Critical Properties of Binary and Ternary Mixtures of Hexane + Methanol, Hexane + Carbon Dioxide, Methanol + Carbon Dioxide, and Hexane + Carbon Dioxide + Methanol

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Critical properties of both binary mixtures (hexane + methanol, hexane + carbon dioxide, and methanol + carbon dioxide) and a ternary mixture (hexane + carbon dioxide + methanol) were measured by using a high-pressure view cell with visual observation. The critical lines of the binary mixtures are continuous over the whole composition range between the critical points of the two pure components. The critical pressure of the binary mixtures of hexane + carbon dioxide and methanol + carbon dioxide shows a maximum, while the critical temperature of the binary mixture of hexane + methanol shows a minimum with the composition.

1. Introduction

Synthesis of methanol from syngas under supercritical conditions using hexane as a solvent is a promising process, since it can improve the conversion and enhance the heat- and mass-transfer efficiencies, and the single-stage conversion of carbon monoxide can be higher than 90%.[1,2] The reacting mixture consists of mainly CO, H_2, CO_2, hexane, and methanol. To capitalize on the unique characteristics of the reaction medium under supercritical conditions, it is essential to be cognizant of the critical properties of the reacting mixture, since the reaction composition and related critical properties of the reacting mixture change along the reaction course. Although a series of work has focused on the critical properties of the related mixtures,[3−13] more data are necessary to determine the phase behaviors of the reacting mixture and the operating parameters for the methanol synthesis under supercritical conditions.

The critical properties of mixtures can be determined from the disappearance of a meniscus on slow heating through the critical point or the reappearance of a meniscus on slow cooling,[14] and it is customary to note that the reappearance of the meniscus is usually a sharper phenomenon than the disappearance. A constant-volume view cell was useful to observe such changes.[15]

In this work, the critical properties of both binary mixtures (hexane + methanol, hexane + carbon dioxide, and methanol + carbon dioxide) and a ternary mixture (hexane + carbon dioxide + methanol) were measured by using a high-pressure view cell with visual observation.

2. Experimental Section

Methanol (>99.5%) from Beijing Chemical Corporation was purified and dried by refluxing with magnesium and iodine, followed by distillation, and hexane (>97.0%) supplied by Tianjin Tian-Da Chemical factory was purified by passing through columns containing silica gel and alumina, as described in our previous work.[16] Carbon dioxide (>99.95%) from the Beijing Analytical Instrument Corporation was used without further treatment. The purity of all the compounds was determined by gas chromatography and was >99.5 mol %.

A constant-volume view cell similar to that in the literature was used in this work.[15] The apparatus consisted of a high-pressure view cell of 18.00 cm^3, a temperature-controlled air bath, and a pressure sensor. The glass windows were attached to the front and back of the cell to permit full visibility of all the contents in the cell. The temperature and pressure were controlled to within ±0.1 K and ±0.01 MPa, respectively.

Before each measurement, the view cell was first evacuated with a vacuum pump. A known mass of hexane, methanol, or the mixture of hexane + methanol was then charged into the cell. The carbon dioxide was pressurized into the cell through a sampling tube. The amount of the mixture in the cell was controlled in such a way that the density of the mixture should be close to or slightly higher than its critical density, which was a priori unknown. After that, the view cell was heated with stirring. With increase of the temperature, the pressure increased and the gas−liquid interface became flat and faint and eventually vanished at the critical point. After a uniform phase of the supercritical fluid in the cell was formed, the temperature of the air thermostat was decreased gradually. At temperatures close to the critical point, the strong red-glow critical opalescence could be observed. With the decrease of the temperature to the critical value, the fluid color went from colorless to yellow, to red-yellow, and to black. Then the meniscus reappeared in the middle of the view cell and two phases were formed. The temperature and pressure readings in the temperature decreasing mode were made at the moment when complete darkness was observed. To make a successful measurement, attention should be paid to ensure that the density of fluid in the cell is close to or slightly higher than its critical density. Good stirring/shaking is necessary to keep the content in the cell uniform. For each measurement, the temperature-increasing and -decreasing processes were repeated at least three times, and an average of the temperature and pressure readings was taken as the values reported here. The accuracies of

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10.1021/je034127q CCC: $25.00
Published on Web 10/07/2003

Table 1. Critical Properties of Pure Substances

	T_c/K		P_c/MPa		ρ_c/g·cm^{-3}	
substance	this work	Reid et al.[17]	this work	Reid et al.[17]	this work	Reid et al.[17]
carbon dioxide	304.5	304.1	7.42	7.38	0.473	0.469
hexane	507.4	507.5	3.02	3.01	0.231	0.232
methanol	512.6	512.6	8.12	8.09	0.276	0.271

Table 2. Critical Properties of Binary Mixtures of Hexane (1) + Methanol (2), Hexane (1) + Carbon Dioxide (2), and Methanol (1) + Carbon Dioxide (2)

x_2	T_c/K	P_c/MPa	x_2	T_c/K	P_c/MPa
Hexane (1) + Methanol (2)					
0	507.4	3.02	0.555	480.6	5.32
0.072	504.6	3.35	0.633	480.4	5.52
0.120	502.0	3.54	0.717	483.3	5.94
0.178	499.8	3.79	0.787	488.6	6.27
0.244	495.9	4.01	0.816	492.5	6.75
0.320	492.1	4.20	0.860	498.0	7.19
0.398	486.7	4.81	0.914	502.5	7.52
0.452	484.3	4.91	0.961	508.9	7.91
0.498	481.9	5.10	1	512.6	8.12
Hexane (1) + Carbon Dioxide (2)					
0	507.4	3.02	0.780	387.0	11.72
0.202	494.4	4.20	0.836	365.6	11.36
0.373	486.4	5.39	0.897	344.8	10.18
0.418	479.5	6.03	0.935	332.9	9.43
0.498	468.7	7.18	0.955	321.8	8.72
0.557	457.5	8.37	0.979	311.9	7.96
0.640	438.7	9.87	0.986	308.2	7.71
0.687	429.4	10.41	1	304.5	7.42
0.750	399.9	11.61			
Methanol (1) + Carbon Dioxide (2)					
0	512.6	8.12	0.668	414.3	16.34
0.072	507.2	8.80	0.713	408.2	16.26
0.169	494.6	10.33	0.786	384.8	15.76
0.244	485.4	11.54	0.810	374.3	15.07
0.327	473.2	12.84	0.862	354.7	13.75
0.383	460.5	14.00	0.893	346.7	12.95
0.446	451.1	14.74	0.912	333.3	11.04
0.495	442.8	15.27	0.965	313.4	8.29
0.572	423.9	16.32	1	304.5	7.42

the critical temperature, critical pressure, and mole fraction were estimated within ±0.3 K, ±0.03 MPa, and ±0.003, respectively.

3. Results and Discussion

3.1. Pure Substances. To check the reliability of the technique and the apparatus, the critical properties of pure hexane, methanol, and carbon dioxide were measured. As shown in Table 1, the agreement between the critical temperature and pressure measured in this work and those in the literature was satisfactory.[17] The difference between our measured density and the literature values indicated that the critical temperature and pressure could be obtained within the required uncertainty using a relatively wide range of density of the mixture, provided it was higher than the critical density. The measured critical density is the fluid density at which the critical properties were obtained, and therefore, it is not very accurate.

3.2. Binary Mixtures. The critical properties of the binary mixtures of hexane + methanol, hexane + carbon dioxide, and methanol + carbon dioxide were listed in Table 2.

For the binary mixture of hexane (1) + methanol (2), as shown in Figure 1, the critical lines are continuous over the whole composition range between the critical points of the two pure components; the critical pressure increases monotonically with the content of methanol, while the critical temperature shows a minimum at $x_2 \approx 0.60$. The

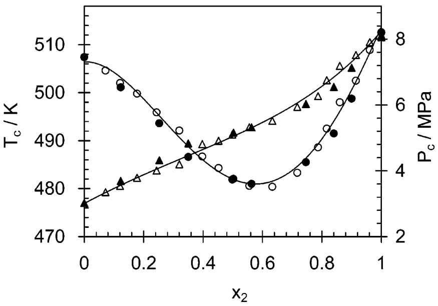

Figure 1. Critical properties of the binary mixture of hexane (1) + methanol (2): ○, critical temperatures in this work; △, critical pressures in this work; ●, critical temperatures by de Loos et al.;[5] ▲, critical pressures by de Loos et al.[5]

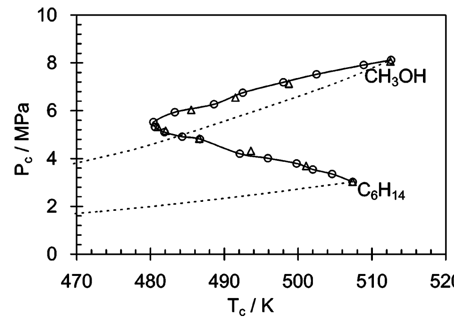

Figure 2. Projection of the critical pressure versus the critical temperature for the binary mixture of hexane (1) + methanol (2): ○, this work; △, de Loos et al.;[5] dotted lines, the vapor pressure of each pure component below the critical temperature.[17]

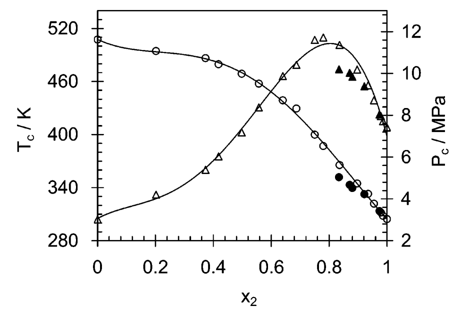

Figure 3. Critical properties of the binary mixture of hexane (1) + carbon dioxide (2): ○, critical temperatures in this work; △, critical pressures in this work; ●, critical temperatures by Choi et al.;[6] ▲, critical pressures by Choi et al.[6]

present data agree well with those of de Loos et al.,[5] which are also plotted in Figure 1. The critical point locus in the $P-T$ projection was shown in Figure 2. Since the binary mixture exhibits partial miscibility at low temperature, it should belong to type II fluid phase behavior with a critical end point of the nature $l_1 = l_2 + g$ at about 306.8 K according to the classification of van Konynenburg and Scott.[18]

For the binary mixture of hexane (1) + carbon dioxide (2), as shown in Figure 3, the critical lines are also continuous over the whole composition range. However, the critical pressure passes through a maximum at $x_2 \approx 0.78$, while the critical temperature decreases with the content of carbon dioxide. The data of Choi and Yeo[6] are also given in Figure 3. They recorded only several points in the carbon dioxide-rich region, and these show considerable deviation from this work. However, the critical points in their work were determined by experimentally tracing the intersection point of the dew point and the bubble point loci on the $P-T$ projections. The critical point locus in the $P-T$ projection was shown in Figure 4. It should belong to type I fluid

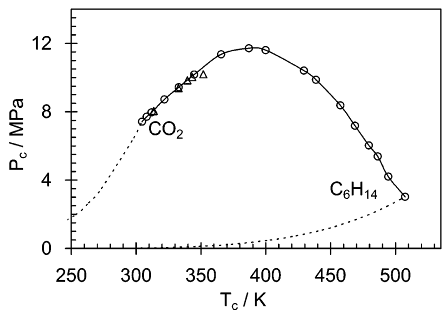

Figure 4. Projection of the critical pressure versus the critical temperature for the binary mixture of hexane (1) + carbon dioxide (2): ○, this work; △, Choi et al.;[6] dotted lines, the vapor pressure of each pure component below the critical temperature.[17]

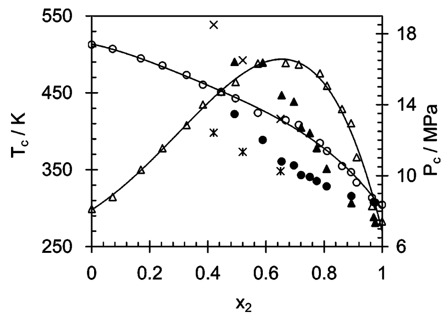

Figure 5. Critical properties of the binary mixture of methanol (1) + carbon dioxide (2): ○, critical temperatures in this work; △, critical pressures in this work; ●, critical temperatures by Yeo et al.;[7] ▲, critical pressures by Yeo et al.;[7] ∗, critical temperatures by Semenova et al.;[8] ×, critical pressures by Semenova et al.[8]

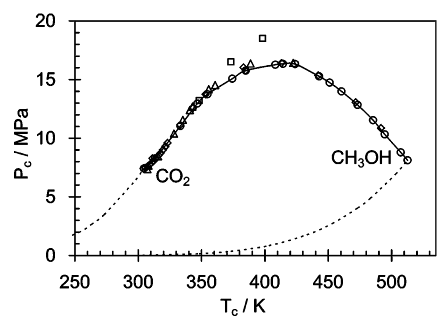

Figure 6. Projection of the critical pressure versus the critical temperature for the binary mixture of methanol (1) + carbon dioxide (2): ○, this work; △, Yeo et al.;[7] □, Semenova et al.;[8] ◇, Brunner et al.;[9] dotted lines, the vapor pressure of each pure component below the critical temperature.[17]

phase behavior according to the classification of van Konynenburg and Scott,[18] although this binary mixture may exhibit a metastable immiscibility at low temperature.[19]

For the binary mixture of methanol (1) + carbon dioxide (2), as shown in Figure 5, the critical lines are also continuous over the whole composition range; the critical pressure passes through a maximum at $x_2 \approx 0.67$, while the critical temperature decreases monotonically with the content of carbon dioxide. The critical points determined by Yeo et al.[7] and Semenova et al.[8] were also shown in Figure 5, and there exist significant differences among all these works. The critical point locus in the $P-T$ projection was shown in Figure 6. The critical points of this work, by Yeo et al.,[7] and by Brunner[9] are overlapped in the $P-T$ projection, which may suggest that the differences are caused by the uncertainties in the mixture composition. Unfortunately, the composition data by Brunner cannot be found.[9] The critical parameters of this mixture by Semenova et al.[8] differ from those by others in both Figures 5 and 6; they were obtained through interpolation and therefore might be less reliable. Since the binary mixture exhibits partial miscibility at lower temperature, it should belong to type II fluid phase behavior according to the classification of van Konynenburg and Scott.

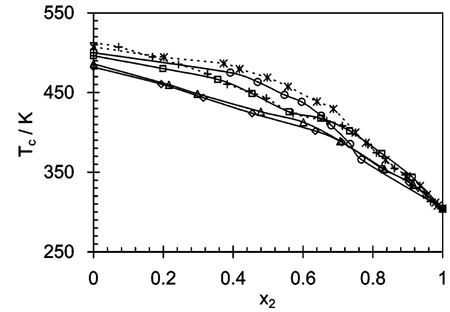

Figure 7. Critical temperature of the ternary mixture of hexane (1) + carbon dioxide (2) + methanol (3): +, $x_1 = 0$; △, $x_1/x_3 = 1/3$; ◇, $x_1/x_3 = 1$; □, $x_1/x_3 = 3$; ○, $x_1/x_3 = 5$; ∗, $x_3 = 0$.

Table 3. Critical Properties of the Ternary Mixture of Hexane (1) + Carbon Dioxide (2) + Methanol (3)

x_1	x_2	x_3	T_c/K	P_c/MPa
		$x_1/x_3 = 1/3$		
0.250	0	0.750	485.9	6.18
0.196	0.216	0.588	459.7	8.57
0.176	0.298	0.527	448.4	9.72
0.130	0.479	0.391	426.0	11.47
0.100	0.601	0.299	412.7	12.32
0.073	0.707	0.220	389.0	12.34
0.042	0.833	0.125	354.1	11.90
0.021	0.916	0.063	334.3	9.90
0	1	0	304.5	7.42
		$x_1/x_3 = 1$		
0.500	0	0.500	481.9	5.10
0.403	0.194	0.403	460.6	6.94
0.342	0.315	0.342	443.5	8.15
0.273	0.454	0.273	424.0	9.75
0.183	0.635	0.183	401.8	10.88
0.145	0.711	0.145	387.7	11.04
0.087	0.826	0.087	354.9	10.68
0.049	0.903	0.049	337.3	9.50
0	1	0	304.5	7.42
		$x_1/x_3 = 3$		
0.750	0	0.250	496.2	4.07
0.601	0.199	0.200	480.1	5.81
0.483	0.356	0.161	466.5	7.22
0.409	0.454	0.136	448.7	8.65
0.330	0.560	0.110	425.8	9.96
0.262	0.650	0.087	417.8	10.38
0.200	0.733	0.067	402.0	10.89
0.131	0.826	0.044	373.3	10.91
0.066	0.913	0.022	343.7	9.56
0	1	0	304.5	7.42
		$x_1/x_3 = 5$		
0.833	0	0.167	500.0	3.74
0.507	0.392	0.101	475.0	6.74
0.442	0.470	0.088	463.3	7.81
0.377	0.547	0.076	446.9	9.18
0.337	0.596	0.067	438.2	9.72
0.290	0.652	0.058	420.8	10.63
0.266	0.681	0.053	408.7	11.09
0.221	0.735	0.044	385.3	11.34
0.194	0.767	0.039	365.9	10.95
0	1	0	304.5	7.42

3.3. Ternary Mixtures. The critical properties of the ternary mixture with a fixed hexane/methanol mole ratio of 1/3, 1, 3, or 5 were shown in Table 3 and Figures 7 and 8. Just like the case of the binary mixture of hexane + carbon dioxide, the critical temperature decreases mono-

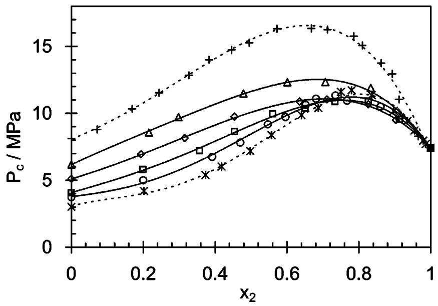

Figure 8. Critical pressure of the ternary mixture of hexane (1) + carbon dioxide (2) + methanol (3): +, $x_1 = 0$; △, $x_1/x_3 = 1/3$; ◇, $x_1/x_3 = 1$; □, $x_1/x_3 = 3$; ○, $x_1/x_3 = 5$; ∗, $x_3 = 0$.

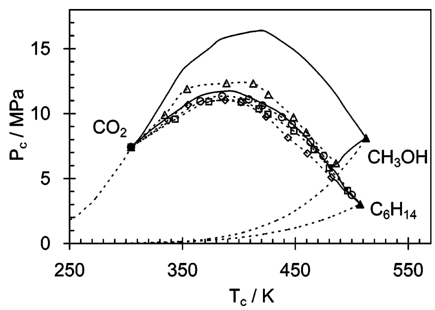

Figure 9. Projection of the critical pressure versus the critical temperature: solid line, binary mixtures; dotted lines, the vapor pressure of each pure component below the critical temperature;[17] dotted lines with symbols, the ternary mixture of hexane (1) + carbon dioxide (2) + methanol (3) (△, $x_1/x_3 = 1/3$; ◇, $x_1/x_3 = 1$; □, $x_1/x_3 = 3$; ○, $x_1/x_3 = 5$).

tonically with the mole fraction of carbon dioxide in the system, while the critical pressure shows a maximum.

The loci of critical points in the $P-T$ projection were shown in Figure 9. If the direct lines were drawn between the critical points of each two pure components, the loci of the critical point and the vapor pressure were placed in the different sides of these direct lines for the binary mixtures of hexane + carbon dioxide and methanol + carbon dioxide, while they were placed in the same side for the binary mixture of hexane + methanol. The critical loci of the ternary mixture with a hexane/methanol ratio > 1/3 were placed near that of the binary mixture of hexane + carbon dioxide.

4. Conclusions

The critical properties of both binary mixtures (hexane + methanol, hexane + carbon dioxide, and methanol + carbon dioxide) and a ternary mixture (hexane + carbon dioxide + methanol) were measured by using a high-pressure view cell with visual observation. The critical lines of the binary mixtures are continuous over the whole composition range between the critical points of the two pure components. The critical pressure of the binary mixtures of hexane + carbon dioxide and methanol + carbon dioxide shows a maximum, while the critical temperature of the binary mixture of hexane + methanol shows a minimum with the composition. The binary mixtures of methanol + carbon dioxide and hexane + methanol belong to type II fluid phase behavior, while the binary mixture of carbon dioxide + hexane should belong to type I, according to the classification of van Konynenburg and Scott.

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Received for review June 26, 2003. Accepted September 5, 2003. The authors are grateful for the financial support of the State Key Fundamental Research Project of China.

JE034127Q