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Measurement of Critical Points and Phase Behavior of $CH_3OH + CO + CO_2$ Ternary Mixture

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An apparatus for determining the critical points and phase behavior is described. The apparatus was used to investigate the phase behavior of pure CO_2 and the ternary mixture of $CH_3OH + CO + CO_2$. The critical points were obtained from both the critical opalescence and the isothermal compressibility. The critical temperature and critical pressure of CO_2, determined by this method, agreed well with literature values. The critical points and the homogeneous points of the ternary mixtures were determined in the CO_2-rich region.

Introduction

Supercritical mixtures are of increasing interest in many processes, such as chemical reactions, particle production, materials processing, and biological processes. The critical parameters are important to understand the phase changes of the fluids. To exploit the advantages of a supercritical fluid (SCF), the mixture should be homogeneous, and supercritical. Therefore, knowledge of critical parameters is crucial. The data of critical points for pure compounds and some binary mixtures are abundant.[1−6] However, experimental data on critical phenomena of ternary mixtures are scarce.[7,8]

The carbonylation of methanol in supercritical (SC) CO_2 is an effective method for producing acetic acid. Conversion may be much higher if the reaction takes place in SC CO_2.

To study this, the critical points of the ternary mixture $CH_3OH + CO + CO_2$ are required. In this work, we have constructed an apparatus for determining the critical points of mixtures and the ternary mixture has been studied in the CO_2-rich region.

Experimental Apparatus and Procedures

Materials. CO_2 and CO were purchased from Beijing Analytical Instrumental Factory, and their purities were 99.995% and 99.95%, respectively. Methanol was supplied by Beijing Chemical Agent Corporation and had a purity of >99.7%.

Apparatus. Figure 1 shows the schematic diagram of the apparatus used for measuring critical points. It consists of a high-pressure view cell, a constant-temperature water bath, a high-pressure pump, a pressure gauge, a magnetic stirrer, and a gas tank.

The high-pressure view cell is designed specially for this work. It consists of a stainless steel body, a stainless steel piston, two borosilicate windows, two tightening-components, and the seals. The piston in the cell can be moved up and down by a screw, with the volume of the cell changing in the range from 20 cm^3 to 50 cm^3. The cell can be used up to 20 MPa. A range of phenomena in the high-pressure cell can be observed through the windows. The cell is immersed in the water bath, and the temperature of the water bath is controlled within ±0.1 K using a Haake-D8 controller. The temperature is measured by an accurate mercury thermometer of better than ±0.05 K. The pressure gauge is composed of a pressure transducer (Model FOXBORO/ICT) and an indicator. It is uncertain to ±0.025 MPa.

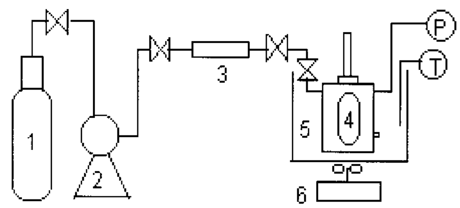

Figure 1. Schematic diagram of the apparatus used for measuring critical points: 1, gas tank; 2, high-pressure pump; 3, sample bomb; 4, high-pressure volume-variable cell; 5, water bath; 6, magnetic stirrer.

Experimental Procedures. The air in the view cell is evacuated by a vacuum pump. A known mass of methanol is charged into the view cell. Then carbon monoxide is added. The mole ratio of methanol and carbon monoxide in the mixture is controlled. The desirable mass of carbon monoxide is calculated from the pressure, the temperature, and the volume of the view cell. A sample bomb (20 mL) with known mass of carbon monoxide is connected to the view cell, and the carbon monoxide is filled into the view cell slowly until the desired pressure is reached. The mass of carbon monoxide added is determined from the mass of the sample bomb before and after filling the cell. At the end, the view cell is charged with CO_2 using another sample bomb of 41 mL (CO_2 was charged into the sample bomb through a pump until approximately 20 MPa before the experiment). It is charged in the same way as carbon monoxide. The mass of CO_2 in the cell is known by the mass difference of the sample bomb before and after filling. The composition of the mixture can be calculated from the masses of the components in the view cell. It is estimated that the mole fractions of the components are accurate to ±0.0002.

After the mixture with a desired composition is filled into the high-pressure view cell, the critical point is estimated by a method using the PR equation of state.[9] The measurements are performed near the estimated critical point. The

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Table 1. Critical Points for the Ternary Mixture CH_3OH (1) + CO (2) + CO_2 (3)

x_1	x_2	T_c/K	P_c/MPa	x_1	x_2	T_c/K	P_c/MPa
0.0371	0.0396	307.8	8.57	0.0328	0.0166	309.3	8.14
0.0437	0.0466	308.4	8.81	0.0389	0.0196	310.3	8.29
0.0549	0.0586	309.8	9.32	0.0520	0.0217	312.6	8.76
0.0656	0.0664	308.6	9.58	0.0593	0.0247	312.6	8.86
0.0775	0.0785	308.1	10.07	0.0639	0.0215	313.9	9.00
0.0809	0.0822	304.9	10.23	0.0713	0.0240	314.7	9.26
0.0903	0.0917	302.7	10.48	0.0795	0.0268	315.5	9.44
0.1019	0.1036	299.9	10.75	0.1028	0.0328	315.2	9.70
0.0251	0.0827	303.5	8.96	0.1137	0.0362	316.0	10.06
0.0313	0.1032	303.1	9.36	0.1211	0.0366	313.8	10.07
0.0399	0.1276	298.4	10.35	0.1356	0.0410	314.6	10.46
0.0449	0.1435	296.4	10.75	0.1481	0.0447	318.0	11.30
0.0503	0.1609	293.3	11.10	0.1624	0.0491	327.8	12.98

pressure of the system is increased by moving the piston down until a homogeneous liquidlike phase is observed. The system is allowed to equilibrate for at least 60 min at the desired temperature. Then the pressure is decreased via turning the piston and the corresponding pressure and volume changes are recorded at constant temperature. After the measurement at this temperature, the experiments are conducted at other temperatures with the same procedure until the strongest opalescence is observed and the compressibility can be calculated. It is estimated that the measurements of the critical temperatures and the critical pressures can be accurate to 0.2 K and 0.03 MPa.

Results and Discussions

For a pure fluid, the opalescence is the strongest and the isothermal compressibility is the highest.[10] We combine these two principles to determine the critical point of CO_2. The measured critical temperature and pressure are respectively 304.2 K and 7.39 MPa, which are in good agreement with the literature data (304.20 K, 7.3834 MPa).[11]

According to McHugh and Krukonis,[12] the mixture critical point is described to be the pressure and temperature at which critical opalescence is observed for a slight change in either pressure or temperature. At the same time, a slight change in temperature or pressure causes a dramatic change in the amount of gas phase and liquid phase at the critical point. In our experiments, the mixture in the cell changes from a single phase to about 50 vol % liquid phase and 50 vol % vapor phase when the pressure is adjusted by only 0.1−0.2 bar. For a mixture, it has not been proven theoretically whether the isothermal compressibility reaches its highest at the critical point. It was observed in our experiments that the isothermal compressibility increased when the system approached to the critical point, but the compressibility near the critical point was not very sensitive to temperature and pressure. In this work, we judge the critical points of the mixtures mainly on the basis of the dramatic change of the phase amount and the strongest critical opalescence, which occur at the critical point.

Table 1 lists the critical temperature and the pressure of the ternary mixture CH_3OH + CO + CO_2 with different compositions. The mole ratios of CH_3OH and CO (CH_3OH/CO) are approximately 3:1, 1:1, and 1:3 in the mixtures.

Figure 2 shows the critical temperature versus the mole fraction of methanol for the ternary mixture CH_3OH + CO + CO_2 at different mole ratios of CH_3OH/CO. It can be found that the critical temperature of the ternary mixture is higher at larger values of the ratio CH_3OH/CO. At CH_3OH/CO = 3:1, the critical temperature of the mixture increases with the content of methanol in the mixture,

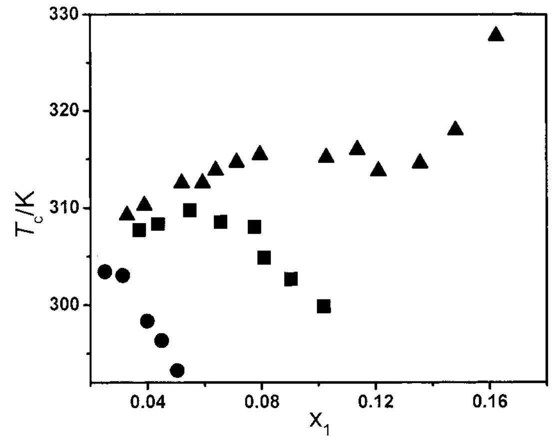

Figure 2. Projection of the critical temperature versus the mole fraction of CH_3OH for the ternary mixture CH_3OH (1) + CO (2) + CO_2 (3) at different values of x_1/x_2: ■, x_1/x_2 = 1:1; ●, x_1/x_2 = 1:3; ▲, x_1/x_2 = 3:1.

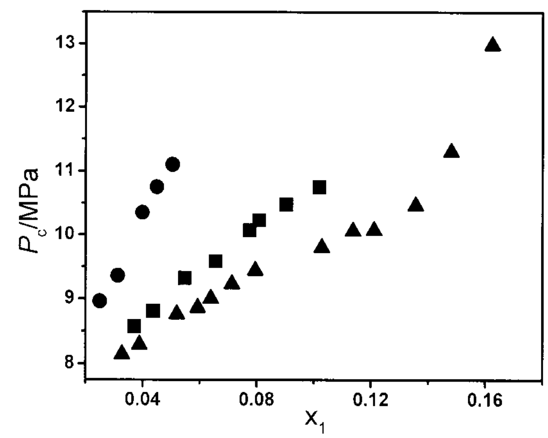

Figure 3. Projection of the critical pressure versus the mole fraction of CH_3OH for the ternary mixture CH_3OH (1) + CO (2) + CO_2 (3) at different values of x_1/x_2: ■, x_1/x_2 = 1:1; ●, x_1/x_2 = 1:3; ▲, x_1/x_2 = 3:1.

especially at higher methanol concentration. At CH_3OH/CO = 1:1, the critical temperature increases slightly with methanol concentration at the beginning and then decreases. The critical temperature of the ternary mixture decreases rapidly at CH_3OH/CO = 1:3. The above phenomenon is easy to understand because the critical temperature of a mixture depends on the critical temperatures of the components and the intermolecular interactions in the mixture. The critical temperature of CO is much lower than that of methanol. Thus, CH_3OH/CO is one of the main factors to affect the critical temperature of the ternary mixture.

The critical pressure of the ternary mixture CH_3OH + CO + CO_2 as a function of the mole fraction of CH_3OH at different ratios CH_3OH/CO is illustrated in Figure 3. Figure 3 shows that the critical pressure increases with the concentration of methanol at a fixed ratio CH_3OH/CO. The critical pressure is more sensitive to the concentration of CH_3OH at lower CH_3OH/CO ratio. At fixed methanol concentration, the critical pressure decreases with the increase of CH_3OH/CO ratio.

Figure 4 shows the projection of the critical pressure versus the critical temperature for the ternary mixture CH_3OH + CO + CO_2 at different mole ratios of CH_3OH/CO. It can be found that the critical temperature increases as the ratio CH_3OH/CO increases. At ratio CH_3OH/CO = 1:1 and 1:3, the critical pressure increases with the

Table 2. Temperatures and Pressures of Phase Separation for the Ternary Mixture CH_3OH (1) + CO (2) + CO_2 (3)

T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
$x_1 = 0.0371$, $x_2 = 0.0396$		$x_1 = 0.0903$, $x_2 = 0.0917$		$x_1 = 0.0449$, $x_2 = 0.1435$		$x_1 = 0.1137$, $x_2 = 0.0362$	
307.2	8.54	299.9	10.17	294.2	10.64	316.3	10.15
$x_1 = 0.0437$, $x_2 = 0.0466$		302.3	10.38	296.2	10.72	317.7	10.39
308.3	8.80	302.9	10.52	$x_1 = 0.0503$, $x_2 = 0.1609$		318.9	10.61
308.7	8.84	304.2	10.75	292.1	11.08	320.0	10.78
$x_1 = 0.0549$, $x_2 = 0.0586$		306.4	11.06	292.8	11.11	320.5	10.81
309.4	9.29	$x_1 = 0.1019$, $x_2 = 0.1036$		293.0	11.10	321.3	10.95
310.2	9.35	298.2	10.68	$x_1 = 0.0328$, $x_2 = 0.0166$		$x_1 = 0.1211$, $x_2 = 0.0366$	
310.7	9.41	299.1	10.78	309.0	8.12	352.6	9.86
311.2	9.47	299.8	10.85	309.2	8.14	353.2	9.96
312.2	9.57	301.3	11.23	$x_1 = 0.0389$, $x_2 = 0.0196$		353.3	10.03
313.7	9.73	302.7	11.40	308.2	8.11	354.1	10.15
$x_1 = 0.0656$, $x_2 = 0.0664$		304.2	11.43	310.5	8.32	$x_1 = 0.1356$, $x_2 = 0.0410$	
307.7	9.48	305.7	11.84	311.3	8.37	314.8	10.51
308.8	9.60	307.7	12.17	$x_1 = 0.0520$, $x_2 = 0.0217$		315.8	10.62
319.2	9.62	$x_1 = 0.0251$, $x_2 = 0.0827$		311.4	8.64	316.3	10.74
309.7	9.66	303.5	8.96	312.4	8.74	316.9	10.84
310.7	9.84	303.7	8.93	$x_1 = 0.0593$, $x_2 = 0.0247$		$x_1 = 0.1481$, $x_2 = 0.0447$	
$x_1 = 0.0775$, $x_2 = 0.0785$		304.2	8.93	311.2	8.70	318.2	11.30
307.2	10.03	$x_1 = 0.0313$, $x_2 = 0.1032$		311.9	8.81	319.5	11.56
307.8	10.09	302.2	9.05	312.4	8.84	321.4	11.85
309.2	10.33	303.2	9.07	$x_1 = 0.0639$, $x_2 = 0.0215$		323.1	12.17
$x_1 = 0.0809$, $x_2 = 0.0822$		303.8	9.38	313.5	8.96	324.7	12.39
303.2	10.22	304.2	9.34	313.7	8.99	326.2	12.56
305.2	10.29	304.4	9.28	314.2	9.06	327.7	12.82
305.8	10.32	305.2	9.29	$x_1 = 0.0713$, $x_2 = 0.0240$		$x_1 = 0.1624$, $x_2 = 0.0491$	
		$x_1 = 0.0399$, $x_2 = 0.1276$		313.6	9.06	318.6	10.85
		298.2	10.35	314.6	9.21	320.9	11.53
				314.9	9.256	323.6	12.00
				316.7	9.60	325.7	12.39
				$x_1 = 0.1028$, $x_2 = 0.0328$		327.0	12.59
				314.9	9.74	308.1	13.01

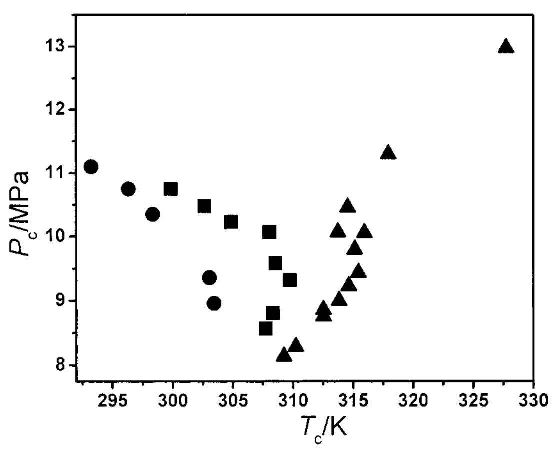

Figure 4. Projection of the critical pressure versus the critical temperature for the ternary mixture CH_3OH (1) + CO (2) + CO_2 (3) at different values of x_1/x_2: ■, x_1/x_2 = 1:1; ●, x_1/x_2 = 1:3; ▲, x_1/x_2 = 3:1.

decrease of the critical temperature. However, the critical pressure decreases with the decrease of the critical temperature at CH_3OH/CO = 3:1.

The pressures at which the mixtures begin to change from one phase into two phases are important for homogeneous chemical processes. If the temperature is critical, the pressure is the critical pressure. There are many processes conducted below the critical temperature. The mixture is generally homogeneous if the pressure is higher than the phase-separating pressure at a certain temperature. The phase-separating data at different conditions are listed in Table 2. The data in Table 2 are dew points above the critical temperature and bubble points below the critical temperature. These points were obtained by visual observation of the reappearance of a meniscus. It can be found from Table 2 that the phase-separating pressure of the mixture increases as the concentration of CO increases at the same mole fraction of CH_3OH. At a fixed composition, the phase-separating pressure increases with the increase of the temperature.

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