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Pressure−Density−Temperature Behavior of CO_2/Acetone, CO_2/Toluene, and CO_2/Monochlorobenzene Mixtures in the Near-Critical Region

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An isochoric technique was used to perform $P-\rho-T$ measurements of CO_2/acetone, CO_2/toluene, and CO_2/monochlorobenzene mixtures where the mol fraction of CO_2 is 0.9 at temperatures from 313.2 to 393.2 K, the density of mixtures varied from 2.91 to 15.77 mol/L, and the determined pressure ranged from 4.19 to 43.06 MPa. The dew points for the above mixtures were also obtained using a visual observation method. The Peng−Robinson equation of state was used to represent the experimental data, and a good agreement was obtained between experimental data and correlated results.

Introduction

The use of supercritical fluids as solvents is of great interest because of their liquidlike solvency and gaslike transport features; specific interest in CO_2 is magnified by its perceived green properties such as nonflammability, relative nontoxicity, and relative chemical inertness.[1−3] The critical temperature of CO_2 is close to room temperature, and it is naturally abundant, which makes it attractive. However, the dipole of CO_2 is almost zero, rendering poor solvency for polar substances. So, usually modifiers or entrainers are used to improve its solvent character; the characteristics they impart include polarity, aromaticity, chirality, etc.[4]

Acetone, toluene, and monochlorobenzene (MCB) are commonly used solvents in the chemical and polymer industry; they are also commonly used as cosolvents to modify CO_2. Day and Chang et al.[5,6] determined the densities and $P-x-y$ diagram for CO_2/acetone mixtures at temperatures from 291.15 to 313.13 K up to 8 MPa. Giacobbe[7] measured the solubility of CO_2 in acetone at temperatures of 293.15 and 303.15 K up to 1 MPa. Katayama et al.[8] obtained the vapor−liquid data at temperatures of 298.15 and 313.15 K up to 8 MPa for CO_2/acetone mixtures. Sebastin et al.,[9] Ng et al.,[10] Kim et al.,[11] and Tochigi et al.[12] investigated the vapor−liquid equilibria for CO_2/toluene mixtures. Reaves et al.[13] determined the critical properties of CO_2/acetone and CO_2/toluene mixtures. Walther and Maurer[14] measured vapor−liquid equilibrium of CO_2/MCB mixtures. All of these studies were focused on the vapor−liquid equilibrium or the critical-point loci of the mixtures. Undoubtedly, such results can provide us with fundamental information for the use of such mixtures. However for a supercritical fluid, the knowledge of density is of great importance because some other properties of the supercritical fluid such as its solvency are believed to have a more direct relation with density.[15] The main objective of this study is to measure the pressure−density−temperature ($P-\rho-T$) behavior of CO_2/acetone, CO_2/toluene, and CO_2/MCB binary systems in the near-critical region (where the mol fraction of the cosolvent is 0.1). The Peng−Robinson equation of state (PR EOS) was considered with respect to correlating the experimental data.

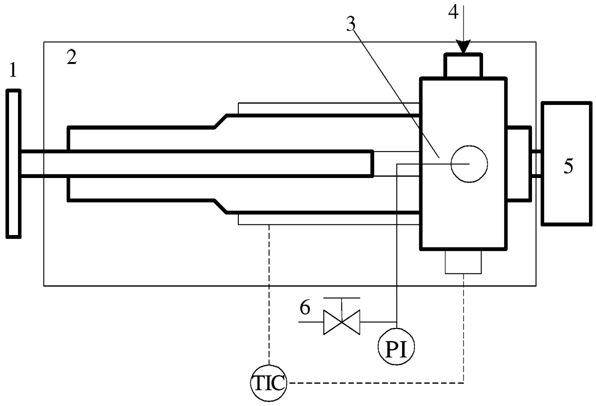

Figure 1. Schematic diagram of phase monitor. 1, Syringe pump; 2, cabinet enclosure; 3, view cell; 4, light source; 5, CCD camera; 6, inlet and outlet where PI is the pressure indicator and TIC is the temperature indicator and controller.

Experimental Section

Materials. Carbon dioxide (purity 99.99%) was purchased from Praxair Specialty Gases and Equipment. Toluene (purity 99.5%) and acetone (purity 99.5%) were purchased from EMC Chemicals, Inc. Monochlorobenzene (purity 99.5%) was purchased from Fisher Chemical Company. All materials were used without further purification.

Apparatus and Method. Figure 1 is the schematic diagram of the phase monitor (Supercritical Fluid Technology, Inc.) used in this study to measure the $P-\rho-T$ behavior and the dew points of CO_2/acetone, CO_2/toluene, and CO_2/MCB systems. A vessel with a total volume of 14 mL was used as an equilibrium cell. There are two quartz windows on the vessel, and a CCD camera was connected to a monitor, which allows the visual observation of the

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phase behavior and liquid level at various conditions. When the liquid meniscus or the last drop of liquid disappears, the dew point appears. The pressure was transmitted by a pressure transducer (±13.8 kPa) to a mounted indicator and then recorded. The fluid temperature was detected by a resistant temperature detector (RTD) with a precision of ±0.1 K. The temperature of the total system was automatically controlled by a temperature-control unit. A magnetic mixer was used to expedite the establishment of phase equilibrium. Fruther details about the apparatus can be found elsewhere.[16]

The $P-\rho-T$ behavior for CO_2/acetone, CO_2/toluene, and CO_2/MCB were measured using an isochoric technique. A certain amount of sample was charged into a fixed volume container, and the temperature was changed in selected increments. When the pressure at each temperature point is measured, an isochore can be obtained. A description of this technique can also be found elsewhere.[17] The mass of the charged sample was determined using a high-precision balance (±0.1 mg). In this study, a high-pressure bomb was used to transfer carbon dioxide to the vessel. The mass of carbon dioxide can be obtained from the mass of the bomb before and after the transferring operation.

The volume of the equilibrium cell was calibrated by using pure CO_2. The experimental procedure was as follows: a given amount of CO_2 was charged into the cell, and then the system was heated to a designated temperature; when the equilibrium was established, the equilibrium pressure and the mass of CO_2 were recorded. According to the density of CO_2 at the temperature and pressure, the volume of the cell was then obtained.

Modeling

For pure CO_2, an equation of state proposed by Huang et al.[18] was used to represent the experimental data and obtain the volume of the view cell by fitting the experimental data, which is a model with 27 parameters developed uniquely for pure CO_2. It was claimed that the density calculation with this equation is reliable to within 0.1−0.2% outside the critical region and to within 1% near the critical point.

For the mixtures involved in this study, first the Sanchez−Lacomb equation of state (SL EOS)[19,20] and the PR EOS[21] were used to correlate the experimental data. SL EOS is a lattice−fluid model proposed by Sanchez and Lacomb originally for polymer−polymer solutions. Recently, it has also been used in systems where supercritical CO_2 is involved.[22,23] When the SL EOS and the PR EOS were used for fitting the experimental data (here, only data in a single phase region was used), the average deviations of pressures for CO_2/acetone mixtures are 5.9 and 2.7%, whereas for CO_2/toluene mixtures, the deviations are 6.3 and 2.1%, respectively, and for CO_2/MCB mixtures are 8.4 and 2.3%, respectively. The average deviation of a property X was calculated by following equation

$$\text{error } \% = \left(\frac{\sum_{i=1}^{N} \left(\frac{X_i^{\text{exp}} - X_i^{\text{cal}}}{X_i^{\text{exp}}} \right)^2}{N} \right)^{1/2} \times 100 \qquad (1)$$

where N is the number of points. The superscript exp denotes the experimental value and cal denotes calculated results by EOSs.

Of the two equations, the PR EOS shows a better correlation of the data. Therefore, the PR EOS was used to describe the further experimental data of this study. The mixing rule of the PR EOS is as follows

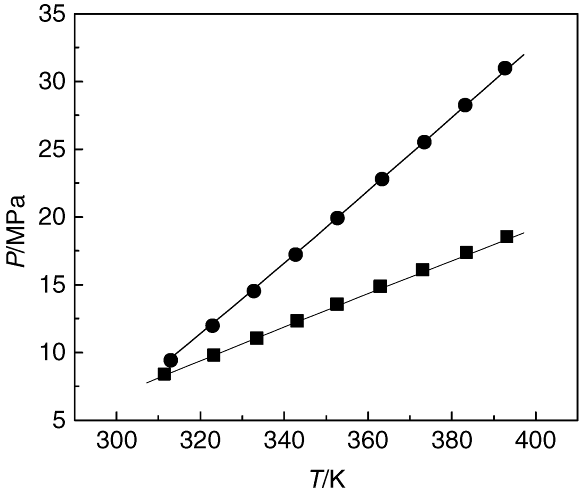

Figure 2. Comparison of experimental data and calculated results. ●, 13.58 mol·L^{-1}; ■, 8.23 mol·L^{-1}; solid line, correlated by EOS (Huang et al.).[18]

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad (2)$$

$$b = \sum_i x_i b_i \qquad (3)$$

$$a_{ij} = (1 - \delta_{ij}) a_i^{1/2} a_j^{1/2} \qquad (4)$$

where x_i is the mole fraction of component i and δ_{ij} is the binary interaction parameter. The values of δ_{ij} were obtained by fitting the present experimental data. The parameters a_i and b_i of pure substances are calculated from critical properties and the acentric factor.

Results and Discussion

To check and confirm the accuracy of the method and apparatus, $P-\rho-T$ measurements were made on pure CO_2 along isochores at densities of 13.58 and 8.23 mol/L. The experimental data are shown in Figure 2, together with the correlation results from the EOS proposed by Huang et al.[18] The volume of the cell was obtained by fitting all the experimental data in Figure 2. The average deviation of the measured pressure is 0.88%, and the maximum deviation is 1.3%. The uncertainty of the volume of the cell was estimated to be less than 1.5%. It can be seen from Figure 2 that the agreement between the experimental data and the correlated results is satisfactory.

Table 1 provides the experimental $P-\rho-T$ data for CO_2/acetone, CO_2/toluene, and CO_2/MCB mixtures, where the mole fraction of CO_2 is 0.9. The estimated uncertainty of the density is less than 1.5%. Figures 3−5 show the isotherms for the CO_2/acetone, CO_2/toluene, and CO_2/MCB mixtures. In these figures, the points with different legends represent the experimental data. The solid lines are the calculated results from the PR EOS, and the dotted lines are the dew point lines. The estimated uncertainties for temperature and pressure at the dew point are less than ±0.5 K and ±0.2 MPa, respectively. Above the dew-point line, the mixture is a single phase. Below the dew point line, the mixture is in the two-phase region. It can be found that the CO_2/acetone system has the largest single-phase area, which implies that acetone has the highest extent of miscibility with CO_2.

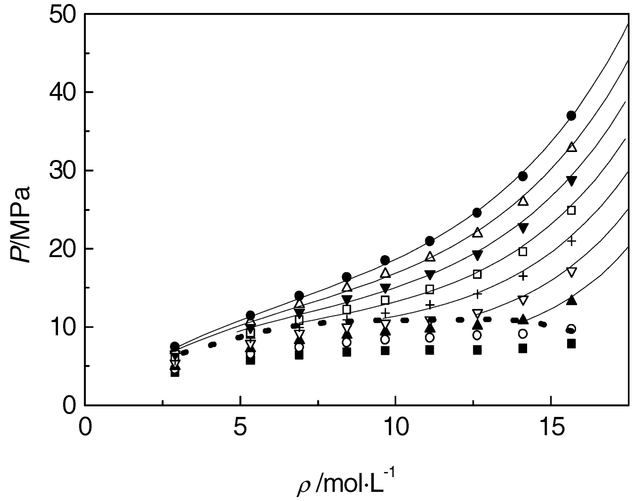

Figure 3. Isotherm for the CO_2−acetone system (mol fraction of CO_2 is 0.9). ●, 393.2 K; △, 383.2 K; ▼, 373.2 K; □, 363.2 K; +, 353.2 K; ▽, 343.2 K; ▲, 333.2 K; ○, 323.2 K; ■, 313.2 K. The dotted line is the dew-point line. Solid lines are correlated results by the PR EOS.

Table 1. Experimental $P-\rho-T$ Data for CO_2/Acetone, CO_2/Toluene, and CO_2/MCB Mixtures (Mol Fraction of CO_2 Is 0.9)

ρ/	T/K								
mol·L^{-1}	313.2	323.2	333.2	343.2	353.2	363.2	373.2	383.2	393.2
	P/MPa								
	CO_2/Acetone								
15.66	7.85	9.68	13.26	17.15	20.99	24.87	28.81	32.84	36.99
14.10	7.22	9.11	10.80	13.55	16.52	19.60	22.77	25.98	29.24
12.63	7.03	8.88	10.10	11.82	14.19	16.71	19.29	21.91	24.57
11.11	7.03	8.59	9.75	10.90	12.82	14.78	16.80	18.85	20.92
9.67	6.95	8.33	9.40	10.44	11.78	13.41	15.08	16.77	18.47
8.43	6.78	7.98	8.96	9.93	10.89	12.19	13.57	14.95	16.33
6.90	6.39	7.39	8.29	9.15	9.95	10.85	11.87	12.90	13.93
5.34	5.76	6.54	7.22	7.88	8.56	9.22	9.93	10.65	11.41
2.91	4.19	4.60	4.98	5.38	5.76	6.14	6.54	6.99	7.42
	CO_2/Toluene								
15.77	8.53	11.00	15.35	19.79	24.39	28.99	33.58	38.33	43.06
13.75	8.04	9.76	11.60	13.68	16.66	19.78	23.11	26.44	29.82
12.25	7.85	9.42	10.96	12.63	14.26	16.38	18.81	21.34	24.00
10.14	7.54	8.95	10.29	11.59	12.85	14.08	15.33	16.89	18.67
8.44	7.19	8.54	9.69	10.73	11.83	12.83	13.81	14.88	15.99
6.70	6.76	7.78	8.71	9.55	10.36	11.19	11.97	12.74	13.50
2.98	4.40	4.74	5.07	5.41	5.74	6.06	6.39	6.77	7.11
	CO_2/MCB								
15.76	9.22	11.00	14.34	18.47	22.85	27.36	31.77	36.29	40.78
13.54	8.28	10.22	12.14	14.03	16.29	19.05	22.12	25.42	28.73
11.95	8.10	9.87	11.67	13.40	15.20	16.89	18.67	20.87	23.37
10.14	7.85	9.47	10.85	12.23	13.66	15.06	16.43	17.84	19.18
8.03	7.51	8.75	9.77	10.76	11.77	12.91	14.03	15.08	16.11
5.84	6.72	7.55	8.28	8.99	9.67	10.31	10.96	11.66	12.49
3.02	4.60	4.94	5.27	5.58	5.93	6.26	6.58	6.93	7.29

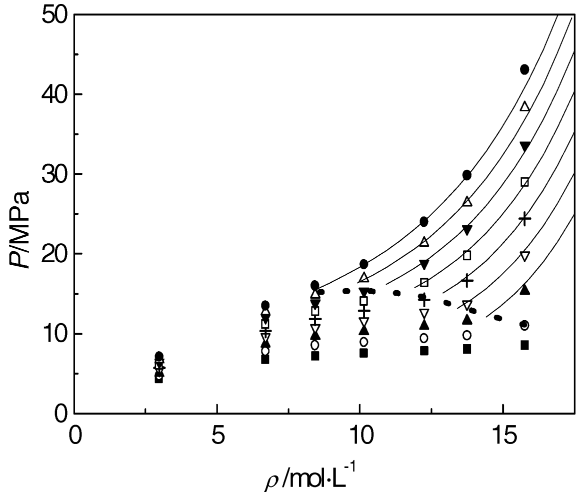

Figure 4. Isotherms of the CO_2−toluene system (mol fraction of CO_2 is 0.9). ●, 393.2 K; △, 383.2 K; ▼, 373.2 K; □, 363.2 K; +, 353.2 K; ▽, 343.2 K; ▲, 333.2 K; ○, 323.2 K; ■, 313.2 K. The dotted line is the dew-point line. Solid lines are correlated results by the PR EOS.

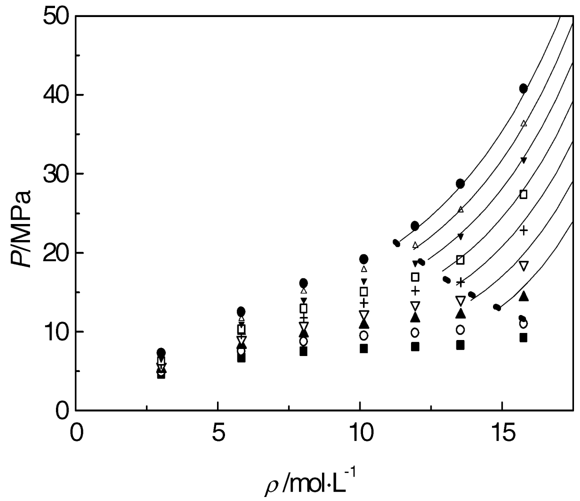

Figure 5. Isotherms of the CO_2−MCB system (mol fraction of CO_2 is 0.9). ●, 393.2 K; △, 383.2 K; ▼, 373.2 K; □, 363.2 K; +, 353.2 K; ▽, 343.2 K; ▲, 333.2 K; ○, 323.2 K; ■, 313.2 K. The dotted line is the dew-point line. Solid lines are correlated results by the PR EOS.

Table 2. Experimental Dew Points for CO_2/Acetone, CO_2/Toluene, and CO_2/MCB mixtures (Mol Fraction of CO_2 Is 0.9)

CO_2/acetone			CO_2/toluene			CO_2/MCB		
ρ	T	P	ρ	T	P	ρ	T	P
mol·L^{-1}	K	MPa	mol·L^{-1}	K	MPa	mol·L^{-1}	K	MPa
15.66	322.1	9.5	15.77	323.6	11.1	15.76	326.6	11.6
14.10	334.4	11.0	13.75	341.2	13.0	13.54	349.0	15.1
12.63	338.2	10.9	12.25	357.0	14.9	11.95	377.4	19.4
11.11	343.0	10.9	10.14	374.4	15.5			
9.67	347.2	10.8	8.44	386.0	15.2			
8.43	352.1	10.8						
6.90	357.1	10.3						
5.39	363.0	9.2						

Table 3 shows the regressed binary interaction parameters of the PR EOS for the mixtures and the deviations of pressures between experimental data and calculated results. It is found that the average deviations of pressures are all at almost the same level (2−3%). The PR EOS was originally developed for real gases, whereas the SL EOS was based on a lattice−fluid model and originally developed for macromolecules. The results of the present study show that the PR EOS has high performance for a system comprised of CO_2 and small molecules under the experimental conditions. In Table 3, only the data for the single-phase region were correlated. However, an attempt was also made to fit all the experimental data with the PR EOS, and the average deviations of pressure for CO_2/acetone, CO_2/toluene, and CO_2/MCB mixtures were 8.4%, 7.9%, and 5.6%, respectively. Higher deviations occurred if all of the experimental data were to be fitted, which mainly resulted from the uncertainty of predicting the phase transformation.

Table 3. Deviations between Experimental Data and Calculated Results

	δ_{ij}	no. data points	average deviation of P^a
CO_2/acetone	−0.03	41	2.7%
CO_2/toluene	0.08	16	2.1%
CO_2/MCB	0.13	12	2.3%

[a] The average deviation of pressure are defined by the following equation,

$$\left(\frac{\sum_{i=1}^{N}\left(\frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{P_i^{\text{exp}}}\right)^2}{N}\right)^{1/2} \times 100$$

in which N is the number of data points

Conclusions

The $P-\rho-T$ data for CO_2/acetone, CO_2/toluene, and CO_2/MCB mixtures (mol fraction of CO_2 is 0.9) were obtained using a phase monitor and dew points for the mixtures were also determined by visual observation. The data obtained were represented fairly well by the PR EOS.

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