Vapor−Liquid Equilibrium Data of (Carbon Dioxide + Methyl Propionate) and (Carbon Dioxide + Propyl Propionate) at Pressures from (1.00 to 12.00) MPa and Temperatures from (313.0 to 373.0) K[†]

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High-pressure vapor−liquid equilibrium data for (methyl propionate + carbon dioxide) and (propyl propionate (PP) + carbon dioxide) were measured at pressures from (1.00 to 12.00) MPa and temperatures in the range from (313.0 to 373.0) K. Experimental results were correlated with the Peng−Robinson equation of state with the two-parameter van der Waals mixing rule. At the same time, the Henry's coefficient and partial molar enthalpy change and partial molar entropy change of CO_2 during dissolution at different temperature were also calculated.

Introduction

Vapor−liquid equilibrium (VLE) data containing supercritical CO_2 (SC-CO_2) are important for the design, development, and operation of supercritical fluid separation processes. The main method of obtaining phase equilibrium data is by experimentation. Several review articles on high-pressure fluid phase equilibrium experimental methods and systems have been published.[1−3] Most of these studies have focused on supercritical (SC) carbon dioxide because it is an inexpensive, nontoxic, and environmentally benign solvent. In this study, we measured the VLE data for two binary mixtures of carbon dioxide with methyl propionate and propyl propionate, respectively. The experimental temperatures are at 313.0 K, 333.0 K, 353.0 K, and 373.0 K, with pressures in the range from (1.00 to 12.00) MPa.

Experimental Section

Materials and Their Purities. Carbon dioxide (molar fraction purity > 0.9999) was provided by Tianjin Gas Company, and both the methyl propionate and propyl propionate (both of mass fraction purity > 0.9985) were supplied by Aladdin Reagent Company. They were degassed before use at 268.0 K for 2 h.

Experimental Apparatus and Procedures. The experimental apparatus which has been described proviously[4−6] is shown in Figure 1. The main part of the apparatus is a high-pressure view cell of 100 cm^3. There is a moveable piston inside the cylinder autoclave. The piston separates the content in the cell from the pressure medium (oil). The pressure is generated manually with an operated screw-driven pump and is measured with a pressure sensor. This pressure sensor (model CYB-20S) with a certainty of ± 0.05 % and the pressure displayer (model DP-A) were previously calibrated by a standard pressure gauge. The quartz window permitted observation of the phase behavior of the content. The content in the cell was stirred by a magnetic stirrer which was powered with a back and forth moved magnet outside the heat jacket. The temperature was measured with a calibrated thermocouple inside the cell. The accuracy of the pressure was ± 0.01 MPa, and the accuracy of the temperature was ± 0.1 K.

Before each measurement, the view cell was first evacuated with a vacuum pump. An ester with known mass was charged into the cell, and then the carbon dioxide was pressured into the cell from the sample valve. The pressure and temperature were adjusted to designated values. After termination of stirring, the phase equilibrium was achieved when the constant pressure was maintained for 2 h at the given temperature. The samples of liquid and vapor phases were taken from the lower and the upper valves, respectively, then put into the previously evacuated and weighted small steel vessel through the needle valve and capillary (the volumes were known). During this isothermal process, the pressure inside the autoclave was kept constant by pushing the piston toward the chamber with the screw-driven pump; therefore, the phase equilibria were maintained through operation. The total mass of the sample taken was weighted using a balance with an accuracy of 0.0001 g. The volume of the sample was determined by measuring the distance between the positions of the piston before and after taking the sample, Δl, and the known inner diameter of the autoclave. The positions of the piston were measured with the help of a Hall probe (model SS541AT) connected to the piston. The uncertainty of Δl was 0.01 mm. The cooled sample vessel was connected to a glass bulb of known volume. The temperature of the bulb was measured by a thermometer with a precision of 0.1 K. The pressure inside the bulb was measured with an absolute-pressure meter with a precision of 10 Pa. Because the pressure of the desorbed gas was very low {about (10 to 20) kPa}, the mass of CO_2 was easily calculated using the equation of state of ideal gas. The mass of CO_2 was also calculated using a mass different method (the mass of the vessel before being connected to the glass bulb minus the mass of the vessel after desorbed CO_2). The densities of the vapor and liquid were obtained by the appropriate mass divided by the volume of each phase. Finally, the molar volumes of the mixture were obtained from the densities and the mole fractions of two phases. The above procedures were all repeated three times. The experimental data listed in Table 1 are the mean values of the measurements. The estimated uncertainty of the mole fractions of the vapor and liquid phases is below 0.001. The uncertainty in reported densities and mole volumes is estimated to be within 0.5 %.

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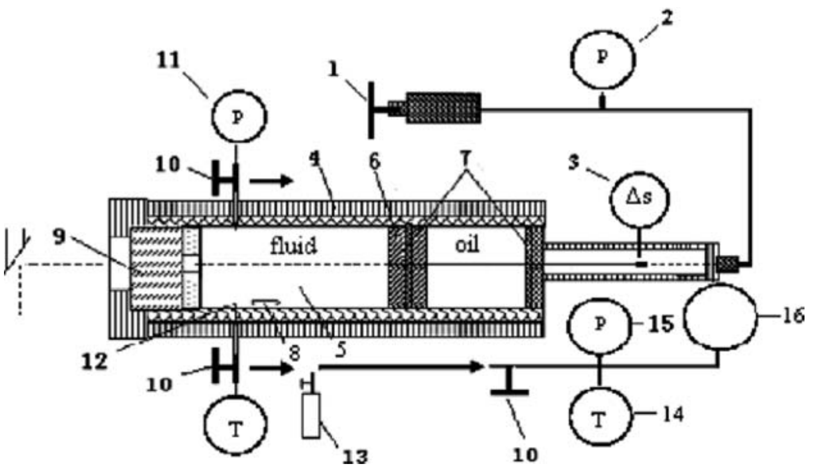

Figure 1. Schematic diagram of the high-pressure apparatus: 1, screw-driven pump; 2, pressure meter; 3, hall probe; 4, heat jacket; 5, autoclave; 6, position; 7, O-ring; 8, stirrer; 9, quartz window; 10, sample valves; 11, pressure sensor; 12, thermocouple; 13, small steel vessel; 14, thermometer; 15, vacuum meter; 16, glass bulb.

Correlations

The experimental data were correlated with the Peng−Robinson equation of state and the conventional mixing rules. The Peng−Robinson equation of state has the following form

$$p = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)} \tag{1}$$

where p, T, and V_m represent the pressure, temperature, and molar volume, respectively. R is the mole gas constant; b is the covolume parameter; and a is the energy parameter.

For a pure fluid, the parameter b is given by

$$b = 0.07780\frac{RT_c}{p_c} \tag{2}$$

whereas $a(T)$, a function of temperature, is given by

$$a(T) = a(T_c)\alpha(T) \tag{3}$$

$$a(T_c) = 0.45724\frac{R^2T_c^2}{p_c} \tag{4}$$

$$\alpha(T) = [1 + k(1 - T_r^{0.5})]^2 \tag{5}$$

where T_c, T_r, and p_c represent the critical temperature, reduced temperature, and critical pressure, respectively.

The value of k depends on the acentric factor, ω, according to

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (0 \le \omega \le 0.5) \tag{6}$$

The critical data ($p_{c,i}$, $T_{c,i}$) were taken from the literature,[7] and the acentric factors (ω's) can be obtained by fitting the functions to vapor pressure data.[7]

For a binary mixture, the common procedure is to write mixing rules that are quadratic in mole fraction

$$b_M = g_1^2b_1 + g_2^2b_2 + 2g_1g_2b_{12} \tag{7}$$

$$a_M = g_1^2a_1(T) + 2g_1g_2a_{12}(T) + g_2^2a_2(T) \tag{8}$$

where g_i is either x or y and a_i and b_i are the values of the pure components.

$a_1(T)$ (or $a_2(T)$) and b_1 (or b_2) refer to the pure-component values, and b_{12} and $a_{12}(T)$ are binary parameters. It is convenient to express these in the form as the following

$$b_{12} = \frac{1}{2}(b_1 + b_2)(1 - c_{12})$$

$$a_{12}(T) = [a_1(T)a_2(T)]^{0.5}(1 - k_{12})$$

where c_{12} and k_{12} are adjustable parameters and depend only on temperature.

The fugacity coefficient ϕ_i for a component i in a mixture is given by

$$\ln \phi_i = \frac{b_i}{b_M}\left(\frac{pV_m}{RT} - 1\right) - \ln\frac{p(V_m - b_M)}{RT} - \frac{a_M}{2\sqrt{2}b_MRT}\left[\frac{2\sum_i g_ia_{12}}{a_M} - \frac{b_i}{b_M}\right]\ln\frac{V_m + (1 + \sqrt{2})b_M}{V_m + (1 - \sqrt{2})b_M} \tag{9}$$

For a binary vapor−liquid equilibrium system at temperature T and pressure p, the equilibrium equations are

$$f_1^v = f_1^l \quad \text{or} \quad \phi_1^vy_1 = \phi_1^lx_1 \tag{10}$$

and

$$f_2^v = f_2^l \quad \text{or} \quad \phi_2^vy_2 = \phi_2^lx_2 \tag{11}$$

Table 1. Vapor−Liquid of {Carbon Dioxide (1) + Methyl Propionate (2)} and {Carbon Dioxide (1) + Propyl Propionate (2)} at Temperatures T and Pressures P As a Function of Mole Fractions x_1 and y_1 along with Densities ρ with Mole Volume V and Ratios of Mole Fractions of 1 and 2 in the Vapor to That in the Liquid K_1 and K_2

{carbon dioxide (1) + methyl propionate (2)}

p/MPa	x_1	ρ_l/g·cm^{-3}	$V_{m,l}$/cm^3·mol^{-1}	y_1	ρ_g/g·cm^{-3}	$V_{m,g}$/cm^3·mol^{-1}	K_1	K_2
				T = 313.0 K				
1.00	0.3321	0.9870	74.35	0.9812	0.0245	1829.68	2.955	0.028
2.00	0.4384	0.9707	70.78	0.9852	0.0438	1019.43	2.247	0.026
3.00	0.5349	0.9460	68.14	0.9819	0.0726	617.03	1.836	0.039
4.00	0.6435	0.9250	64.53	0.9819	0.1241	360.97	1.526	0.051
5.00	0.7649	0.8869	61.27	0.9753	0.1801	250.34	1.275	0.105
6.00	0.8355	0.8401	60.99	0.9660	0.3103	146.62	1.156	0.207
7.00	0.9058	0.7676	62.72	0.9137	0.5463	87.49	1.009	0.916
				T = 333.0 K				
3.00	0.4501	0.9058	75.29	0.9870	0.0528	844.17	2.193	0.024
4.00	0.5358	0.9102	70.78	0.9874	0.0822	542.02	1.843	0.027
5.00	0.6338	0.9172	65.54	0.9887	0.1000	444.97	1.560	0.031
6.00	0.7185	0.9162	61.54	0.9774	0.1541	291.98	1.360	0.080
7.00	0.7867	0.9112	58.59	0.9716	0.1856	243.80	1.235	0.133
8.00	0.8443	0.8700	58.45	0.9495	0.2436	189.75	1.125	0.324
9.00	0.8821	0.8432	58.33	0.9025	0.4200	114.98	1.023	0.827
				T = 353.0 K				
2.00	0.3125	0.8702	85.33	0.9422	0.0412	1129.69	3.015	0.084
3.00	0.3711	0.8656	82.80	0.9502	0.0484	954.36	2.561	0.079
4.00	0.4215	0.8664	80.16	0.9486	0.0689	671.43	2.251	0.089
5.00	0.4811	0.8695	76.86	0.9456	0.0988	469.57	1.966	0.105
6.00	0.5563	0.8579	74.04	0.9460	0.1165	398.08	1.701	0.122
7.00	0.6038	0.8543	71.91	0.9420	0.1432	325.08	1.560	0.146
8.00	0.6866	0.8510	67.91	0.9352	0.1965	238.43	1.362	0.207
9.00	0.7392	0.8243	67.30	0.9023	0.2800	172.50	1.221	0.375
10.00	0.8125	0.7910	66.06	0.8601	0.3894	128.80	1.059	0.746
				T = 373.0 K				
3.00	0.3282	0.8250	89.16	0.9213	0.0444	1068.98	2.807	0.117
4.00	0.3961	0.8214	85.92	0.9255	0.0616	767.50	2.337	0.123
5.00	0.4511	0.8121	83.92	0.9228	0.0817	580.13	2.046	0.141
6.00	0.5166	0.7982	81.77	0.9246	0.0983	481.36	1.790	0.156
7.00	0.5685	0.7828	80.46	0.9222	0.1224	387.44	1.622	0.180
8.00	0.6251	0.7637	79.21	0.9189	0.1484	320.54	1.470	0.216
9.00	0.6694	0.7447	78.62	0.9123	0.2126	225.11	1.363	0.265
10.00	0.7097	0.7226	78.57	0.9011	0.2833	170.67	1.270	0.341
11.00	0.7523	0.6985	78.60	0.8845	0.3716	132.08	1.176	0.466
12.00	0.8121	0.6750	77.43	0.8432	0.4512	112.81	1.038	0.835

{carbon dioxide (1) + propyl propionate (2)}

p/MPa	x_1	ρ_l/g·cm^{-3}	$V_{m,l}$/cm^3·mol^{-1}	y_1	ρ_g/g·cm^{-3}	$V_{m,g}$/cm^3·mol^{-1}	K_1	K_2
				T = 313.0 K				
1.00	0.2710	0.8250	116.96	0.9892	0.0220	2035.35	3.650	0.015
2.00	0.4001	0.8869	98.31	0.9942	0.0429	1035.38	2.485	0.010
3.00	0.5071	0.9083	87.51	0.9941	0.0652	681.36	1.960	0.012
4.00	0.6290	0.9085	77.83	0.9928	0.1068	416.84	1.578	0.019
5.00	0.7510	0.9086	68.16	0.9976	0.1537	287.40	1.328	0.010
6.00	0.8616	0.8939	60.37	0.9963	0.2444	181.12	1.156	0.027
7.00	0.9475	0.8945	53.42	0.9610	0.6463	72.42	1.014	0.743
				T = 333.0 K				
2.00	0.3446	0.8970	101.66	0.9819	0.0403	1124.15	2.849	0.028
3.00	0.3901	0.8681	101.27	0.9812	0.0588	771.32	2.515	0.031
4.00	0.4837	0.8344	97.28	0.9700	0.0772	597.93	2.005	0.058
5.00	0.5720	0.8134	91.98	0.9700	0.1080	427.41	1.696	0.070
6.00	0.6650	0.7923	85.98	0.9653	0.1269	366.42	1.452	0.104
7.00	0.7286	0.7708	82.43	0.9811	0.1800	252.00	1.347	0.070
8.00	0.7741	0.7306	82.49	0.9725	0.2475	185.78	1.256	0.122
9.00	0.8615	0.7000	77.10	0.9735	0.2767	165.91	1.130	0.191
10.00	0.9049	0.6458	78.74	0.9145	0.4468	112.26	1.011	0.899
				T = 353.0 K				
2.00	0.3001	0.8580	110.01	0.9375	0.0271	1789.67	3.124	0.089
3.00	0.3446	0.8530	106.90	0.9496	0.0496	960.26	2.756	0.077
4.00	0.3901	0.8495	103.49	0.9610	0.0682	686.33	2.464	0.064
5.00	0.4477	0.8465	98.96	0.9609	0.0898	521.33	2.146	0.071
6.00	0.5007	0.8344	95.82	0.9631	0.1239	376.57	1.924	0.074
7.00	0.5583	0.8069	93.94	0.9609	0.1650	283.73	1.721	0.089

Table 1 Continued

{carbon dioxide (1) + methyl propionate (2)}

p / MPa	x_1	ρ_l / $g\cdot cm^{-3}$	$V_{m,l}$ / $cm^3\cdot mol^{-1}$	y_1	ρ_g / $g\cdot cm^{-3}$	$V_{m,g}$ / $cm^3\cdot mol^{-1}$	K_1	K_2
8.00	0.6241	0.7938	89.52	0.9499	0.2206	215.81	1.522	0.133
9.00	0.6939	0.7813	84.52	0.9364	0.2767	175.57	1.350	0.208
10.00	0.7545	0.7887	78.20	0.9023	0.3330	153.26	1.196	0.398
11.00	0.8198	0.7700	73.99	0.8701	0.4566	116.85	1.061	0.721
				$T = 373.0$ K				
2.00	0.2551	0.7000	139.48	0.9093	0.0220	2296.84	3.565	0.122
3.00	0.2685	0.7448	129.79	0.9073	0.0429	1181.22	3.379	0.127
4.00	0.2943	0.7863	120.58	0.9075	0.0652	776.99	3.084	0.131
5.00	0.3240	0.8085	114.62	0.9073	0.0860	589.24	2.800	0.137
6.00	0.3599	0.8044	111.99	0.8984	0.1082	474.26	2.496	0.159
7.00	0.3865	0.8132	108.43	0.8932	0.1463	353.31	2.311	0.174
8.00	0.4242	0.8167	104.64	0.8824	0.1901	276.00	2.080	0.204
9.00	0.4968	0.7992	100.39	0.8744	0.2522	210.32	1.760	0.250
10.00	0.5686	0.7998	93.85	0.8686	0.3042	175.74	1.528	0.305
11.00	0.6172	0.7834	91.35	0.8532	0.3341	163.33	1.382	0.384
12.00	0.7036	0.7547	86.58	0.8268	0.4604	122.66	1.175	0.584

where f is fugacity and ϕ is fugacity coefficient.

The fitting was performed at each temperature by minimizing the following objective function

$$F = 5\sum_{i=1}^{N}\left(\frac{p - p_{cal}}{p}\right)^2 + \sum_{i=1}^{N}\sum_{j=1}^{M}\left(\frac{y_j - y_{j,cal}}{y_j}\right)^2 \qquad (12)$$

where the subscript cal represent calculated values.

Results and Discussion

Isothermal vapor−liquid equilibria for (CO_2 + methyl propionate) and (CO_2 + propyl propionate) were measured at temperatures of (313.0, 333.0, 353.0, and 373.0) K at pressures between (1.00 and 12.00) MPa. The results are listed in Table 1, where x_1 and y_1 are the mole fractions of CO_2 in the liquid phase and vapor phase, respectively. The molar volumes at different temperatures (T) and pressures (p) were obtained from densities and mole fractions. The mixture volumes (V_m) are defined as

$$V_{m,l} = \frac{x_1M_1 + x_2M_2}{\rho_l} = \frac{x_1M_1 + (1 - x_1)M_2}{\rho_l} \qquad (13)$$

$$V_{m,g} = \frac{y_1M_1 + y_2M_2}{\rho_g} = \frac{y_1M_1 + (1 - y_1)M_2}{\rho_g} \qquad (14)$$

where $V_{m,l}$ and $V_{m,g}$ represent the molar volumes of the liquid phase and the vapor phase, respectively, while M_1 and M_2 indicate the relative molar masses of CO_2 and ester, respectively. The vapor−liquid ratio of CO_2 (1) and methyl or propyl propionate (2) is defined as follows as

$$K_1 = \frac{y_1}{x_1} \text{ and } K_2 = \frac{y_2}{x_2}$$

They were also calculated and listed in Table 1.

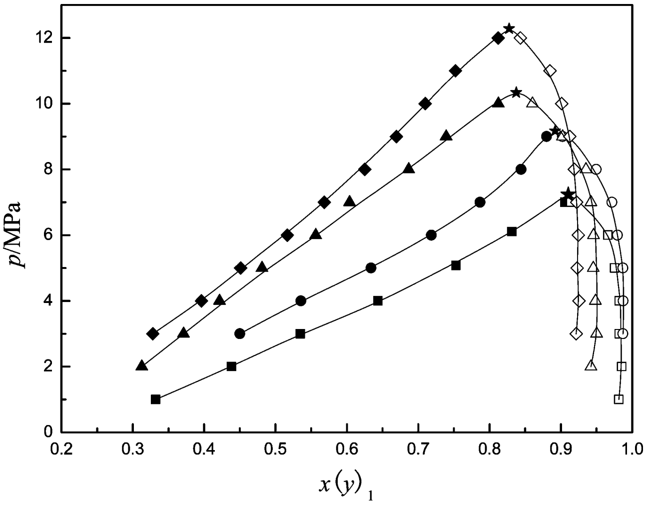

Figure 2. p−x $(y)_1$ of {carbon dioxide (1) + methyl propionate (2)} at four temperatures: ■ and □, $T = 313.0$ K; ● and ○, $T = 333.0$ K; ▲ and Δ, $T = 353.0$ K; ◆ and ◇, $T = 373.0$ K; and ★, estimated critical points; —, results obtained from the equation of state. Solid points represent the liquid phase, and unfilled symbols represent the gas phase.

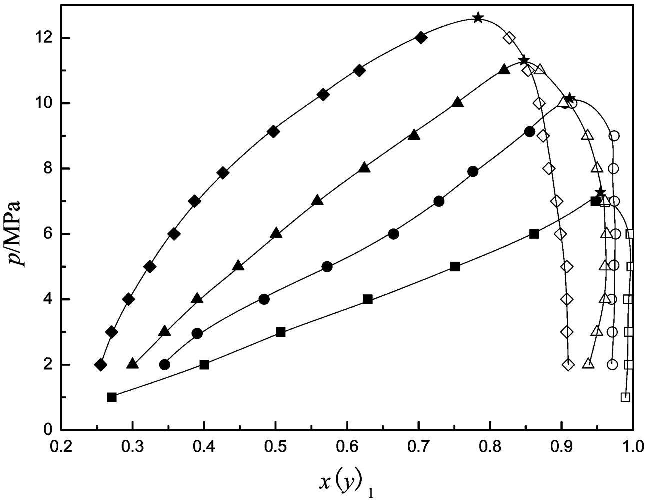

Figure 3. p−x $(y)_1$ of {carbon dioxide (1) + propyl propionate (2)} at four temperatures: ■ and □, $T = 313.0$ K; ● and ○, $T = 333.0$ K; ▲ and Δ, $T = 353.0$ K; ◆ and ◇, $T = 373.0$ K; ★, estimated critical points; —, eqution of state. Solid points represent the liquid phase, and unfilled symbols represent the gas phase.

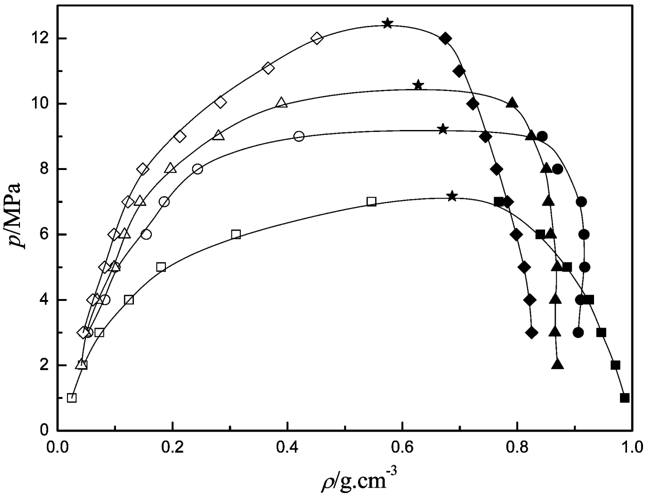

Figure 4. $p-\rho$ of {carbon dioxide (1) + methyl propionate (2)} at four temperatures: ■ and □, $T = 313.0$ K; ● and ○, $T = 333.0$ K; ▲ and Δ, $T = 353.0$ K; ◆ and ◇, $T = 373.0$ K; ★, estimated critical points; —, obtained from the equation of state. Solid points represent the liquid phase, and unfilled symbols represent the gas phase.

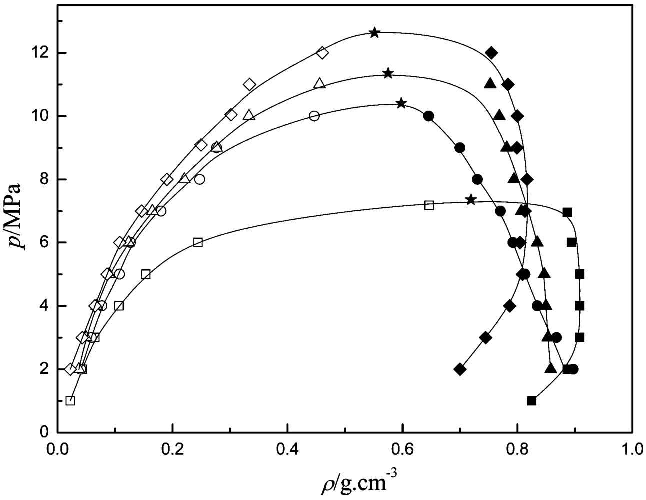

Figure 5. $p-\rho$ of {carbon dioxide (1) + propyl propionate (2)} at four temperatures: ■ and □, $T = 313.0$ K; ● and ○, $T = 333.0$ K; ▲ and Δ, $T = 353.0$ K; ◆ and ◇, $T = 373.0$ K; ★, estimated critical points; —, equation of state results. Solid points represent the liquid phase, and unfilled symbols represent the gas phase.

Figure 2 and Figure 3 give the $p-x$ diagrams, while Figure 4 and Figure 5 give $p-\rho$ diagrams. In these four figures, the estimated critical points were also given. Figure 6 and Figure 7 show isothermal $k-p$ diagrams.

1. Effect of Pressure on The Solubility and Henry's Coefficients of SC-CO$_2$ in Liquid Esters. The solubilities of supercritical CO$_2$ in methyl propionate and propyl propionate increase with increasing pressures at a constant temperature, which results in the decrease of densities and molar volumes in the liquid phases. In addition, the solubilities of the two esters in SC CO$_2$ are also increased with increasing pressure at the same temperature, thus resulting in the increasing densities and decreasing molar volumes in the vapor phases. Finally, this behavior makes the properties (densities and compositions) of the liquid and vapor very close. The cross points of the two lines are the critical pressure, p_c, critical density, ρ_c, and critical composition, x_c, of systems at this temperature. The estimated critical values are listed in Table 3.

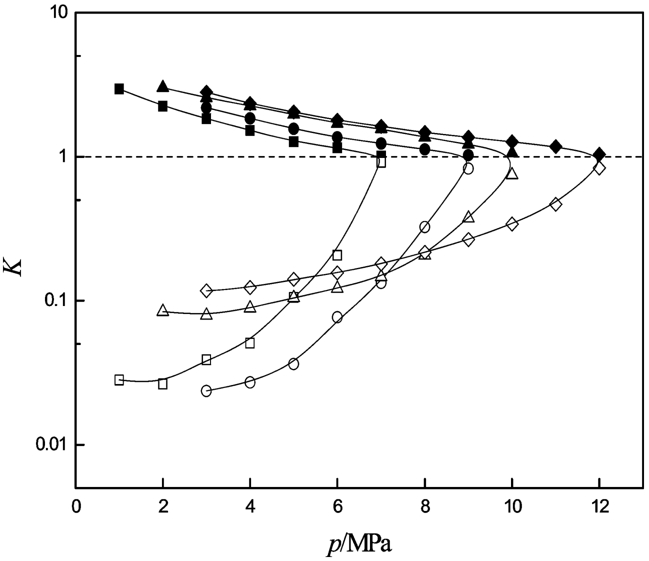

Figure 6. $K-p$ of {carbon dioxide (1) + methyl propionate (2)} at four temperatures: ■ and □, $T = 313.0$ K; ● and ○, $T = 333.0$ K; ▲ and Δ, $T = 353.0$ K; ◆ and ◇, $T = 373.0$ K; —, equation of state results. Solid points represent the liquid phase, and unfilled symbols represent the gas phase.

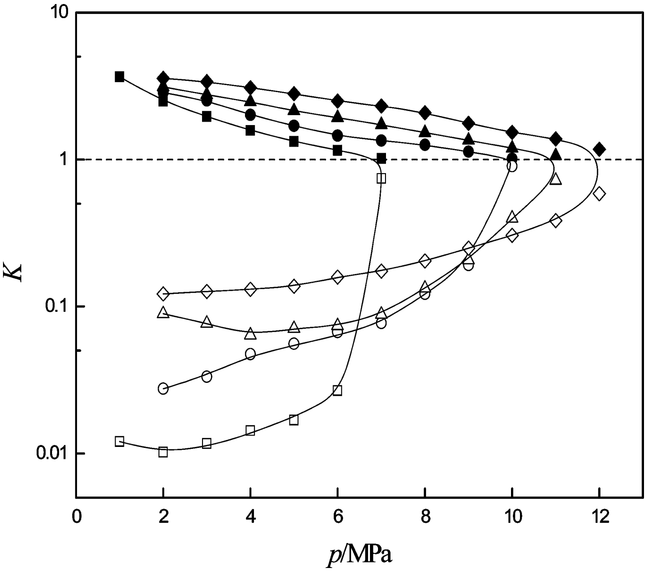

Figure 7. $K-p$ of {carbon dioxide (1) + methyl propionate (2)} at four temperatures: ■ and □, $T = 313.0$ K; ● and ○, $T = 333.0$ K; ▲ and Δ, $T = 353.0$ K; ◆ and ◇, $T = 373.0$ K; ★, estimated critical points; —, equation of state results. Solid points represent the liquid phase, and unfilled symbols represent the gas phase.

Since the experimental temperatures are higher than the critical temperature of CO$_2$ and the pressures are not very high, we can assume reasonably that neglecting all gas-phase nonideality as well as the effect of pressure on the liquid and also neglecting the interactions between solute and solvent because CO$_2$ and the esters are all nonpolar. Using the data in Table 1 and Table 2, the diagrams with the partial pressures of CO$_2$ in gas phases against the mole fractions (solubilities) in the liquid are shown in the figures. From these figures, it was observed that the solubilities of supercritical CO$_2$ in the esters were proportional to its partial pressure in the gas phase in a certain range

$$p_1 = H\cdot x_1 \qquad (15)$$

Table 2. Equation of State Parameters and Errors in Calculated Pressure p_{are} and Mole Fraction y_{are} for {Carbon Dioxide (1) + Methyl Propionate (2)} and {Carbon Dioxide (1) + Propyl Propionate (2)} at Temperature T

{carbon dioxide (1) + methyl propionate (2)}					{carbon dioxide (1) + propyl propionate (2)}				
T/K	k_{12}	c_{12}	$^a p_{ARE}$/%	$^b y_{ARE}$/%	T/K	k_{12}	c_{12}	$^a p_{ARE}$/%	$^b y_{ARE}$/%
313.0	0.12	−0.16	8.09	1.04	313.0	0.13	−0.10	7.67	0.29
333.0	−0.27	−0.05	3.99	0.99	333.0	0.15	−0.09	6.31	1.56
353.0	−0.01	0.40	5.69	1.26	353.0	0.32	−0.10	7.63	2.54
373.0	0.02	0.42	3.36	0.93	373.0	0.09	−0.02	15.78	4.93

[a] Average relative errors of p: $p_{are} = (\sum_{i=1}^{n} (p_{exp,i} - p_{cal,i})/(p_{exp,i}))/n$. [b] Average relative errors of y: $y_{are} = (\sum_{i=1}^{n} (y_{exp,i} - y_{cal,i})/(y_{exp,i}))/n$.

Table 3. Estimated Critical Pressure P_c, Critical Density ρ_c, and Critical Composition of {Carbon Dioxide (1) + Methyl Propionate (2)} and {Carbon Dioxide (1) + Propyl Propionate (2)} at Critical Temperatures T_c

T_c/K	p_c/MPa	x_1	ρ_c/g·cm^{-3}
{Carbon Dioxide (1) + Methyl Propionate (2)}			
304.0	7.38	1.0000	0.4664
313.0	7.44	0.9103	0.6866
333.0	9.17	0.8921	0.6707
353.0	10.34	0.8377	0.6277
373.0	12.28	0.8275	0.5742
531.0	4.01	0.0000	0.3115
{Carbon Dioxide (1) + Propyl Propionate (2)}			
304.0	7.38	1.0000	0.4664
313.0	7.49	0.9564	0.7242
333.0	10.15	0.9137	0.5980
353.0	11.31	0.8476	0.5750
373.0	12.62	0.7833	0.5516
571.0	3.06	0.0000	0.2940

Table 4. Henry's Coefficients H of {Carbon Dioxide (1) + Methyl Propionate (2)} and {Carbon Dioxide (1) + Propyl Propionate (2)} at Temperatures T

{Carbon Dioxide (1) + Methyl Propionate (2)}				
T/K	313.0	333.0	353.0	373.0
H/MPa	9.53	10.72	17.05	14.94
{Carbon Dioxide (1) + Propyl Propionate (2)}				
T/K	313.0	333.0	353.0	373.0
H/MPa	8.40	10.43	21.78	32.74

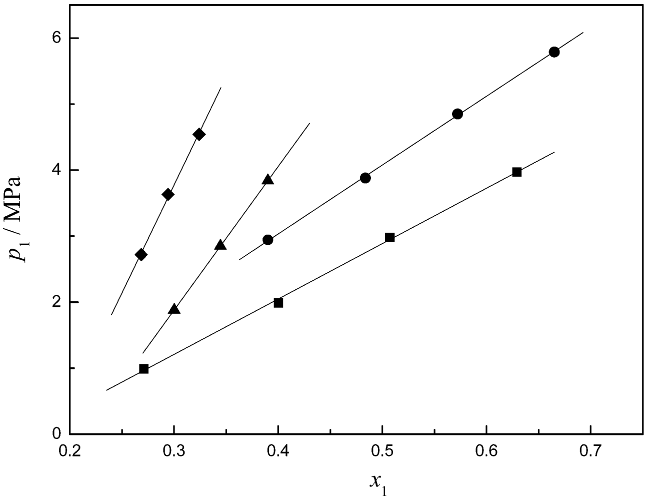

Figure 9. p_1−x_1 of {carbon dioxide (1) + propyl propionate (2)} in the linear range at four temperatures: ■, T = 313.0 K; ●, T = 333.0 K; ▲, T = 353.0 K; ◆, T = 373.0 K; —, estimated from an equation of state.

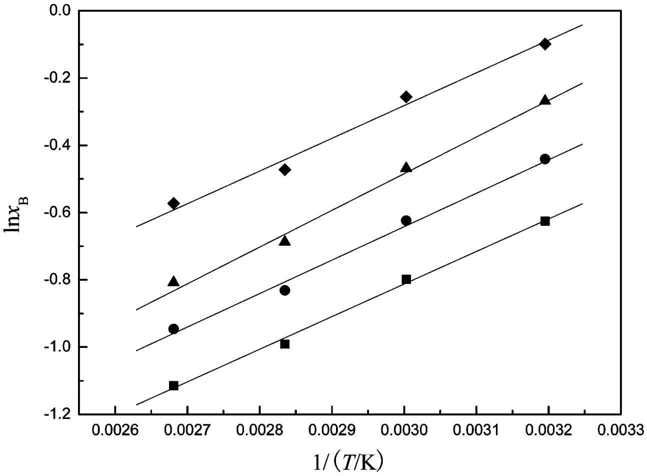

Figure 10. ln x_B as a function of 1/T for the {carbon dioxide (1) + methyl propionate (2)} system at four pressures: ■, p = 3.00 MPa; ●, p = 4.00 MPa; ▲, p = 5.00 MPa; ◆, p = 7.00 MPa; —, results obtained from an equation of state.

where H is Henry's coefficient which only depends on the temperature. The H values at four temperatures for the two systems were listed in Table 4, and $p_{CO_2} \sim x_1$ lines were presented in Figure 8 and Figure 9. At the constant temperature, the H value is constant; i.e., the relations between p_{CO_2} and x_1 are linear and the fitting correlation coefficients are all greater than 0.9990. From Figure 10 and Figure 11, it was shown that Henry's law appeared to hold to high pressures and large solubilities for the investigated SC-CO$_2$ and ester systems.

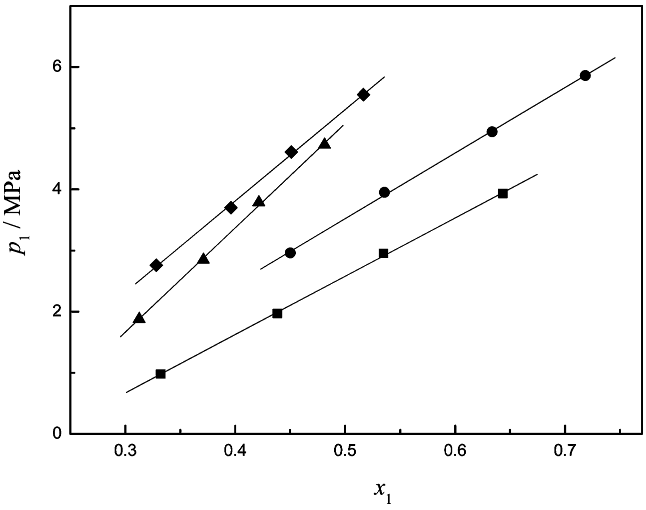

Figure 8. p_1−x_1 of {carbon dioxide (1) + methyl propionate (2)} in the linear range at four temperatures: ■, T = 313.0 K; ●, T = 333.0 K; ▲, T = 353.0 K; ◆, T = 373.0 K; —, estimated from an equation of state.

2. Effect of Temperature on the Solubility of SC CO$_2$ in the Esters. From Table 1, Figure 2, and Figure 3, it can be observed that the solubilities of SC-CO$_2$ in esters decrease with rising temperature at the constant pressures. The temperature derivative of the solubility, as calculated from the Gibbs−Helmholtz equation, is directly related to either the partial molar enthalpy or the partial molar entropy of the gaseous solute in the liquid phase. If there are no

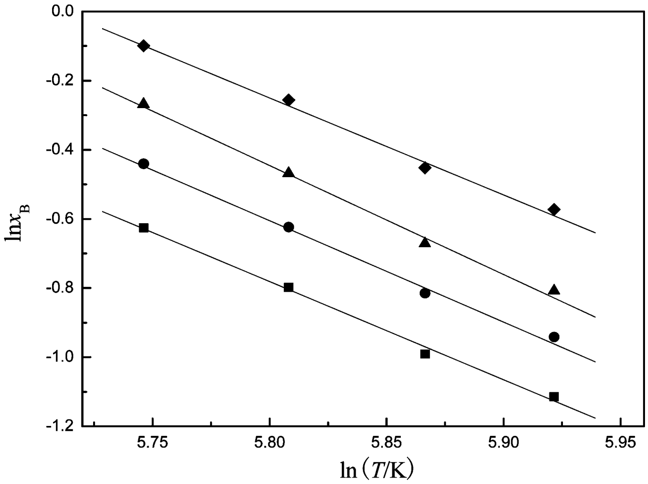

Figure 11. ln x_B as a function of ln T for the {carbon dioxide (1) + methyl propionate (2)} system at four pressures: ■, p = 3.00 MPa; ●, p = 4.00 MPa; ▲, p = 5.00 MPa; ◆, p = 7.00 MPa; —, results obtained from an equation of state.

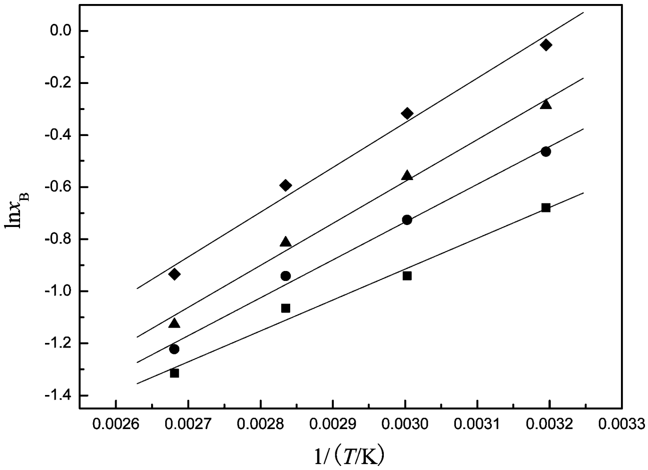

Figure 12. ln x_B as a function of 1/T for the {carbon dioxide (1) + propyl propionate (2)} system at four pressures: ■, p = 3.00 MPa; ●, p = 4.00 MPa; ▲, p = 5.00 MPa; ◆, p = 7.00 MPa; —, results obtained from an equation of state.

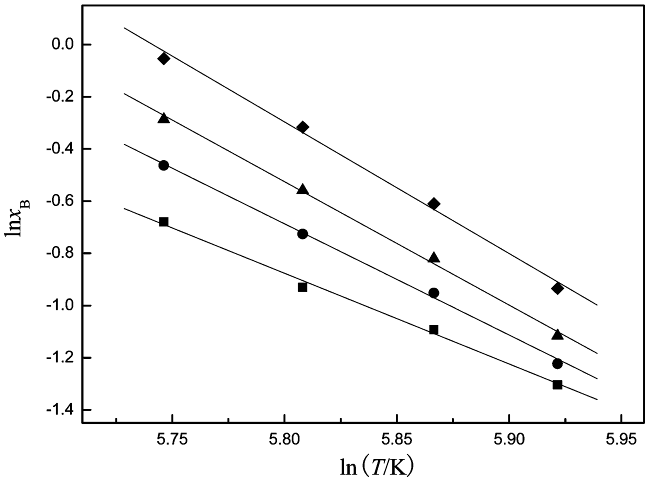

Figure 13. ln x_B as a function of ln T for the {carbon dioxide (1) + propyl propionate (2)} system at four pressures: ■, p = 3.00 MPa; ●, p = 4.00 MPa; ▲, p = 5.00 MPa; ◆, p = 7.00 MPa; —, results obtained from an equation of state.

Table 5. Partial Molar Enthalpy Change (ΔH_B) and Partial Molar Entropy change (ΔS_B) of {Carbon Dioxide (1) + Methyl Propionate (2)} and {Carbon Dioxide (1) + Propyl Propionate (2)} at Pressure *P*

p/MPa	ΔH_B/kJ·mol^{-1}	ΔS_B/J·mol^{-1}
{Carbon Dioxide (1) + Methyl Propionate (2)}		
3.00	−8.06	−23.62
4.00	−8.28	−24.38
5.00	−9.07	−26.20
7.00	−8.09	−23.33
{Carbon Dioxide (1) + Propyl Propionate (2)}		
3.00	−9.87	−28.89
4.00	−12.09	−35.43
5.00	−13.40	−39.29
7.00	−14.28	−41.94

specific chemical interactions and solvations between solute and solvent, it can be obtained by the equation

$$\left\{\frac{\partial \ln x_B}{\partial\left(\frac{1}{T}\right)}\right\}_p = -\frac{\Delta H_B}{R} \tag{16}$$

and

$$\left\{\frac{\partial \ln x_B}{\partial \ln T}\right\}_p = \frac{\Delta S_B}{R} \tag{17}$$

where x_B is the mole fraction of gaseous CO_2 (solute) at saturation and ΔH_B and ΔS_B are the partial molar enthalpy change and the partial molar entropy change of CO_2 during dissolution, respectively. The fitted lines are shown in Figure 10 to Figure 13, and the calculated ΔH_B and ΔS_B are listed in Table 5.

To understand the significance of the enthalpy and entropy change, it is convenient to divide the dissolution process into two parts: condensation and mixing. The latter is commonly much lower in quantity. Since CO_2 is readily soluble (relatively a large x_1) and its temperature coefficient of solubility is negative and large in quantity, the enthalpy of condensation of pure solute dominates the dissolution process. It shows that the difference in cohesive energy densities is very small.

Conclusions

VLE data for (carbon dioxide + methyl propionate) and (carbon dioxide + propyl propionate) were measured at temperatures of 313.0 K, 333.0 K, 353.0 K, and 373.0 K at pressures up to 12.00 MPa. The experimental results were also correlated with the Peng−Robinson equation of state with the two-parameter van der Waals mixing rule and obtained a good agreement. At the same time, the densities and mole volumes of vapor and liquid phases for the two binary systems are presented in this paper. Furthermore, the Henry's coefficients (H), dissolution enthalpy (ΔH_B), and dissolution entropy (ΔS_B) of SC CO_2 in the esters at different temperature were also calculated.

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