ exiting the sample cylinders passed through a sample train that consisted of two 30 cm³ test tubes in series (not shown). This was done to capture any propylene carbonate that may have exited the cylinder with the CO₂. These tubes were carefully weighed before and after venting the CO₂. The cylinders were then attached to a vacuum pump and evacuated for about 5 min while the cylinder remained in ice water. The cylinder was then carefully cleaned, dried, and weighed to determine the amount of propylene carbonate in the cylinder. The weight percent propylene carbonate was then calculated from the mass of the sample and the mass of the propylene carbonate that remained in the cylinder after removing all of the CO₂.

A second analytical technique was used for determining the concentration in some of the vapor samples that contained very little propylene carbonate. The CO₂ from the sample cylinders was removed as described above, and a small amount of toluene was weighed into each sample cylinder. The cylinders were shaken vigorously to solubilize all of the propylene carbonate into the added toluene. Multiple aliquots of this liquid were then withdrawn from the cylinder and analyzed by gas chromatography (GC). The mass of propylene carbonate in each sample was determined by the GC analyses, and the weight percent propylene carbonate was determined from the mass of propylene carbonate and the total mass of the sample. This GC technique was used for propylene carbonate compositions of less than about 0.1 wt % propylene carbonate.

The estimated uncertainty in the reported vapor-phase compositions below 0.1 wt % propylene carbonate is ±10%. This uncertainty decreases to about ±5% of the reported propylene carbonate concentration for the remaining vapor analysis results. The uncertainty in each reported liquid composition is estimated to be within ±1% of the reported propylene carbonate concentration on a weight basis.

Materials. The propylene carbonate used was obtained from Aldrich Chemical with a specified minimum purity of 99.92%. The carbon dioxide used was instrument grade obtained from US Welding and had a specified purity of 99.99%.

Results and Analysis

Isothermal vapor–liquid equilibrium data were measured at 298.15 K, 308.15 K, 333.15 K, and 373.15 K over a pressure range from 41 to 206.8 bar. The results are listed in Table 1, where x_2 and y_2 are the mole fractions of carbon dioxide in the liquid phase and vapor phase, respectively.

The phase equilibrium data obtained were modeled using the Soave–Redlich–Kwong (SRK) equation of state. The SRK equation of state has a relatively simple form and is widely used in engineering calculations of fluid phase equilibria.¹

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)} \quad (1)$$

Table 1. Experimental Vapor–Liquid Equilibrium Data for Propylene Carbonate (1)–Carbon Dioxide (2) Mixtures

<i>T</i> /K	<i>P</i> /bar	x_2	y_2	<i>T</i> /K	<i>P</i> /bar	x_2	y_2
298.15	41.37	0.4373	0.999 986	333.15	137.90	0.6161	0.993 943
298.15	61.24	0.7091	0.999 890	333.15	172.37	0.6737	0.985 220
308.15	55.16	0.4788	0.999 951	333.15	206.84	0.7318	0.972 790
308.15	82.74	0.6774	0.993 807	373.15	55.16	0.2122	0.999 532
308.15	110.32	0.7234	0.986 651	373.15	82.74	0.2989	0.999 169
308.15	137.90	0.7608	0.982 810	373.15	110.32	0.3720	0.998 521
333.15	55.16	0.3313	0.999 898	373.15	137.90	0.4366	0.997 762
333.15	82.74	0.4577	0.999 576	373.15	172.37	0.5043	0.995 416
333.15	110.32	0.5558	0.998 546	373.15	206.84	0.5559	0.991 521

Table 2. Critical Properties and Acentric Factors of Pure Components

component	<i>T</i> _c /K	<i>P</i> _c /bar	ω
propylene carbonate	625.15 ³	57.05 ³	0.707
carbon dioxide ⁴	304.1	73.8	0.239

Table 3. Antoine Coefficients–Propylene Carbonate

<i>A</i>	<i>B</i>	<i>C</i>
9.6179	4097.7	184.78

where the parameters $a(T)$ and b are determined from pure component properties and with appropriate mixing rules. Cubic equations of state often utilize van der Waals mixing rules for mixtures; however, in this paper the mixing rules developed by Kwak and Mansoori² have been used. The temperature-dependent parameter $a(T)$ is replaced by the temperature-independent parameters c and d , which are obtained from an expansion of $a(T)$ in terms of RT .

$$a(T) = c + dRT - 2\sqrt{cdRT} \quad (2)$$

The parameters of the mixture are then evaluated from

$$b = \sum_i^n \sum_j^n x_i x_j (1 - k_{ij}) \left[\frac{(b_i^{1/3} + b_j^{1/3})^3}{2} \right] \quad (3)$$

$$c = \sum_i^n \sum_j^n x_i x_j (1 - l_{ij}) \sqrt{c_i c_j} \quad (4)$$

$$d = \sum_i^n \sum_j^n x_i x_j (1 - m_{ij}) \left[\frac{(d_i^{1/3} + d_j^{1/3})^3}{2} \right] \quad (5)$$

Details of the data reduction and use of the mixing rules can be found in the Supporting Information. The critical constants, T_c and P_c , and the acentric factor, ω , of the pure components are summarized in Table 2. The acentric factor for propylene carbonate was calculated using the method presented in ref 4 and the following Antoine vapor pressure equation.

$$\ln P_{vp} = A - \frac{B}{(T + C)} \quad (6)$$

where P_{vp} is the vapor pressure in bar, T is the temperature in degrees Celsius, and the Antoine coefficients, obtained from and experimentally verified by Huntsman Corporation, are presented in Table 3.

The values for k_{ij} , l_{ij} , and m_{ij} were evaluated by a weighted least-squares fit. The weighting was determined

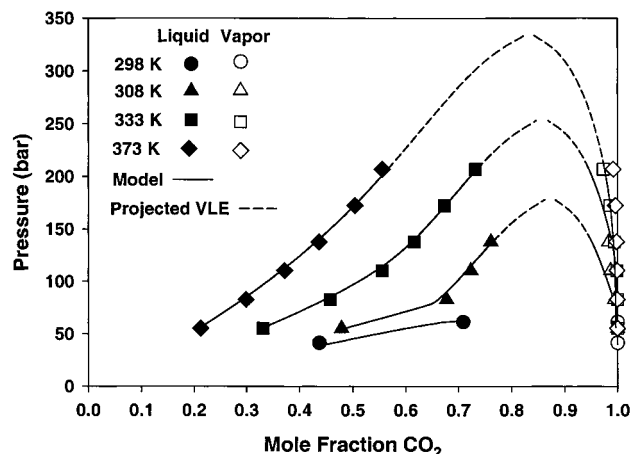


Figure 2. Propylene carbonate-CO₂ VLE.

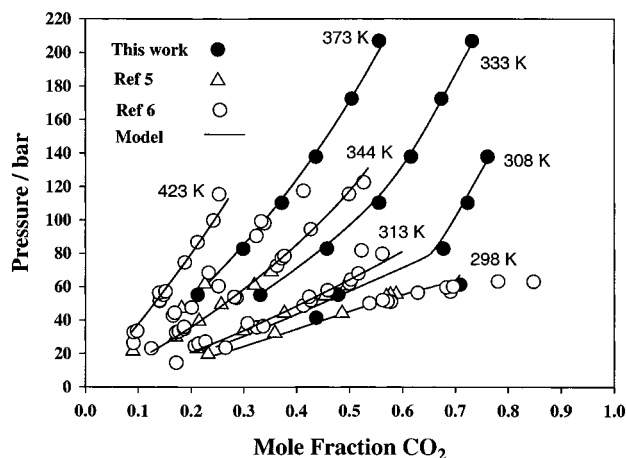


Figure 3. Comparison of high-pressure propylene carbonate-CO₂ VLE.

on the basis of the experimental uncertainties in the liquid and vapor mole fractions.

$$\min(S) = \sum \left[\frac{(y_{\text{exp}} - y_{\text{calc}})^2}{(\sigma_y)^2} \right] + \sum \left[\frac{(x_{\text{exp}} - x_{\text{calc}})^2}{(\sigma_x)^2} \right] \quad (7)$$

where σ_y is the experimental uncertainty in the vapor mole

fraction and σ_x is the experimental uncertainty in the liquid mole fraction.

The values obtained for the three binary fitting parameters are $k_{ij} = -0.037$, $l_{ij} = -0.114$, and $m_{ij} = -0.067$. The results of the correlation are shown in Figure 2. The solid lines represent the isotherms calculated using the interaction parameters k_{ij} , l_{ij} , and m_{ij} obtained from the correlation. The dashed lines represent the projected VLE predicted by the described model and using the presented interaction parameters. It can be seen that the agreement between the experimental and calculated values is quite good for both the liquid and vapor phases, especially at higher temperatures.

The open symbols in Figure 3 show the highest pressure VLE data available for the propylene carbonate-carbon dioxide system, in the literature, compared to the current experimental data (closed symbols). It can be seen that the current data extend the pressure range previously reported. Where experiments were conducted at the same temperature, agreement is noted between the data presented here and VLE data published elsewhere. All the propylene carbonate + carbon dioxide VLE data (this work as well as refs 5 and 6) were modeled using the interaction parameters k_{ij} , l_{ij} , and m_{ij} mentioned above, and the results of the liquid equilibrium correlation are represented by the solid lines in Figure 3. Only isotherms at 298 K and above have been modeled, and again, good agreement is seen between the experimental and calculated values.

A similar modeling procedure was carried out for published vapor-liquid equilibrium data for carbon dioxide and various esters. As in the previous analysis, the correlation utilized three interaction parameters and minimized the difference between the experimental CO₂-ester mole fractions and the calculated mole fractions. These parameter values and the source of the experimental CO₂-ester VLE data are shown in Table 4.

Conclusions

Our results show that the vapor-liquid equilibrium in the system propylene carbonate + carbon dioxide is well represented by the SRK equation of state with three interaction parameters, especially at higher temperatures. It can be seen from Table 4 that this correlation also accurately models other CO₂-ester VLE data.

Table 4. SRK Model for Binary Mixtures-Carbon Dioxide + Component 1

component 1	chemical formula	no. of data points	<i>T</i> /K	<i>P</i> /bar	ref	k_{ij}	l_{ij}	m_{ij}	σ_x , avg % error	σ_y , avg % error
methyl acetate	CH ₃ COOCH ₃	22	298.15-313.15	6.5-80	7	-0.179	-0.035	0.136	0.009, 1.9%	0.011, 0.7%
ethyl acetate	CH ₃ CH ₂ COOCH ₃	42	303.15-323.15	20-90	8-10	-0.353	-0.208	0.035	0.013, 1.5%	0.004, 0.3%
propyl acetate	CH ₃ (CH ₂) ₂ COOCH ₃	56	303.15-323.15	20-92	11	-0.331	-0.144	0.125	0.012, 1.3%	0.002, 0.1%
ethyl propanoate	CH ₃ CH ₂ COOCH ₂ CH ₃	74	303.15-323.15	17-92	12	-0.249	-0.108	-0.101	0.012, 1.3%	0.002, 0.1%
methyl myristate	CH ₃ (CH ₂) ₁₂ COOCH ₃	17	313.15-343.15	72-160	13	-0.391	0.101	0.300	0.009, 0.9%	0.003, 0.2%
methyl palmitate	CH ₃ (CH ₂) ₁₄ COOCH ₃	25	313.15-343.15	62-183	13	-0.453	0.030	0.501	0.006, 0.5%	0.003, 0.2%
methyl oleate	CH ₃ (CH ₂) ₇ (CH)=CH(CH ₂) ₇ COOH ₃	25	313.15-343.15	72-200	13	-0.448	0.043	0.536	0.008, 0.6%	0.004, 0.3%
methyl stearate	CH ₃ (CH ₂) ₁₆ COOCH ₃	22	313.15-343.15	60-198	13	-0.473	-0.001	0.495	0.008, 0.8%	0.002, 0.1%
propylene carbonate	CH ₃ CHCH ₂ OCCO	18	298.15-373.15	41-207	^a	-0.037	-0.114	-0.067	0.011, 1.6%	0.013, 0.8%

^a This work.

Acknowledgment

The authors thank Huntsman Corporation for providing the funding to obtain the data from the Weltec Research Company, Inc., which were used in this study.

Supporting Information Available:

Additional text detailing the Soave–Redlich–Kwong equation of state, mixing rules, and model equations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Soave, G. Equilibrium Constants From a Modified Redlich-Kwong Equation of State. *Chem. Eng. Sci.* **1972**, *27*, 1197–1203.
- (2) Kwak, T. Y.; Mansoori, G.; van der Waals, A. Mixing Rules For Cubic Equations of State. Applications For Supercritical Fluid Extraction Modeling. *Chem. Eng. Sci.* **1986**, *41*, 1303–1309.
- (3) Page, S. H.; Raynie, D. E.; Goates, S. R.; Lee, M. L. Predictability and Effect of Phase Behavior of CO₂/Propylene Carbonate in Supercritical Fluid Chromatography. *J. Microcolumn Sep.* **1991**, *3*, 355–369.
- (4) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed; McGraw-Hill: New York, 1987.
- (5) Mantor, P. D.; Abib, O.; Song, K. Y.; Kobayashi, R. Solubility of Carbon Dioxide in Propylene Carbonate at Elevated Pressures and Higher than Ambient Temperature. *J. Chem. Eng. Data* **1982**, *27*, 243–245.
- (6) Zubchenko, Y. P.; Shakhova, S. F.; Wei, T.; Titelman, L. I.; Kaplan, L. K. Phase Equilibria and Volume Relationships in the System Propylene Carbonate-Carbon Dioxide. *Zh. Prikl. Khim.* **1971**, *44*, 2044–2047.
- (7) Ohgaki, K.; Katayama, T. J. Isothermal Vapor-Liquid Equilibria for Systems Ethyl Ether-Carbon Dioxide and Methyl Acetate-Carbon Dioxide at High Pressures. *J. Chem. Eng. Data* **1975**, *20*, 264–267.
- (8) Wagner, Z.; Pavlicek, J. Vapor-Liquid Equilibrium in the Carbon Dioxide-Ethyl Acetate System at High Pressure. *Fluid Phase Equilib.* **1994**, *97*, 119–126.
- (9) Chrisochoou, A.; Schaber, K.; Bolz, U. Phase Equilibria for Enzyme-Catalyzed Reactions in Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **1995**, *108*, 1–14.
- (10) Vazquez, da Silva, M.; Barbosa, D.; Ferreira, P. O.; Mendonca, J. High-Pressure Phase Equilibrium Data for the Systems Carbon Dioxide/Ethyl Acetate and Carbon Dioxide/Isoamyl Acetate at 295.2, 303.2, and 313.2 K. *Fluid Phase Equilib.* **2000**, *175*, 193–33.
- (11) Wagner, Z. Vapor-Liquid at High Pressure in the System Containing Carbon Dioxide and Propyl Acetate. *Fluid Phase Equilib.* **1995**, *110*, 175–182.
- (12) Wagner, Z. Vapor-Liquid in the Carbon Dioxide–Ethyl Propanoate System at Pressures from 2 to 9 MPa and Temperatures from 303 to 323K. *Fluid Phase Equilib.* **1995**, *112*, 125–129.
- (13) Inomata, H.; Kondo, T.; Hirohama, S.; Arai, K. Vapor-Liquid Equilibria for Binary Mixtures of Carbon Dioxide and Fatty Acid Methyl Esters. *Fluid Phase Equilib.* **1989**, *46*, 41–52.

Received for review May 14, 2001. Accepted December 13, 2001.

JE010151X