

ARTICLE

Vapor-Liquid Equilibrium Data of Carbon Dioxide+Methyl Propionate and Carbon Dioxide+Propyl Propionate Systems

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High-pressure vapor-liquid equilibrium data for the binary systems of methyl propionate+carbon dioxide and propyl propionate+carbon dioxide were measured at pressure from 1.00 MPa to 12.00 MPa and temperature in the range from 313 K to 373 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, partial molar enthalpy change and partial molar entropy change of CO₂ during dissolution at different temperature were also calculated.

Key words: Carbon dioxide, Methyl propionate, Propyl propionate, Vapor-liquid equilibrium data, Henry's coefficient

I. INTRODUCTION

CO₂ is used in biochemical engineering, pharmaceutical industry, and food industry because it is an inexpensive, nontoxic, and environmentally benign solvent. Vapor-liquid equilibrium (VLE) data containing supercritical CO₂ are important for the design, development, and operation of supercritical fluid separation processes [1, 2]. Several review articles on high-pressure fluid phase equilibrium experimental methods and systems have been published [3–5]. Acrylate is one of critical materials in organic synthesis intermediates, polymers and natural rubber latex. Supercritical CO₂ is used to substitute for traditional toxic organic solvents in solution rafting modification of natural rubber [6].

Vapor-liquid equilibrium data of supercritical CO₂ and acrylate are very important for improvement of grafting modification technology, but high pressure phase equilibrium data have not been published. In this study, we measured the VLE data for two binary mixtures of carbon dioxide with methyl propionate and propyl propionate by using the high-pressure vapor-liquid equilibrium measurement apparatus. The experimental temperatures are 313, 333, 353, and 373 K with pressure range from 1 MPa to 12 MPa. At the same time, the Henry's coefficient, partial molar enthalpy and partial molar entropy of CO₂ during dissolution at different temperature were also calculated.

II. EXPERIMENTS

A. Materials and their purities

Carbon dioxide (molar fraction purity >0.9999) was provided by Tianjin Gas Company and the methyl propionate and propyl propionate (mass fraction purity >0.9985) were supplied by Aladdin Reagent Company. They were degassed before use at 268 K for 2 h.

B. Experimental apparatus and procedures

In this work, the main part of the experimental apparatus is a high-pressure view cell of 100 cm³. There is a moveable piston inside the cylinder autoclave [7, 8]. The piston separates the content in the cell from the pressure medium. The pressure is generated with a manually 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 is attached to the front of the cell to permit full visibility of all the contents in the cell. The contents inside the autoclave were stirred with a magnetic stirrer. 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

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dioxide was pressured into the cell. 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 the liquid and vapor phases were taken from the lower and the upper valves respectively, and then got 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 was weighted using a balance with an accuracy of 0.1 mg.

The volume of the sample was determined by measuring the distance Δl between the positions of the piston before and after taking the sample, 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 volume of the sample Δl was ± 0.1 mm. The cooled vessel of the sample was connected to a glass bulb of known volume. The bulb's temperature was measured with a thermometer. The pressure inside bulb was measured with an absolute-pressure meter with a precision of 10 Pa. Because the pressure of the desorbed gas was very low (10–20 kPa), the mass of CO₂ was easily calculated using the equation of state of an ideal gas. The mass of CO₂ was also calculated using a mass different method (the mass of vessel before being connected to the glass bulb minus the mass of the vessel after desorbed CO₂). 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 mixture were obtained from the densities and the molar fractions of two phases. The above procedures were all repeated for three times. The experimental data listed in Table I and Table II are the mean value of the measurements. The estimated uncertainty of the molar fractions of the vapor and liquid phases is below 0.1%. The uncertainty of reported densities and molar volumes are estimated to be within $\pm 0.5\%$.

C. 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 [9–11]

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

where p , T , and V_m respectively represent the pressure, temperature, and molar volume. R is the mole gas con-

stant, b is the co-volume parameter, and a is the energy parameter.

For a pure fluid, the parameter b is given by

$$b = 0.07780 \frac{RT_c}{p_c} \quad (2)$$

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

$$a(T) = a(T_c)\alpha(T) \quad (3)$$

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

$$\alpha(T) = \left[1 + k(1 - T_r^{1/2}) \right]^2 \quad (5)$$

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

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (6)$$

$(0 \leq \omega \leq 0.5)$

The critical data ($p_{c,i}$, $T_{c,i}$) were taken from the literature, and the acentric factors (ω) can be obtained by fitting the functions to vapor pressure data [8].

For a binary mixture, the common procedure is to write mixing rules that are quadratic in molar fraction [12]:

$$b_M = g_1^2 b_1 + g_2^2 b_2 + 2g_1 g_2 b_{12} \quad (7)$$

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

where g_i is either x or y , 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:

$$b_{12} = \frac{1}{2}(b_1 + b_2)(1 - c_{12}) \quad (9)$$

$$a_{12}(T) = [a_1(T)a_2(T)]^{1/2}(1 - k_{12}) \quad (10)$$

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

$$\ln \phi_i = \frac{b_i}{b_M} \left(\frac{pV_m}{RT} - 1 \right) - \ln \frac{p(V_m - b_M)}{RT} - \frac{a_M}{2\sqrt{2}b_M RT} \left(\frac{2}{a_M} \sum_i g_i a_{12} - \frac{b_i}{b_M} \right) \cdot \ln \frac{V_m + (1 + \sqrt{2})b_M}{V_m + (1 - \sqrt{2})b_M} \quad (11)$$

For a binary liquid mixture at temperature T and pressure p with molar fractions x_1 and x_2 in equilibrium

TABLE I Vapor-liquid equilibrium data of CO₂(1)+MP(2) systems at various temperatures and pressures.

| T/K | p/MPa | $x_{1,\text{exp}}$ | $x_{1,\text{cal}}$ | $Dev(x)$ | $y_{1,\text{exp}}$ | $y_{1,\text{cal}}$ | $Dev(y)$ | K_1 | K_2 |
|-------|----------------|--------------------|--------------------|----------|--------------------|--------------------|----------|--------|--------|
| 313 | 1.00 | 0.3321 | 0.3329 | -0.0008 | 0.9812 | 0.9836 | -0.0024 | 2.9545 | 0.0281 |
| | 2.00 | 0.4384 | 0.4394 | -0.0010 | 0.9852 | 0.9875 | -0.0023 | 2.2473 | 0.0264 |
| | 3.00 | 0.5349 | 0.5390 | -0.0041 | 0.9819 | 0.9895 | -0.0076 | 1.8357 | 0.0389 |
| | 4.00 | 0.6435 | 0.6502 | -0.0067 | 0.9819 | 0.9922 | -0.0103 | 1.5259 | 0.0508 |
| | 5.00 | 0.7649 | 0.7802 | -0.0153 | 0.9753 | 0.9948 | -0.0195 | 1.2751 | 0.1051 |
| | 6.00 | 0.8355 | 0.8512 | -0.0157 | 0.9660 | 0.9842 | -0.0182 | 1.1562 | 0.2067 |
| | 7.00 | 0.9058 | 0.8989 | 0.0069 | 0.9137 | 0.9067 | 0.0070 | 1.0087 | 0.9161 |
| 333 | 3.00 | 0.4501 | 0.4471 | 0.0030 | 0.9870 | 0.9805 | 0.0065 | 2.1928 | 0.0236 |
| | 4.00 | 0.5358 | 0.5333 | 0.0025 | 0.9874 | 0.9829 | 0.0045 | 1.8429 | 0.0271 |
| | 5.00 | 0.6338 | 0.6320 | 0.0018 | 0.9887 | 0.9859 | 0.0028 | 1.5600 | 0.0309 |
| | 6.00 | 0.7185 | 0.7255 | -0.0070 | 0.9774 | 0.9869 | -0.0095 | 1.3603 | 0.0803 |
| | 7.00 | 0.7867 | 0.7989 | -0.0122 | 0.9716 | 0.9867 | -0.0151 | 1.2350 | 0.1331 |
| | 8.00 | 0.8443 | 0.8691 | -0.0248 | 0.9495 | 0.9774 | -0.0279 | 1.1246 | 0.3243 |
| | 9.00 | 0.8821 | 0.8742 | 0.0079 | 0.9025 | 0.8944 | 0.0081 | 1.0231 | 0.8270 |
| 353 | 2.00 | 0.3125 | 0.3165 | -0.0040 | 0.9422 | 0.9543 | -0.0121 | 3.0150 | 0.0841 |
| | 3.00 | 0.3711 | 0.3739 | -0.0028 | 0.9502 | 0.9574 | -0.0072 | 2.5605 | 0.0792 |
| | 4.00 | 0.4215 | 0.4255 | -0.0040 | 0.9486 | 0.9575 | -0.0089 | 2.2505 | 0.0889 |
| | 5.00 | 0.4811 | 0.4890 | -0.0079 | 0.9456 | 0.9611 | -0.0155 | 1.9655 | 0.1048 |
| | 6.00 | 0.5563 | 0.5630 | -0.0067 | 0.9460 | 0.9574 | -0.0114 | 1.7005 | 0.1217 |
| | 7.00 | 0.6038 | 0.6136 | -0.0098 | 0.9420 | 0.9573 | -0.0153 | 1.5601 | 0.1464 |
| | 8.00 | 0.6866 | 0.6912 | -0.0046 | 0.9352 | 0.9415 | -0.0063 | 1.3621 | 0.2068 |
| | 9.00 | 0.7392 | 0.7373 | 0.0019 | 0.9023 | 0.9000 | 0.0023 | 1.2206 | 0.3746 |
| | 10.00 | 0.8125 | 0.7924 | 0.0201 | 0.8601 | 0.8388 | 0.0213 | 1.0586 | 0.7461 |
| 373 | 3.00 | 0.3282 | 0.3304 | -0.0022 | 0.9213 | 0.9275 | -0.0062 | 2.8071 | 0.1171 |
| | 4.00 | 0.3961 | 0.4003 | -0.0042 | 0.9255 | 0.9353 | -0.0098 | 2.3365 | 0.1234 |
| | 5.00 | 0.4511 | 0.4581 | -0.0070 | 0.9228 | 0.9371 | -0.0143 | 2.0457 | 0.1406 |
| | 6.00 | 0.5166 | 0.5251 | -0.0085 | 0.9246 | 0.9399 | -0.0153 | 1.7898 | 0.1560 |
| | 7.00 | 0.5685 | 0.5785 | -0.0100 | 0.9222 | 0.9385 | -0.0163 | 1.6222 | 0.1803 |
| | 8.00 | 0.6251 | 0.6331 | -0.0080 | 0.9189 | 0.9306 | -0.0117 | 1.4700 | 0.2163 |
| | 9.00 | 0.6694 | 0.6678 | 0.0016 | 0.9123 | 0.9102 | 0.0021 | 1.3629 | 0.2653 |
| | 10.00 | 0.7097 | 0.7189 | -0.0092 | 0.9011 | 0.9128 | -0.0117 | 1.2697 | 0.3407 |
| | 11.00 | 0.7523 | 0.7477 | 0.0046 | 0.8845 | 0.8791 | 0.0054 | 1.1757 | 0.4663 |
| | 12.00 | 0.8121 | 0.8034 | 0.0087 | 0.8432 | 0.8342 | 0.0090 | 1.0383 | 0.8345 |

$$Dev(x)=x_{\text{exp}}-x_{\text{cal}}, Dev(y)=y_{\text{exp}}-y_{\text{cal}}.$$

with its vapor with molar fractions y_1 and y_2 , the equilibrium equations are

$$f_1^v = f_1^l \quad \text{or} \quad \phi_1^v y_1 = \phi_1^l x_1 \quad (12)$$

$$f_2^v = f_2^l \quad \text{or} \quad \phi_2^v y_2 = \phi_2^l x_2 \quad (13)$$

where f is fugacity and ϕ is coefficient of fugacity.

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

$$F = 5 \sum_{i=1}^N \left(\frac{p - p_{\text{cal}}}{p} \right)^2 + \sum_{i=1}^N \sum_{j=1}^M \left(\frac{y_j - y_{j,\text{cal}}}{y_j} \right)^2 \quad (14)$$

where the subscript cal represent calculated values.

III. RESULTS AND DISCUSSION

Isothermal vapor-liquid equilibrium data of carbon dioxide (CO₂)+methyl propionate (MP) and CO₂+propyl propionate (PP) (CO₂(1)+MP(2) and CO₂(1)+PP(2)) systems were measured at 313, 333, 353, and 373 K at pressures between 1.00 and 12.00 MPa. The results are listed in Tables I and II, where x_1 and y_1 are the molar fractions of CO₂ in the liquid phase and vapor phase, respectively. The correlated results of two binary systems with the Peng-Robinson equation of state and the conventional mixing rules are listed in Table III.

Figures 1 and 2 give the p - x diagrams of CO₂(1)+MP(2) and CO₂(1)+PP(2), respectively. Changes of

TABLE II Vapor-liquid equilibrium data of CO₂(1)+PP(2) systems at various temperatures and pressures.

| T/K | p/MPa | $x_{1,\text{exp}}$ | $x_{1,\text{cal}}$ | $Dev(x)$ | $y_{1,\text{exp}}$ | $y_{1,\text{cal}}$ | $Dev(y)$ | K_1 | K_2 |
|-------|----------------|--------------------|--------------------|----------|--------------------|--------------------|----------|--------|--------|
| 313 | 1.00 | 0.2710 | 0.2647 | 0.0063 | 0.9892 | 0.9662 | 0.0230 | 3.6502 | 0.0148 |
| | 2.00 | 0.4001 | 0.4012 | -0.0011 | 0.9942 | 0.9970 | -0.0028 | 2.4849 | 0.0097 |
| | 3.00 | 0.5071 | 0.5087 | -0.0016 | 0.9941 | 0.9973 | -0.0032 | 1.9604 | 0.0120 |
| | 4.00 | 0.6290 | 0.6320 | -0.0030 | 0.9928 | 0.9976 | -0.0048 | 1.5784 | 0.0194 |
| | 5.00 | 0.7510 | 0.7514 | -0.0004 | 0.9976 | 0.9982 | -0.0006 | 1.3284 | 0.0096 |
| | 6.00 | 0.8616 | 0.8635 | -0.0019 | 0.9963 | 0.9985 | -0.0022 | 1.1563 | 0.0267 |
| | 7.00 | 0.9475 | 0.9436 | 0.0039 | 0.9610 | 0.9570 | 0.0040 | 1.0142 | 0.7429 |
| 333 | 2.00 | 0.3446 | 0.3487 | -0.0041 | 0.9819 | 0.9937 | -0.0118 | 2.8494 | 0.0276 |
| | 3.00 | 0.3901 | 0.3947 | -0.0046 | 0.9812 | 0.9929 | -0.0117 | 2.5153 | 0.0308 |
| | 4.00 | 0.4837 | 0.4951 | -0.0114 | 0.9700 | 0.9928 | -0.0228 | 2.0054 | 0.0581 |
| | 5.00 | 0.5720 | 0.5853 | -0.0133 | 0.9700 | 0.9926 | -0.0226 | 1.6958 | 0.0701 |
| | 6.00 | 0.6650 | 0.6832 | -0.0182 | 0.9653 | 0.9918 | -0.0265 | 1.4516 | 0.1036 |
| | 7.00 | 0.7286 | 0.7367 | -0.0081 | 0.9811 | 0.9920 | -0.0109 | 1.3466 | 0.0696 |
| | 8.00 | 0.7741 | 0.7854 | -0.0113 | 0.9725 | 0.9867 | -0.0142 | 1.2563 | 0.1217 |
| 353 | 9.00 | 0.8615 | 0.8708 | -0.0093 | 0.9735 | 0.9840 | -0.0105 | 1.1300 | 0.1913 |
| | 10.00 | 0.9049 | 0.9006 | 0.0043 | 0.9145 | 0.9101 | 0.0044 | 1.0106 | 0.8991 |
| | 2.00 | 0.3001 | 0.3159 | -0.0158 | 0.9375 | 0.9870 | -0.0495 | 3.1240 | 0.0893 |
| | 3.00 | 0.3446 | 0.3578 | -0.0132 | 0.9496 | 0.9859 | -0.0363 | 2.7557 | 0.0769 |
| | 4.00 | 0.3901 | 0.3998 | -0.0097 | 0.9610 | 0.9848 | -0.0238 | 2.4635 | 0.0639 |
| | 5.00 | 0.4477 | 0.4582 | -0.0105 | 0.9609 | 0.9835 | -0.0226 | 2.1463 | 0.0708 |
| | 6.00 | 0.5007 | 0.5103 | -0.0096 | 0.9631 | 0.9816 | -0.0185 | 1.9235 | 0.0739 |
| 373 | 7.00 | 0.5583 | 0.5686 | -0.0103 | 0.9609 | 0.9786 | -0.0177 | 1.7211 | 0.0885 |
| | 8.00 | 0.6241 | 0.6384 | -0.0143 | 0.9499 | 0.9716 | -0.0217 | 1.5220 | 0.1333 |
| | 9.00 | 0.6939 | 0.7056 | -0.0117 | 0.9364 | 0.9522 | -0.0158 | 1.3495 | 0.2078 |
| | 10.00 | 0.7545 | 0.7210 | 0.0335 | 0.9023 | 0.8623 | 0.0400 | 1.1959 | 0.3980 |
| | 11.00 | 0.8198 | 0.7977 | 0.0221 | 0.8701 | 0.8467 | 0.0234 | 1.0614 | 0.7209 |
| | 2.00 | 0.2551 | 0.2742 | -0.0191 | 0.9093 | 0.9774 | -0.0681 | 3.5645 | 0.1218 |
| | 3.00 | 0.2685 | 0.2877 | -0.0192 | 0.9073 | 0.9723 | -0.0650 | 3.3791 | 0.1267 |
| 373 | 4.00 | 0.2943 | 0.3138 | -0.0195 | 0.9075 | 0.9676 | -0.0601 | 3.0836 | 0.1311 |
| | 5.00 | 0.3240 | 0.3434 | -0.0194 | 0.9073 | 0.9617 | -0.0544 | 2.8003 | 0.1371 |
| | 6.00 | 0.3599 | 0.3814 | -0.0215 | 0.8984 | 0.9520 | -0.0536 | 2.4962 | 0.1587 |
| | 7.00 | 0.3865 | 0.4045 | -0.0180 | 0.8932 | 0.9348 | -0.0416 | 2.3110 | 0.1741 |
| | 8.00 | 0.4242 | 0.4327 | -0.0085 | 0.8824 | 0.9000 | -0.0176 | 2.0802 | 0.2042 |
| | 9.00 | 0.4968 | 0.4861 | 0.0107 | 0.8744 | 0.8555 | 0.0189 | 1.7601 | 0.2496 |
| | 10.00 | 0.5686 | 0.5371 | 0.0315 | 0.8686 | 0.8204 | 0.0482 | 1.5276 | 0.3046 |
| 373 | 11.00 | 0.6172 | 0.5689 | 0.0483 | 0.8532 | 0.7865 | 0.0667 | 1.3824 | 0.3835 |
| | 12.00 | 0.7036 | 0.6655 | 0.0381 | 0.8268 | 0.7820 | 0.0448 | 1.1751 | 0.5843 |

the p - x diagrams were consistent with that of general binary system. Solubilities of CO₂ in acrylate increase with rising pressure at the given temperature, which results in the decrease of density and molar volume in the liquid phase. In addition, the increasing concentration of acrylate in vapor phase with increasing pressure leads to the increasing densities and decreasing molar volumes in the vapor phases. Finally, this behavior makes the properties of the liquid and vapor very close. The cross point of the two lines is the critical pressure, p_c and critical composition, x_c , of systems at this temperature. The estimated critical values are

listed in Table IV.

The vapor-liquid ratio of CO₂(1) and MP(2) or PP(2) are defined as:

$$K_1 = y_1/x_1 \quad (15)$$

$$K_2 = y_2/x_2 \quad (16)$$

They were also calculated and listed in Tables I and II. Figure 3 shows isothermal K - p diagrams. At a constant pressure, K_1 is always larger than K_2 . Lines of K_1 - p and K_2 - p cross in the line of $K=1$, which means $K_1=K_2=1$ at critical point.

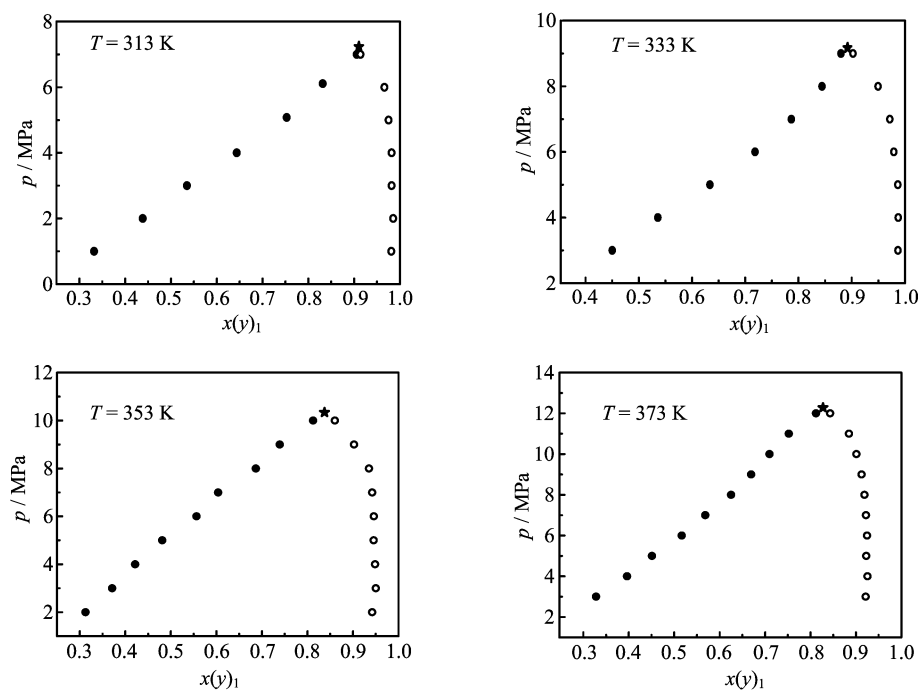


FIG. 1 p - $x(y)_1$ diagrams of CO₂(1)+MP(2) system at four temperatures. Solid points represent the liquid phase, unfilled symbols represent the gas phase.

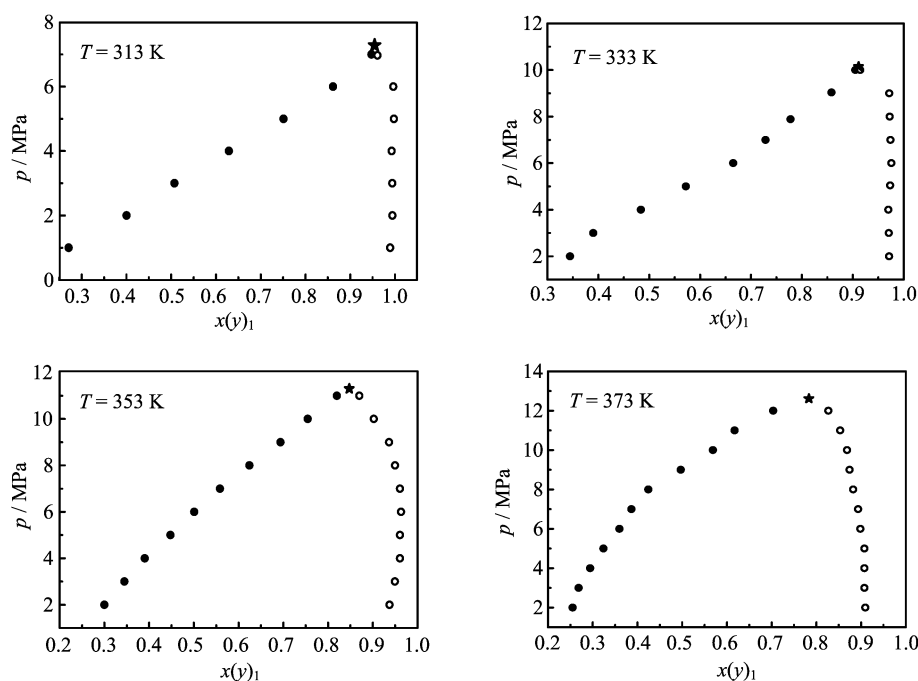


FIG. 2 p - $x(y)_1$ diagrams of CO₂(1)+PP(2) system at four temperatures. Solid points represent the liquid phase, unfilled symbols represent the gas phase.

A. Effect of pressure on the solubility and Henry's coefficients of CO₂ in liquid esters

Since the experimental temperatures are higher than the critical temperature of CO₂ and the pressures are not very high, we can assume reasonably that neglecting

all gas-phase non-ideality as well as the effect of pressure on the liquid, and also neglecting the interactions between solute and solvent because CO₂ and esters are all non-polar. Using the data in Table I, Table II, and Table III, the diagrams with the partial pressures of

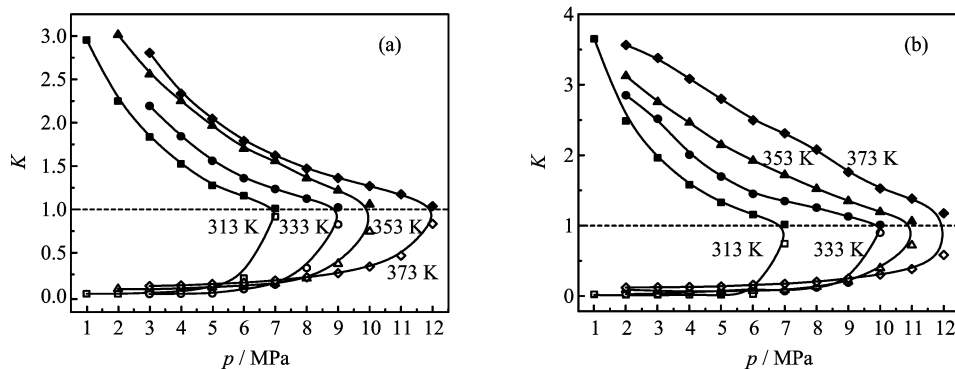


FIG. 3 K - p diagrams of $\text{CO}_2(1)+\text{MP}(2)$ (a) and $\text{CO}_2(1)+\text{PP}(2)$ (b) systems at four temperatures. Solid points represent the liquid phase (K_1), unfilled symbols represent the gas phase (K_2), and solid lines represent the fitted.

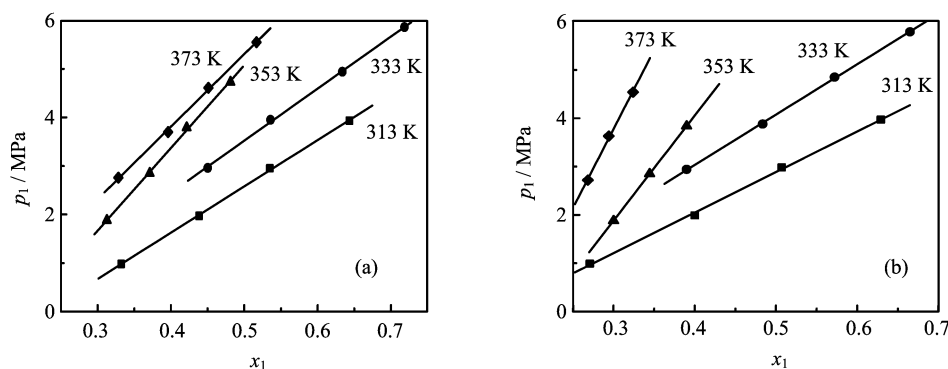


FIG. 4 p_1 - x_1 diagrams of $\text{CO}_2(1)+\text{MP}(2)$ (a) and $\text{CO}_2(1)+\text{PP}(2)$ (b) systems in the linear range at four temperatures. Solid lines represent the fitted.

TABLE III Critical pressure and critical composition of $\text{CO}_2(1)+\text{MP}(2)$ and $\text{CO}_2(1)+\text{PP}(2)$ systems at various temperatures.

| $\text{CO}_2(1)+\text{MP}(2)$ | | | $\text{CO}_2(1)+\text{PP}(2)$ | | |
|-------------------------------|------------------|--------|-------------------------------|------------------|--------|
| T_c/K | p_c/MPa | x_1 | T_c/K | p_c/MPa | x_1 |
| 304 | 7.38 [8] | 1.0000 | 304 | 7.38 [8] | 1.0000 |
| 313 | 7.44 | 0.9103 | 313 | 7.49 | 0.9564 |
| 333 | 9.17 | 0.8921 | 333 | 10.15 | 0.9137 |
| 353 | 10.34 | 0.8377 | 353 | 11.31 | 0.8476 |
| 373 | 12.28 | 0.8275 | 373 | 12.62 | 0.7833 |
| 531 | 4.01 [8] | 0.0000 | 571 | 3.06 [8] | 0.0000 |

CO_2 in gas phases against the mole fractions (solubilities) in the liquid were plotted. It was observed that the solubility of SC-CO_2 in the esters is proportional to its partial pressure in the gas phase in a certain range [13, 14]:

$$p_1 = Hx_1 \quad (17)$$

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 V and p_1 - x_1 lines were presented in Fig.4. At the constant tempera-

TABLE IV Fitted results for two systems $\text{CO}_2(1)+\text{MP}(2)$ and $\text{CO}_2(1)+\text{PP}(2)$.

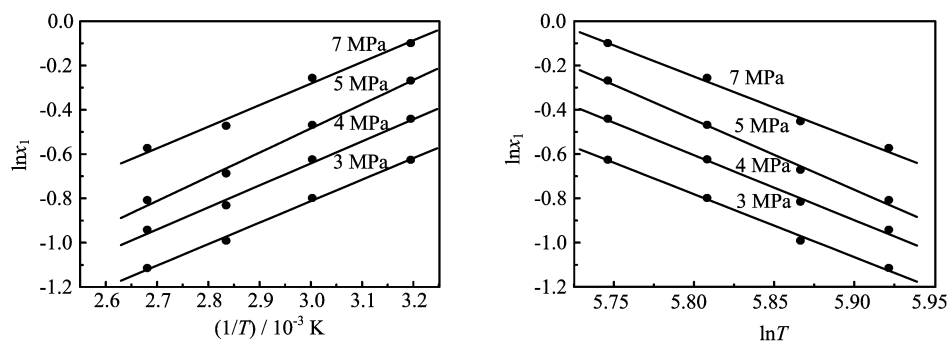
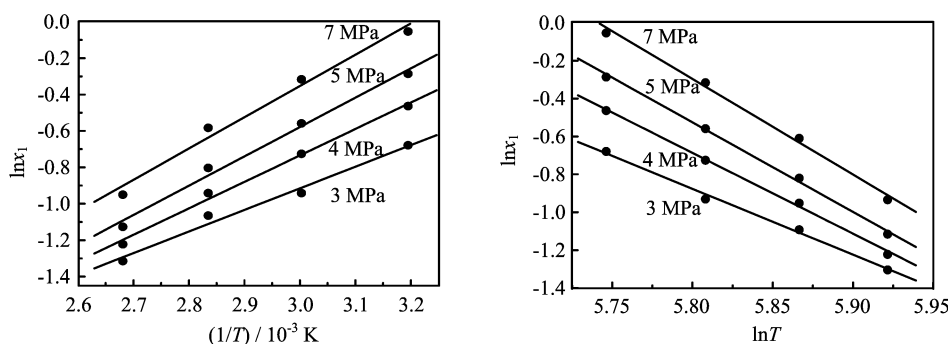
| System | T/K | k_{12} | c_{12} | $p_{\text{ARE}}^{\text{a}}/\%$ | $y_{\text{ARE}}^{\text{b}}/\%$ |
|-------------------------------|--------------|----------|----------|--------------------------------|--------------------------------|
| $\text{CO}_2(1)+\text{MP}(2)$ | 313 | 0.12 | -0.16 | 8.09 | 1.04 |
| | 333 | -0.27 | -0.05 | 3.99 | 0.99 |
| | 353 | -0.01 | 0.40 | 5.69 | 1.26 |
| | 373 | 0.02 | 0.42 | 3.36 | 0.93 |
| $\text{CO}_2(1)+\text{PP}(2)$ | 313 | 0.13 | -0.10 | 7.67 | 0.29 |
| | 333 | 0.15 | -0.09 | 6.31 | 1.56 |
| | 353 | 0.32 | -0.10 | 7.63 | 2.54 |
| | 373 | 0.09 | -0.02 | 15.78 | 4.93 |

^a Average relative errors of p : $p_{\text{ARE}} = \frac{1}{n} \sum_{i=1}^n \frac{p_{\text{exp},i} - p_{\text{cal},i}}{p_{\text{exp},i}}$.

^b Average relative errors of pressure of y :

$$y_{\text{ARE}} = \frac{1}{n} \sum_{i=1}^n \frac{y_{\text{exp},i} - y_{\text{cal},i}}{y_{\text{exp},i}}$$

ture, the H value is constant, *i.e.* the relations between p_1 and x_1 are linear, the fitting correlation coefficients are all greater than 0.9990. From Fig.4, it can be seen that Henry's law appeared to hold to high pressures and large solubilities for the investigated SC-CO_2 and esters systems.

FIG. 5 $\ln x_1-1/T$ and $\ln x_1-\ln T$ diagrams of CO₂(1)+MP(2) systems at four pressures. Solid lines represent the fitted.FIG. 6 $\ln x_1-1/T$ and $\ln x_1-\ln T$ diagrams of CO₂(1)+PP(2) systems at four pressures. Solid lines represent the fitted.TABLE V Henry's coefficients of CO₂(1)+MP(2) and CO₂(1)+PP(2) systems at various temperatures.

| T/K | CO ₂ (1)+MP(2) | | CO ₂ (1)+PP(2) | |
|-----|---------------------------|--------|---------------------------|--------|
| | H | R | H | R |
| 313 | 9.5327 | 0.9998 | 8.3986 | 0.9995 |
| 333 | 10.7225 | 0.9997 | 10.4252 | 0.9999 |
| 353 | 17.0465 | 0.9995 | 21.7777 | 1.0000 |
| 373 | 14.9448 | 0.9995 | 32.7389 | 0.9992 |

TABLE VI Partial molar enthalpy change ΔH_1 (in kJ/mol) and partial molar entropy change ΔS_1 (in J/(mol K)) of CO₂(1)+MP(2) and CO₂(1)+PP(2) systems.

| p/MPa | CO ₂ (1)+MP(2) | | CO ₂ (1)+PP(2) | |
|-------|---------------------------|--------------|---------------------------|--------------|
| | ΔH_1 | ΔS_1 | ΔH_1 | ΔS_1 |
| 3.00 | -8.06 | -23.62 | -9.87 | -28.89 |
| 4.00 | -8.28 | -24.38 | -12.09 | -35.43 |
| 5.00 | -9.07 | -26.20 | -13.40 | -39.29 |
| 7.00 | -8.09 | -23.33 | -14.28 | -41.94 |

B. Effect of temperature on the solubility of SC-CO₂ in the esters

Table I, Table II, Fig.1, and Fig.2 show that the solubilities of SC-CO₂ 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 liquid mixture. If there are no specific chemical interactions and solvation between solute and solvent, it can be obtained by the following equation [15]:

$$\left\{ \frac{\partial \ln x_1}{\partial (1/T)} \right\}_p = -\frac{\Delta H_1}{R} \quad (18)$$

$$\left\{ \frac{\partial \ln x_1}{\partial \ln T} \right\}_p = \frac{\Delta S_1}{R} \quad (19)$$

where x_1 is the molar fraction of gaseous CO₂ (solute) at saturation, ΔH_1 and ΔS_1 are the partial molar enthalpy change and the partial molar entropy change of CO₂ during dissolution, respectively. The fitted lines are shown in Fig.5 and Fig.6, and the calculated ΔH_1 and ΔS_1 are listed in Table VI.

To understand the significance of the enthalpy and entropy change, it is convenient to divided the dissolution process into two parts: condensation and mixing. And the later is common much lower in quantity. Since CO₂ 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 different cohesive energy densities are very small.

IV. CONCLUSION

VLE data for the binary systems of carbon dioxide with methyl propionate and propyl propionate were measured at 313, 333, 353, and 373 K and pressure up to 12 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. Furthermore, the Henry's coefficients H , dissolution enthalpy ΔH_1 , and dissolution entropy ΔS_1 of SC-CO₂ in the esters at different temperature were also calculated.

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