

Vapor–Liquid Equilibria of the Carbon Dioxide + Acetone System at Pressures from (2.36 to 11.77) MPa and Temperatures from (333.15 to 393.15) K

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High-pressure phase equilibrium data p , T , x , ρ , and V_m for the binary carbon dioxide + acetone system were measured at several temperatures (333.15, 353.15, 373.15, and 393.15) K and pressures from (2.36 to 11.77) MPa. The experimental data at 333.15 K are in good agreement with literature data, and the experimental results are correlated by the Peng–Robinson equation.

Introduction

Vapor–liquid equilibrium data 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 of its low critical temperature and pressure, nontoxicity, and low cost.

Understanding the phase behavior of a system containing SC CO₂ and a cosolvent is necessary for the evaluation of models. The cosolvents that are typically selected, for example, alkanes, alcohols, esters, or ketones of low molecular weight, are best suited to the extraction of biomaterials, medicines, and foods.

The phase equilibrium for the binary carbon dioxide + acetone system has been studied by many researchers.^{4–6} However, most studies have been limited to temperatures below 333 K. In this work, we have measured the data (p , T , x , V_m) for the carbon dioxide + acetone system at (333.15, 353.15, 373.15, and 393.15) K over a pressure range from (2.36 to 11.77) MPa, and we have measured the density of the vapor and liquid phases at phase equilibria. In addition, we have estimated the critical-point data (p_c , T_c , x_c , V_c).

Materials. Carbon dioxide (mole fraction purity >0.9999) was provided by the Tianjin Gas Company. Acetone (mass fraction purity >0.995) was obtained from Kewei, which was degassed at 268 K under vacuum for 2 h.

Experimental Apparatus and Procedure. The experimental apparatus used for the vapor–liquid equilibrium measurements is shown in Figure 1. There is a moveable piston inside the cylindrical autoclave. The volume of the cylindrical autoclave can be changed by changing the position of the piston. The pressure was generated with a manually operated screw-driven pump and was measured with a pressure sensor. The quartz window allowed us to observe the phase behavior of the contents. The window and piston were each sealed with O-rings (fluorin rubber). To ensure mixing, the contents of the autoclave were stirred with a magnetic stirrer. Circulated water or a heating jacket adjusted the temperature of the

system. The temperature was measured with a calibrated thermocouple inside the cell. The uncertainty of the pressure was ± 0.01 MPa, and the total uncertainty of the temperature was ± 0.1 K.

Before filling the cell with CO₂ and acetone, we pumped the autoclave. The experimental temperature was adjusted using either water or the heating jacket. After the termination of stirring, the phase equilibria were indicated when a constant pressure was maintained for 2 h at the given temperature. Samples of the liquid and vapor phases were taken from the upper and lower valves, respectively, and then placed into a small steel weighed vessel under vacuum through a needle valve and capillary (with known volumes). The samples were weighed to the nearest 0.0001 g. The cooled sample vessel was connected to a glass bulb of known volume. The bulb's temperature was measured with a thermometer. The bulb's pressure was measured with an absolute-pressure meter with a precision of 10 Pa. The quantity of CO₂ was easily calculated using the state equation for an ideal gas. The mass of CO₂ was also calculated using a weight difference method (the mass of the vessel before being connected to the glass bulb minus the mass of the vessel after the desorption of CO₂). The densities of the vapor and liquid were obtained by dividing the appropriate mass by the volume of the vessel. Finally, the mole volume was obtained from the density and the mole fraction.

Results and Discussion

Isothermal vapor–liquid equilibrium data were measured at (333.15, 353.15, 373.15, and 393.15) K at pressures between (2.36 and 11.77) MPa. The results are listed in Table 1, where $x(\text{CO}_2)$ and $y(\text{CO}_2)$ are the mole fractions of carbon dioxide in the liquid phase and vapor phase, respectively, and $\rho(l)$ and $\rho(g)$ are the densities of the liquid phase and vapor phase, respectively. The molar volumes at different T and p were obtained from the densities and

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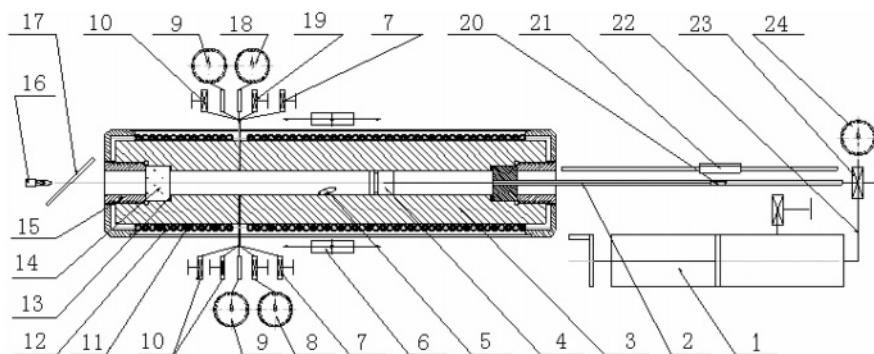


Figure 1. Schematic diagram of the high-pressure apparatus: (1) screw-driven pump; (2) displacement sensor joint pole; (3) autoclave; (4) piston; (5) stirrer; (6) strong magnet; (7) sampling valve; (8) pressure meter for calibration; (9) temperature sensor; (10) input valve; (11) heating jacket; (12) copper tube; (13) O-ring; (14) quartz window; (15) compacting equipment; (16) lamp; (17) viewfinder; (18) pressure sensor; (19) vacuum valve; (20) position sensor; (21) micrometer; (22) oil tube; (23) valve; (24) pressure meter.

Table 1. Experimental Vapor–Liquid Equilibrium Data for the Carbon Dioxide + Acetone System

p MPa	$x(\text{CO}_2)$	$\rho_l \times 10^{-3}$ $\text{kg}\cdot\text{m}^{-3}$	$V_{m,l} \times 10^{-6}$ $\text{m}^3\cdot\text{mol}^{-1}$	$y(\text{CO}_2)$	$\rho_g \times 10^{-3}$ $\text{kg}\cdot\text{m}^{-3}$	$V_{m,g} \times 10^{-6}$ $\text{m}^3\cdot\text{mol}^{-1}$
333.15 K						
8.47	0.8349	0.8011	53.67	0.9442	0.4720	86.90
7.47	0.7299	0.8149	55.09	0.9643	0.1944	209.13
6.47	0.6592	0.8128	56.80	0.9674	0.1503	270.12
5.46	0.6097	0.8146	57.77	0.9656	0.1123	361.81
4.46	0.5499	0.8044	59.85	0.9616	0.0860	473.30
3.46	0.4724	0.7886	62.82	0.9551	0.0595	686.07
2.36	0.3254	0.7704	67.76	0.9421	0.0397	1034.16
8.85 ^a	0.9266	0.7200	57.41	0.9266	0.7200	57.41
353.15 K						
9.27	0.7401	0.7916	56.48	0.9294	0.4332	95.30
8.97	0.7035	0.8158	55.61	0.9483	0.3352	122.15
7.97	0.6729	0.8189	56.08	0.9514	0.2120	192.87
6.97	0.6379	0.8078	57.63	0.9487	0.1668	245.43
5.96	0.5970	0.7994	59.16	0.9519	0.1214	336.73
4.96	0.5624	0.7948	60.29	0.9448	0.0934	439.05
3.96	0.4857	0.7854	62.77	0.9337	0.0720	572.33
9.74 ^a	0.8854	0.6800	61.88	0.8854	0.6800	61.88
373.15 K						
10.47	0.7196	0.7604	59.28	0.8918	0.4050	103.62
9.97	0.6787	0.7666	59.77	0.9054	0.3169	131.65
8.47	0.6279	0.7591	61.56	0.9177	0.2119	195.82
7.38	0.6097	0.7497	62.78	0.9217	0.1440	287.67
5.97	0.5750	0.7257	65.72	0.9229	0.1017	407.11
2.96	0.3919	0.6849	74.46	0.8984	0.0494	847.08
10.95 ^a	0.8377	0.6150	69.83	0.8377	0.6150	69.83
393.15 K						
11.77	0.6865	0.6128	74.53	0.8514	0.3919	108.94
10.47	0.6318	0.6259	74.55	0.8584	0.2369	179.69
8.97	0.5861	0.6237	76.14	0.8687	0.1823	232.49
7.97	0.5592	0.6199	77.39	0.8782	0.1509	279.73
6.36	0.5283	0.6240	77.78	0.8640	0.1072	396.15
5.36	0.4780	0.6226	79.41	0.8621	0.0818	519.58
12.37 ^a	0.7833	0.5400	81.34	0.7833	0.5400	81.34

^a Estimated critical points.

molar fractions. The mixture molar volumes (V_m) are defined as

$$V_{m,l} = \frac{x_1 M_1 + x_2 M_2}{\rho(l)} = \frac{x_1 M_1 + (1 - x_1) M_2}{\rho(l)}$$

and

$$V_{m,g} = \frac{y_1 M_1 + y_2 M_2}{\rho(g)} = \frac{y_1 M_1 + (1 - y_1) M_2}{\rho(g)} \quad (1)$$

where $V_{m,l}$ and $V_{m,g}$ represent the molar volumes of the mixture in the liquid phase and vapor phase, respectively,

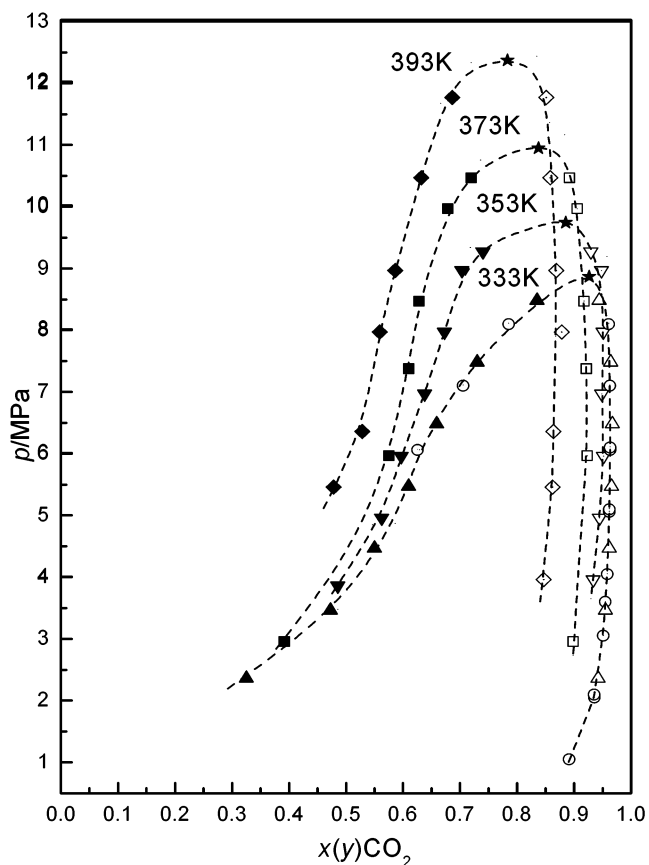


Figure 2. p - $x(y)$ diagram of the carbon dioxide + acetone system: \blacktriangle , 333.15 K; \blacktriangledown , 353.15 K; \blacksquare , 373.15 K; \blacklozenge , 393.15 K; \star , estimated critical points. Solid points represent liquid phases; hollow points represent gas phases. \circ , 333 K, Bamberger.⁴

and M_1 and M_2 indicate the relative molar masses of CO_2 and acetone, respectively.

Figure 2 shows the p - $x(y)$ diagram at four temperatures. The experimental data at 333.15 K are in good agreement with the literature.⁴ The experimental results show that the solubility of CO_2 in acetone increase with increasing pressure. The two curves intersect at the critical points.

Figure 3 gives the isothermal p - ρ curves. The density of the gas phase increases with elevated pressure. In the liquid phase, the solubility of carbon dioxide increases with elevated pressure, which reduces the density of the liquid. At the same time, an increase in pressure causes the density of the liquid to increase, so the density of the liquid

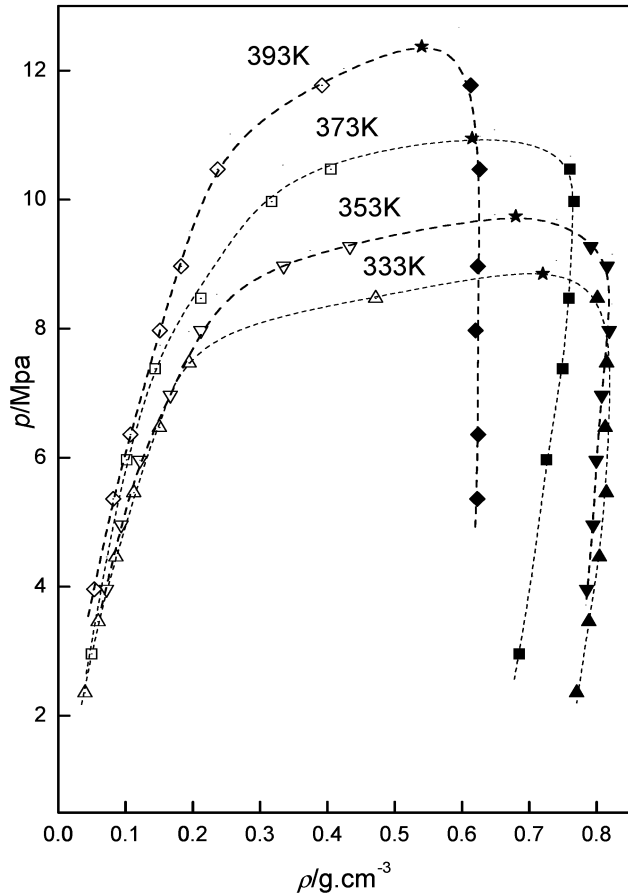


Figure 3. p - ρ diagram of the carbon dioxide + acetone system at four temperatures: Δ , \blacktriangle , 333.15 K; ∇ , \blacktriangledown , 353.15 K; \square , \blacksquare , 373.15 K; \diamond , \blacklozenge , 393.15 K; \star , estimated critical point. Solid points represent liquid phases; hollow points represent gas phases.

phase does not show a noticeable change with increasing pressure.

Correlation of the Experimental Data. In this work, the experimental data was compared with data calculated from the Peng–Robinson (PR)⁷ equation. The PR-EOS has the form

$$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)} \quad (2)$$

with

$$a(T) = a(T_c) \alpha(T) = 0.45724 \frac{R^2 T_c^2 \alpha(T)}{p_c} \quad (3)$$

$$b(T) = 0.07780 \frac{RT_c}{p_c} \quad (4)$$

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

$$m = 0.3746 + 1.54226\omega - 0.26992\omega^2 \quad (6)$$

$$T_r = \frac{T}{T_c} \quad (7)$$

where T_c and p_c are the critical temperature and pressure of the pure components, respectively, and ω is the acentric factor. The values are listed in Table 2.

Table 2. Critical Properties and Acentric Factors for the Pure Components^{8,9}

component	T_c /K	P_c /MPa	ω
carbon dioxide	304.18	7.38	0.225
acetone	508.1	4.701	0.309

Table 3. Interaction Parameters for the Carbon Dioxide + Acetone System

333.15 K	353.15 K	373.15 K	393.15 K
$k_{ij} = -0.04$	$k_{ij} = -0.23$	$k_{ij} = -0.25$	$k_{ij} = -0.19$
$l_{ij} = -0.11$	$l_{ij} = 0.21$	$l_{ij} = 0.06$	$l_{ij} = 0.01$

Table 4. Experimental and Correlated Mole Fractions of CO₂ and Relative Quadratic Deviation Values for the CO₂ + Acetone System at Four Temperatures

p /MPa	x_{exptl}	y_{exptl}	x_{PR}	y_{PR}
$T = 333.15$ K				
8.47	0.8349	0.9442	0.8407	0.9611
7.47	0.7299	0.9643	0.7494	0.9675
6.47	0.6592	0.9674	0.6796	0.9674
5.46	0.6097	0.9656	0.6164	0.9686
4.46	0.5499	0.9616	0.5451	0.9678
3.46	0.4724	0.9551	0.4508	0.9639
2.36	0.3254	0.9421	0.3262	0.9452
RQD ^a			5.67×10^{-4}	6.84×10^{-5}
$T = 353.15$ K				
9.27	0.7401	0.9294	0.7428	0.9349
8.97	0.7035	0.9483	0.7082	0.9393
7.97	0.6729	0.9514	0.6763	0.9463
6.97	0.6379	0.9487	0.6386	0.9491
5.96	0.5970	0.9519	0.5978	0.9508
4.96	0.5624	0.9448	0.5516	0.9521
3.96	0.4857	0.9337	0.4907	0.9432
RQD ^a			1.40×10^{-4}	4.55×10^{-5}
$T = 373.15$ K				
10.47	0.7196	0.8918	0.7314	0.8743
9.97	0.6787	0.9054	0.6976	0.8901
8.47	0.6279	0.9177	0.6462	0.9117
7.38	0.6097	0.9217	0.6139	0.925
5.97	0.5750	0.9229	0.5606	0.9266
2.96	0.3919	0.8984	0.3815	0.8911
RQD ^a			5.45×10^{-4}	1.35×10^{-4}
$T = 393.15$ K				
11.77	0.6865	0.8514	0.6843	0.8246
10.47	0.6318	0.8584	0.6421	0.8366
8.97	0.5861	0.8687	0.5982	0.8572
7.97	0.5592	0.8782	0.5648	0.8687
6.36	0.5283	0.8640	0.5156	0.8810
5.36	0.4780	0.8621	0.4647	0.8753
RQD ^a			3.08×10^{-4}	4.25×10^{-4}

^a RQD is relative quadratic deviation, $\text{RQD} = \sum_{i=1}^n [(x_{\text{exptl},i} - x_{\text{PR},i})/x_{\text{exptl},i}]^2/n$, and n is number of experimental results.

The classic mixing rule with two parameters was used

$$a_M = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} (1 - k_{ij}) \quad (8)$$

$$a_M = \sum_i \sum_j x_i x_j \frac{(b_i + b_j)}{2} (1 - l_{ij}) \quad (9)$$

where x_i is the molar fraction of component i and a_i and b_i are the EOS parameters for the pure components. k_{ij} and l_{ij} are the interaction parameters for the binary mixture i - j . In this work, k_{ij} and l_{ij} were considered to be dependent on temperature because data was collected over a 60 K temperature range (from 333 K to 393 K), but the relationship is ruleless. The values of k_{ij} and l_{ij} are listed in Table 3. The calculated results are listed in Table 4, and the data of Figure 4 is from Table 4. X_{PR} and Y_{PR} are the mole

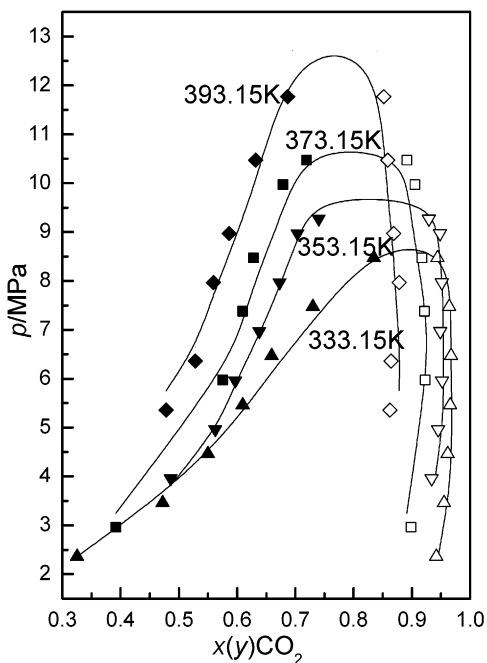


Figure 4. p - $x(y)$ diagram of the carbon dioxide + acetone system. Experimental (point) and correlated data with PR (—) equations of state for the system CO_2 + acetone: \blacktriangle , \blacktriangledown , 333.15 K; \blacksquare , \blacktriangledown , 353.15 K; \blacklozenge , \blacklozenge , 373.15 K; \blacklozenge , \blacklozenge , 393.15 K. Solid points represent the liquid phase; hollow points represent the gas phase.

fractions of carbon dioxide in the liquid phase and vapor phase, respectively, from PR EOS.

Conclusions

The experimental results for the CO_2 + acetone system are given in Tables 1–4 and Figures 2–4. The experimental values were compared with PR EOS and literature⁴ data. The experimental data accurately agree with both the PR equation of state and the literature.

The solubility of CO_2 in acetone drastically increases with elevated pressures at the studied temperatures, but the amount of acetone in the gas phase has not changed obviously with pressure. Similar behavior has been found for carbon dioxide systems containing other esters, such as carbon dioxide–1-alkanol,¹⁰ carbon dioxide–propyl acetate,¹¹ and carbon dioxide + propylene carbonate.¹²

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