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Measurement and Modeling of the High-Pressure Phase Behavior of the Carbon Dioxide + Propene Oxide Binary System

Jia-Jun Wang, Jin-Tang Duan, Long Wang, Xue-Ping Gu, and Lian-Fang Feng*

State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University,
Hangzhou 310027, P. R. China

The phase equilibrium of the binary system carbon dioxide + propene oxide has been determined for carbon dioxide mole fractions from 0.1 to 0.7 and temperatures from (303.2 to 353.2) K. The experimental measurements of bubble points were carried out in an experimental device incorporating a moveable piston and a vision window. A good description of the phase behavior in a wide range of temperatures with the Peng−Robinson equation of state using the one-parameter conventional van der Waals mixing rule has been obtained, on the basis of measured data and literature data for the carbon dioxide + propene oxide system. The binary interaction parameter k_{ij} has been optimized to match experimental data at each temperature separately and found to be temperature-dependent, especially at high temperatures.

Introduction

Generally carbon dioxide (CO_2) is thought of as an inert and relatively unreactive compound. There was no report on polymerization utilizing CO_2 as a monomer, until 1969, when Inoue et al.[1] observed that the copolymerization of CO_2 with an epoxide could form polycarbonate under relatively mild conditions. Since then, many attempts to develop new catalysts and to copolymerize other monomers with CO_2 have been made, which are described in several good reviews of Rokicki and Kuran,[2] Scholsky,[3] Yamazaki et al.,[4] Coates and Moore,[5] and Darensbourg.[6] To consume CO_2, the copolymerization was carried out using CO_2 with ethylene oxide (EO), propene oxide (PO), butylene oxide (BO), and cyclohexene oxide (CHO), and so forth.

We focus on the synthesis of poly(propylene carbonate) (PPC) from CO_2 and propene oxide. The development of such a process would provide a solvent-free alternative to polycarbonate synthesis. CO_2 contributes 43 % by mass to this polymer and thus provides an environmentally benign alternative to phosgene for the introduction of the carbonate functionality in polycarbonates. Not only is this information vital in designing a one-phase reaction system which includes mixtures of PO and carbon dioxide, but it also makes possible the extraction of unreacted monomer from the synthesized polycarbonate using carbon dioxide resulting in a truly organic solvent-free system.[7−9]

For the successful development of such a process, phase behavior plays a significant role. Unfortunately, there are very few data available currently. There is only one literature source[10] reported on the phase equilibrium of this binary system, but at higher temperatures. In this paper attention is focused on the phase behavior of the reactants in the CO_2 + PO copolymerization process. More precise data are provided at temperatures from (303.2 to 353.2) K and CO_2 mole fractions from 0.1 to 0.7 typical for this copolymerization. We present in this paper experimental bubble points of the binary system CO_2 + PO determined visually using an apparatus with a moveable piston and a vision window. In addition, the experimental data and literature data are modeled using the Peng−Robinson equation of state (PR-EoS). A temperature-dependent interaction parameter k_{ij} is obtained to better predict the equilibrium data at a wide temperature scale of (303.2 to 473.2) K.

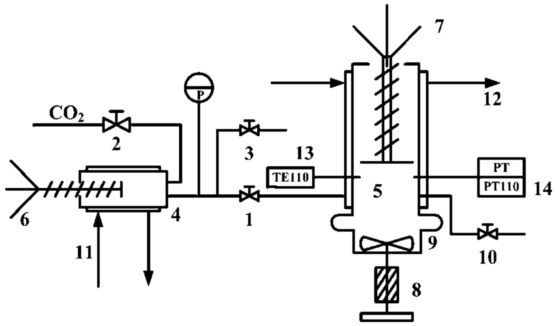

Figure 1. Variable-volume equilibrium cell with a sapphire window and mixer: 1, 2, inlet valve; 3, 10, dumping valve; 4, inlet syringe pump; 5, cell; 6, 7, capstan; 8, magnetic stirrer; 9, CCD camera; 11, 12, thermostatic bath; 13, temperature transducer; 14, pressure transducer.

Experimental Section

Materials. Propene oxide (mass fraction purity > 0.98, GC) was obtained from Lingfeng Chemical Co. (Shanghai). Prior to use, PO was refluxed overnight with calcium hydride and distilled to remove trace elements of water, both under nitrogen atmosphere. Then PO was frozen with liquid nitrogen under high vacuum to remove gases and heated to room temperature afterward. CO_2 with a mass fraction purity better than 0.99995 from Praxair Co. (Shanghai) was used without further purification.

Apparatus and Procedure. The mixtures of CO_2 and PO were observed in a variable-volume, high-pressure view cell (SEPAREX EC600, France). A simplified schematic of the apparatus is shown in Figure 1. The SEPAREX cell can perform measurements of thermodynamic data with precise pressure and temperature control and precise volume control with variable cell volume by adjusting the piston position in the cell.

The SEPAREX cell is a thick-walled, hollow, stainless steel cylinder with an internal diameter of 20 mm. The cell is covered by the jacket and thermostatic bath for temperature control. The temperature is measured using a platinum resistance thermometer with an uncertainty of 0.1 K. A 30 mm length piston is

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* Corresponding author. Tel.: +86 57187951307. Fax: +86 57187951612. E-mail address: fenglf@zju.edu.cn.

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Table 1. Experimental and Calculated Bubble-Point Pressure of CO_2 + PO

$x(CO_2)$	$P_{exp}{}^{a}$/MPa	$P_{cal}{}^{b}$/MPa	dev.^{c}/%	$P_{exp}{}^{a}$/MPa	$P_{cal}{}^{b}$/MPa	dev.^{c}/%	$P_{exp}{}^{a}$/MPa	$P_{cal}{}^{b}$/MPa	dev.^{c}/%
		T/K = 303.2 ± 0.1			T/K = 313.2 ± 0.1			T/K = 323.2 ± 0.1	
0.10	0.588	0.643	9.4	0.980	0.850	13.3	1.100	1.052	4.4
0.20	1.034	1.123	8.6	1.545	1.467	5.0	1.836	1.796	2.2
0.32	1.789	1.793	0.2	2.417	2.314	4.3	2.862	2.811	1.8
0.40	2.290	2.274	0.7	2.973	2.910	2.1	3.479	3.522	1.2
0.50	2.964	2.900	2.1	3.684	3.669	0.4	4.390	4.420	0.7
0.60	3.781	3.566	5.7	4.418	4.457	0.9	5.242	5.343	1.9
0.70	4.337	4.279	1.3	5.236	5.281	0.9	6.089	6.295	3.4
		T/K = 333.2 ± 0.1			T/K = 343.2 ± 0.1			T/K = 353.2 ± 0.1	
0.10	1.239	1.233	0.5	1.530	1.434	3.8	1.728	1.705	1.3
0.20	2.165	2.081	3.9	2.542	2.388	6.1	3.040	2.802	7.8
0.32	3.345	3.244	3.0	3.785	3.699	2.3	4.328	4.299	0.7
0.40	4.046	4.061	0.4	4.704	4.623	1.7	5.306	5.346	0.7
0.50	5.132	5.098	0.7	5.792	5.799	0.1	6.586	6.659	1.1
0.60	6.110	6.165	0.9	6.965	7.006	0.6	7.731	7.980	3.2
0.70	7.038	7.265	3.2	8.079	8.233	1.9	9.012	9.265	2.8

[a] Experimental data. [b] Calculated data with PR-EoS (k_{ij} used is listed in Table 3). [c] dev. = $|P_{exp} - P_{cal}|/P_{exp}$.

introduced at one end of the cell, while a magnetic stirrer with magnetic bar is placed at the other end. The seal-less stirrer can perform efficient mixing inside the cell. The piston actuation by fine thread screw type capstan gives the indication of piston position and precise pressure adjustment. The pressure gauge allows for an uncertainty of the pressure measurement of 5 kPa. Another 50 mL inlet syringe pump with jacket and capstan allows precise CO_2 liquid volume injection to supply precise quantities of liquid in the cell. The composition of the samples is controlled within 0.1 % (CO_2 mole fraction).

The cell mounted on the skid can rotate 180° along the central axis for observation convenience. There are also four circular vision windows in the cell where a cold light source and a CCD camera can be mounted, for numerical visualization and recording on PC. Therefore, we can judge the bubble point with images and videos easily and accurately.

First, the SEPAREX cell is loaded with the desired volume of PO which is gravimetrically determined with an uncertainty of 0.02 mg. Prior to feeding, CO_2 is compressed to 10.0 MPa and cooled to 5 °C through the jacket and thermostatic bath. CO_2 is added very slowly to the cell using a 50 mL inlet syringe pump with an accuracy of 0.05 mL. Meanwhile, the piston in the cell is released at the same speed. This results in an easily controlled, isobaric, isothermal injection of CO_2 into the cell. Once the desired volume of carbon dioxide is introduced, the piston in the cell will compress to increase the cell pressure to 40.0 MPa. The cell is agitated with the magnetic stirrer and heated to the desired operating temperature. When the cell contents achieve equilibrium, the piston is released slowly, resulting in the sample volume's expansion. The pressure of the mixture is lowered until a bubble is observed. Then the cell is agitated again to achieve equilibrium. If the bubble is still present, the pressure is slowly increased by compressing the sample volume. The system is equilibrated by mixing after each addition. The bubble grows smaller and smaller after each pressure increase until it disappears. The highest pressure at which the bubble is observed is referred to as the bubble-point pressure for that mole fraction and temperature.

Results and Discussion

The phase behavior of the CO_2 + PO system was determined at (303.2, 313.2, 323.2, 333.2, 343.2, and 353.2) K. The experimental data are presented in Table 1, and the uncertainty is 0.005 MPa. The values are typically averages of three or four measurements.

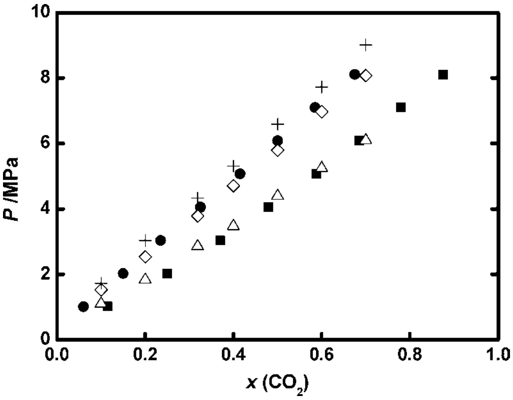

Figure 2. $P-X$ diagram for the binary mixtures of CO_2 + PO: ■, 323.15 K from literature;[10] △, 323.2 K; ◇, 343.2 K; ●, 348.15 K from literature;[10] +, 353.2 K.

Parts of the measured results are compared with previously reported data[10] at temperatures of (323.15 and 348.15) K on the phase behavior of this system in Figure 2. There seems to be a good agreement between two data sets.

Although cubic equations of state are simple, they are suitable for modeling hydrocarbon systems with light gases such as CO_2 over wide ranges of temperature and pressure, including subcritical and supercritical regions. Super et al.[11] and Van Schilt et al.[12] showed that the PR-EoS can be used to describe the phase behavior of carbon dioxide and 1,2-epoxycyclohexane.

The cubic equation of state calculates the properties of a fluid as if it consisted of one component. If the fluid is a mixture, the parameters of the imaginary component must be calculated from the pure-component parameters of the real components, using mixing rules. The PR-EoS[13] would be used for correlating phase equilibrium for the CO_2 + PO system. The PR-EoS, coupled with the classical van der Waals mixing rule with one binary interaction parameter for the attraction parameter, is shown as follows,

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

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} (1 - k_{ij}) \tag{2}$$

$$b = \sum_i \sum_j x_i x_j \left(\frac{b_i + b_j}{2}\right) \tag{3}$$

where P, T, v, R, and k_{ij} stand for the pressure, temperature, molar volume, gas constant, and binary interaction parameter,

Table 2. Pure-Component Parameters Used for the PR-EoS

	T_c	P_c	V_c	mol wt
	K	MPa	$cm^3 \cdot mol^{-1}$	$g \cdot mol^{-1}$
carbon dioxide	304.21	7.383	94	44.0098
propene oxide	488.25	4.920	186	58.08004

Table 3. Average Relative Deviations in Bubble-Point Pressure (ARDP) and Average Absolute Deviations in Vapor-Phase Compositions (AADY) for the CO_2 + PO System Calculated by the PR-EoS

T/K	P range/MPa	k_{ij}	ARDP/%	AADY/%	ref
303.2	0.59 to 4.34	0	4.0		this work
313.2	0.98 to 5.23	0.02	4.0		this work
323.15	1.01 to 8.11	0.03	4.2	1.7	10
323.2	1.10 to 6.09	0.03	2.3		this work
333.2	1.24 to 7.04	0.03	1.8		this work
343.2	1.49 to 8.08	0.03	2.3		this work
348.15	1.01 to 8.11	0.03	1.9	0.5	10
353.2	1.73 to 9.08	0.04	2.5		this work
373.15	2.03 to 9.59	0.04	1.5	0.9	10
398.15	2.03 to 10.13	0.05	3.7	2.3	10
423.15	2.53 to 8.75	0.08	4.5	2.1	10
448.15	4.05 to 7.85	0.09	2.5	4.1	10
473.15	5.32 to 6.59	0.15	4.1		10

respectively. The two characteristic parameters a and b represent the energy parameter and the covolume parameter, respectively. The parameters a and b for a pure component can be calculated with the physical properties of CO_2 and PO (as listed in Table 2) by the following equations,

$$a = 0.45724R^2T_c^{\ 2}/P_c \qquad (4)$$

$$b = 0.07780RT_c/P_c \qquad (5)$$

For the best representation of nonideal systems, we must obtain the binary interaction parameter, k_{ij}, from regression of experimental vapor−liquid equilibrium data. AspenOne 2006 was used to determine the value of the binary interaction parameter that minimized the absolute average percent deviation between the calculated and the experimental composition.

Table 3 presents the best-fit interaction parameter k_{ij}, the average relative deviations in bubble-point pressure (ARDP), and the average absolute deviations in vapor-phase compositions (AADY) of the experimental data, comparing the prediction results. It is shown that the predictions of PR-EoS fit the experimental data well. The ARDP and AADY are calculated by the equations

$$\mathrm{ARDP} = \frac{1}{N_{\mathrm{exp}}}\sum_{i=1}^{N_{\mathrm{exp}}}\left|\frac{P_i^{\mathrm{exp}} - P_i^{\mathrm{calc}}}{P_i^{\mathrm{exp}}}\right| \qquad (6)$$

$$\mathrm{AADY} = \frac{1}{N_{\mathrm{exp}}}\sum_{i=1}^{N_{\mathrm{exp}}}|Y_i^{\mathrm{exp}} - Y_i^{\mathrm{calc}}| \qquad (7)$$

The interaction parameter (k_{ij}) optimized to match the experimental data at each temperature separately is found to be strongly temperature-dependent, especially for high temperatures (see Table 3 and Figure 3). The interaction parameter data for a wide temperature range from (303.2 to 473.2) K were fitted to the following correlation with an 11.19 % average deviation:

$$k_{ij} = -3.31886 + 0.0269T - 7.2471 \cdot 10^{-5}T^2 + 6.575 \cdot 10^{-8}T^3 \qquad (8)$$

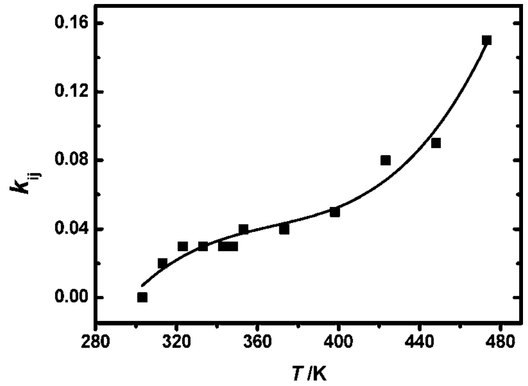

Figure 3. Temperature dependency of the interaction parameter $k_{ij}(T)$: ■, data in Table 3; −, fitted curve (eq 8).

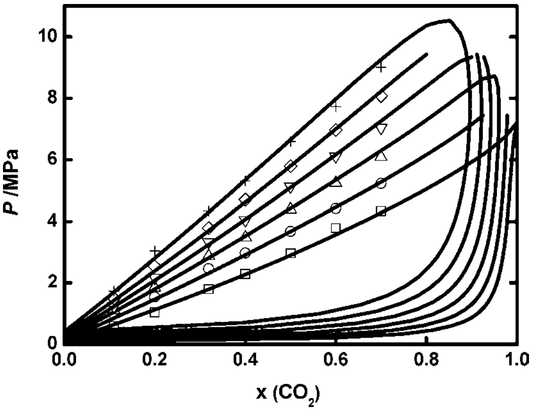

Figure 4. Comparison of our measured data for the CO_2 + PO system and prediction with PR-EoS (k_{ij} used is listed in Table 3): □, 303.2 K; ○, 313.2 K; △, 323.2 K; ▽, 333.2 K; ◇, 343.2 K; +, 353.2 K; −, PR-EoS.

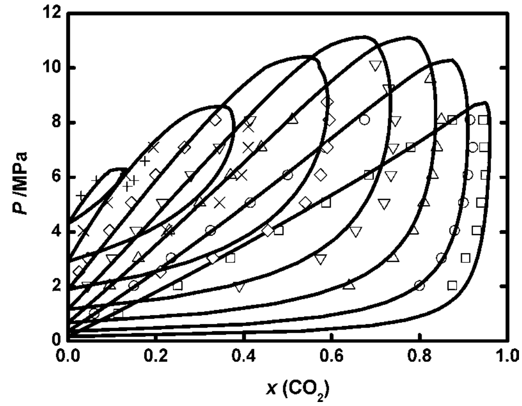

Figure 5. Comparison of literature data[10] for the CO_2 + PO system and prediction with PR-EoS (k_{ij} used is listed in Table 3): □, 323.15 K; ○, 348.15 K; △, 373.15 K; ▽, 398.15 K; ◇, 423.15 K; ×, 448.15 K; +, 473.15 K; −, PR-EoS.

For the low temperature range from (320.2 to 380.2) K, a fixed temperature-independent value for k_{ij}, 0.03, can be acceptable. However, the predictions of phase equilibrium data could be more reliable at higher temperatures if the correlation (eq 8) for the temperature-dependent interaction parameter is used.

The isotherms comparing the PR-EoS results with experimental data are illustrated in Figures 4 (measured data of this work) and 5 (literature data[10]). As can be seen, the PR-EoS with the temperature-dependent interaction parameters leads to a satisfactory prediction of the phase equilibrium data for the CO_2 + PO system. Table 1 also lists the calculated data and the deviation of each experimental point.

Conclusions

New phase-equilibrium data relevant to the copolymerization of CO_2 and propene oxide are reported in this paper. The bubble points of the binary mixtures were measured using a high-pressure experimental apparatus equipped with a variable-volume view cell, at various CO_2 compositions in the range of temperatures close to the requirement of the copolymerization, which gave more precise phase-equilibrium data at low temperatures.

Both experimental bubble-point data and literature data were successfully correlated with the PR-EoS coupled with a conventional one-parameter van der Waals mixing rule. The binary interaction parameter k_{ij} was found to be temperature-dependent, especially at high temperatures. The experimental data and parameters that are reported in this work could be helpful to the design and the further development of the CO_2-based solvent-free alternative to polycarbonate synthesis.

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