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Phase Behavior, Densities, and Isothermal Compressibility of the CO_2 + Ethanol + Dichloromethane Ternary System in Different Phase Regions

Bo Wang, Weize Wu,* Jiawei Chen, Buxing Han,* Zhaofu Zhang, Dong Shen, and Rui Zhang

Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

The phase behavior and critical parameters of the CO_2 (1) + ethanol (2) + dichloromethane (3) ternary system were determined, and the density of the mixtures was measured in both the subcritical and supercritical regions of the system. The isothermal compressibility (K_T) under some typical conditions was calculated using the density data. The data were also calculated using the Peng−Robinson equation of state (PR EOS). The results showed that the density of the mixtures at fixed composition and temperature is very sensitive to pressure as the pressure approaches critical, bubble, and dew pressures in the critical regions (both temperature and composition are close to the critical point of the mixtures). However, the effect of pressure on the density of a subcritical fluid is very limited over the whole pressure range because the composition of the mixture is far from the critical composition.

Introduction

Knowledge of the phase behavior and critical parameters of fluid systems is crucial to the understanding of different chemical processes. This has been an interesting topic for years, and many related papers have been published, including the study of various mixtures.[1−3]

In recent years, scientists and engineers have paid much attention to supercritical fluids (SCFs). Some are attracted by the unusual properties of the SCFs, and others are more interested in their applications. SCFs can be used in many chemical processes, such as extraction and fractions,[4−6] chemical reactions,[7−9] and material processing.[10−12] Supercritical (SC) CO_2 is the most commonly used because it is nontoxic, nonflammable, inexpensive, readily available in large quantities, and has moderate critical temperature and pressure (304.2 K and 7.38 MPa). In practical applications of SCFs, the systems usually consist of the SC solvent and other related components. Therefore, the phase behaviors and critical parameters of the systems should be considered.

In recent years, we have been very interested in how the physical properties of mixtures in different phase regions (subcritical, supercritical) change with pressure, temperature and compositions. In previous papers,[13,14] we studied the phase behavior, critical parameters, densities, and compressibility of CO_2 + pentane, CO_2 + acetone, and CO_2 + pentane + acetone mixtures. In this work, we have determined the critical parameters and phase behavior of the CO_2 (1) + ethanol (2) + dichloromethane (3) ternary system, and the density of the mixture is then determined in different phase regions at different temperatures and pressures. The effect of the phase behavior on the density and isothermal compressibility was then investigated in the critical region and outside the critical region of the mixture. The Peng−Robinson equation of state (PR EOS)[15] was used to calculate the phase behavior, the density, and the isothermal compressibility.

Experimental Section

Materials. CO_2 (99.995%) was supplied by the Beijing Analytical Instrument Factory. Ethanol (>99.9%) and dichloromethane (>99.8%) were analytical grade and were produced by the Beijing Chemical Reagent Plant. All chemicals were used as received.

Apparatus and Procedures. The phase behavior and the densities of the mixtures were determined using a volume-variable view cell, and the apparatus and procedures were similar to those used in our previous paper.[16] The constant-temperature water bath was controlled by a Haake-D8 temperature controller, and the temperature was determined by accurate mercury thermometers with an accuracy of better than ±0.05 K. The pressure gauge was composed of a pressure transducer (Foxboroc/ICT, model 93) and an indicator. Its accuracy was ±0.025 MPa in the pressure range of 0 to 20 MPa.

In a typical experiment, the apparatus was washed thoroughly using different solvents and dried under vacuum. A known amount of a ethanol + dichloromethane mixture was charged after the air in the system was removed by vacuum pump. CO_2 was then added using a sample bomb. The mass of the CO_2 in the system was known from the mass difference of the sample bomb before and after charging the system. The cell was placed into the water bath at a desired temperature. After thermal equilibrium had been reached, the piston in the view cell was moved up and down to change the volume and the pressure of the system, and the phase separation could be observed directly. At the critical point, very strong opalescence was observed, and the meniscus appeared at half-volume after a slight pressure reduction. The volume of the system was known from the position of the piston, which was calibrated accurately using water as a medium. The composition and density of the mixture could be easily known from the masses of the components and the volume of the system. In this work, the molar ratio of ethanol to dichloromethane was 1:1 for all of the experiments.

It is estimated that the accuracy of the density data is $\pm 0.001\ g\cdot cm^{-3}$; the accuracy of the bubble-point pressure,

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* Corresponding authors. E-mail: wzwu@iccas.ac.cn; hanbx@iccas.ac.cn. Fax: 86-10-62562821.

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Table 1. Binary Interaction Parameters k_{ij} in PR EOS for Different Binary Mixtures

	CO_2 + ethanol	CO_2 + dichloromethane	ethanol + dichloromethane
k_{ij}	0.092[a]	0.084[b]	0.051[b]

[a] Reported in ref 15. [b] Obtained by correlating the vapor−liquid equilibrium data in refs 18 and 19.

critical pressure, and dew-point pressure is better than ±0.05 MPa, and that of the bubble-point temperature, critical temperature, and dew-point temperature is better than ±0.1 K. To calculate the compressibility (K_T), we used a B-spline method to smooth the measured density data, and K_T was obtained by differential calculation. It was estimated that the accuracy of the K_T data was better than ±3%.

Correlation. The PR EOS was used to correlate the vapor−liquid equilibrium data and the critical points of the mixtures. The PR EOS and the mixing rules used are as follows.

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \tag{1}$$

The constants a and b can be obtained from the related parameters of pure components using the following equations[17]

$$a = 0.457235\frac{R^2{T_c}^2}{P_c}\alpha \tag{2}$$

$$b = 0.077796\frac{RT_c}{P_c} \tag{3}$$

$$\alpha = [1 + m(1 - \sqrt{\{T\}/\{T_c\}})]^2 \tag{4}$$

$$m = 0.37464 + 1.54266\omega - 0.26922\omega^2 \tag{5}$$

For a mixture, the van der Waals mixing rules are applied[17]

$$a = \sum_i\sum_j x_i x_j a_{ij} \tag{6}$$

$$b = \sum_i x_i b_i \tag{7}$$

$$a_{ij} = (1 - k_{ij})\sqrt{a_{ii}a_{jj}} \tag{8}$$

where T_c, P_c, and ω stand for the critical temperature, critical pressure, and acentric factor; a_{ii} and b_i are parameters of the pure components; and k_{ij} is the binary parameter. The k_{ij} values for the binary mixtures involved in this work (shown in Table 1) have been reported[15] or calculated from the phase equilibrium data reported by other authors.[18,19] The PR EOS and the binary parameters in Table 1 were used to predict the phase behavior of the CO_2 + ethanol + dichloromethane ternary system.

Results and Discussion

Phase Behavior of the Mixture. The critical parameters of CO_2 were measured in this work to verify the reliability of the apparatus again. The critical temperature, critical pressure, and critical density of CO_2 determined in this work are 304.25 K, 7.38 MPa, and 0.462 g·cm^{-3}, respectively, which agree well with the literature data.[20]

Table 2. Experimental Bubble Points, Critical Points, and Dew Points of Carbon Dioxide (1) + Ethanol (2) + Dichloromethane (3) (x_2/x_3 = 1:1) at Different Compositions

x_1	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
0.965	308.15[a]	7.55[a]	310.15[a]	7.75[a]	313.15[b]	8.06[b]	315.15[c]	8.27[c]
	318.15[c]	8.44[c]	320.15[c]	8.47[c]	323.15[c]	8.50[c]	325.15[c]	8.54[c]
	328.15[c]	8.57[c]						
0.952	308.15[a]	7.15[a]	310.15[a]	7.45[a]	313.15[a]	7.86[a]	315.15[a]	8.04[a]
	318.15[b]	8.35[b]	320.15[c]	8.60[c]	323.15[c]	8.87[c]	325.15[c]	9.02[c]
	328.15[c]	9.20[c]						
0.921	308.15[a]	6.93[a]	310.15[a]	7.19[a]	313.15[a]	7.53[a]	315.15[a]	7.72[a]
	318.15[a]	8.22[a]	320.15[a]	8.45[a]	323.15[a]	8.94[a]	325.15[a]	9.12[a]
	328.15[b]	9.15[b]						
0.871	308.15[a]	6.66[a]	310.15[a]	6.85[a]	313.15[a]	7.28[a]	315.15[a]	7.46[a]
	318.15[a]	7.91[a]	320.15[a]	8.23[a]	323.15[a]	8.64[a]	325.15[a]	8.90[a]
	328.15[a]	9.28[a]						
0.790	308.15[a]	6.27[a]	310.15[a]	6.45[a]	313.15[a]	6.84[a]	315.15[a]	7.05[a]
	318.15[a]	7.45[a]	320.15[a]	7.65[a]	323.15[a]	8.05[a]	325.15[a]	8.13[a]
	328.15[a]	8.52[a]						

[a] Bubble point. [b] Critical point. [c] Dew point.

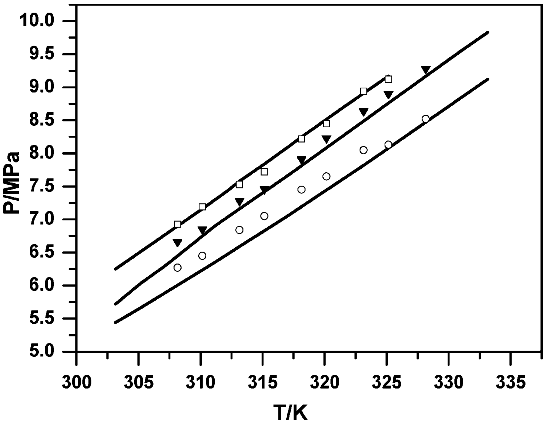

Figure 1. Experimental bubble points of CO_2 (1) + ethanol (2) + dichloromethane (3) ternary mixtures (x_2/x_3 = 1:1) at different temperatures: □, x_1 = 0.921; ▼, x_1 = 0.871; ○, x_1 = 0.790. Lines, calculated results; points, experimental data.

Table 2 summarizes the bubble-point, critical-point, and dew-point temperatures and pressures for the ternary system of different compositions. As expected, T_c and P_c of the mixtures increase with the concentration of ethanol and dichloromethane under our experimental conditions.

Figure 1 illustrates the bubble points of some mixtures as a function of temperature. The results calculated from the PR EOS are also given in the Figure. The bubble-point pressures increase linearly with temperature at a fixed composition, as can be seen from the Figure. The Figure also shows that the calculated results agree well with the experimental data and that the deviation is less than 5%.

Density and Isothermal Compressibility. The densities of the mixture at different temperatures and pressures were measured. The data determined under different conditions are listed in Table 3. As examples, the dependence of the density of the mixture with x_1 = 0.952 (x_2/x_3 = 1:1) on pressure and temperature is illustrated in Figure 2, and the dependence of the density on pressure at 328.15 K is illustrated in Figure 3. The data calculated from the PR EOS is also given in the Figures. It can be seen that the density depends strongly on pressure in the critical region. The deviation of the calculated density data from the experimental results is relatively large, and the deviation is about 30% in some compositions.

Table 3. Densities of CO_2 (1) + Ethanol (2) + Dichloromethane (3) (x_2/x_3 = 1:1) Ternary Mixtures under Different Conditions

P/MPa	ρ/g·cm^{-3}	P/MPa	ρ/g·cm^{-3}	P/MPa	ρ/g·cm^{-3}	P/MPa	ρ/g·cm^{-3}	P/MPa	ρ/g·cm^{-3}
T = 308.15 K		T = 308.15 K		T = 308.15 K		T = 308.15 K		T = 308.15 K	
x_1 = 0.965		x_1 = 0.952		x_1 = 0.921		x_1 = 0.871		x_1 = 0.790	
7.55^a	0.699^a	7.15^a	0.714^a	6.93^a	0.793^a	6.66^a	0.782^a	6.27^a	0.846^a
7.69	0.721	7.41	0.729	7.43	0.811	6.83	0.800	8.74	0.869
7.78	0.730	7.78	0.748	8.19	0.830	7.60	0.817	12.43	0.894
8.00	0.746	8.35	0.765	8.61	0.839	8.94	0.833	14.00	0.900
8.12	0.756	9.10	0.786	9.28	0.849	10.55	0.852	15.68	0.911
8.54	0.780	10.12	0.805	10.22	0.866	12.58	0.869	17.43	0.920
9.68	0.829	11.40	0.825	11.12	0.876	15.13	0.887	18.92	0.931
T = 313.15 K		T = 313.15 K		T = 313.15 K		T = 313.15 K		T = 313.15 K	
x_1 = 0.965		x_1 = 0.952		x_1 = 0.921		x_1 = 0.871		x_1 = 0.790	
8.06^b	0.513^b	7.87^a	0.624^a	7.53^a	0.762^a	7.28^a	0.730^a	6.84^a	0.835^a
8.11	0.535	8.06	0.650	7.72	0.772	7.34	0.750	8.56	0.850
8.16	0.557	8.18	0.658	7.95	0.782	7.38	0.765	10.16	0.869
8.19	0.567	8.41	0.676	8.39	0.800	7.71	0.780	11.34	0.877
8.25	0.594	8.66	0.687	8.88	0.814	8.46	0.797	12.51	0.886
8.35	0.621	8.90	0.636	9.64	0.832	9.51	0.814	14.02	0.597
8.45	0.652	9.91	0.666	10.42	0.847	10.91	0.832	15.34	0.903
8.70	0.685	10.62	0.754	11.63	0.868	11.13	0.882	17.24	0.913
9.02	0.722	12.73	0.792	13.16	0.889	12.67	0.953	18.82	0.922
9.54	0.761	14.27	0.814	15.04	0.910				
T = 318.15 K		T = 318.15 K		T = 318.15 K		T = 318.15 K		T = 318.15 K	
x_1 = 0.965		x_1 = 0.952		x_1 = 0.921		x_1 = 0.871		x_1 = 0.790	
8.44^c	0.501^c	8.35^b	0.517^b	8.22^a	0.719^a	8.01^a	0.734^a	7.45^a	0.808^a
8.51	0.521	8.41	0.484	8.39	0.736	8.40	0.752	8.28	0.827
8.59	0.542	8.52	0.509	8.50	0.745	8.98	0.764	9.46	0.843
8.69	0.569	8.78	0.551	8.95	0.772	9.44	0.776	10.26	0.852
8.78	0.598	9.00	0.570	9.25	0.788	10.34	0.790	11.16	0.860
8.87	0.624	9.71	0.617	9.71	0.805	11.44	0.807	13.25	0.875
8.98	0.657	10.97	0.728	10.37	0.824	12.37	0.817	14.45	0.887
9.10	0.692	12.07	0.752	11.17	0.843	13.20	0.827	15.88	0.893
9.27	0.730	13.67	0.784	12.12	0.861	13.96	0.837	17.35	0.900
9.35	0.751	15.08	0.802	13.37	0.883	15.78	0.852	18.94	0.908
T = 323.15 K		T = 323.15 K		T = 323.15 K		T = 323.15 K		T = 323.15 K	
x_1 = 0.965		x_1 = 0.952		x_1 = 0.921		x_1 = 0.871		x_1 = 0.790	
8.50^c	0.419^c	8.60^c	0.457^c	8.94^a	0.618^a	8.64^a	0.657^a	8.05^a	0.795^a
8.58	0.432	8.72	0.483	8.98	0.630	8.91	0.667	8.90	0.817
8.66	0.446	8.88	0.515	9.03	0.639	9.22	0.677	10.15	0.832
8.75	0.461	9.00	0.538	9.21	0.663	9.66	0.687	10.86	0.839
8.83	0.476	9.27	0.580	9.33	0.675	10.25	0.701	11.62	0.847
9.08	0.527	9.46	0.603	9.46	0.688	11.00	0.716	12.57	0.856
9.22	0.559	9.76	0.629	9.60	0.701	11.80	0.730	13.51	0.863
9.42	0.603	10.77	0.686	10.00	0.730	12.96	0.744	14.65	0.875
9.60	0.653	13.18	0.756	11.44	0.793	14.20	0.758	15.78	0.881
9.98	0.720	14.18	0.775	12.78	0.830	15.30	0.760	18.61	0.897
T = 328.15 K		T = 328.15 K		T = 328.15 K		T = 328.15 K		T = 328.15 K	
x_1 = 0.965		x_1 = 0.952		x_1 = 0.921		x_1 = 0.871		x_1 = 0.790	
8.57^c	0.370^c	9.20^c	0.398^c	9.15^b	0.598^b	9.28^a	0.671^a	8.52^a	0.771^a
8.68	0.381	9.38	0.428	9.26	0.619	9.45	0.683	8.73	0.780
8.91	0.410	9.68	0.473	9.49	0.652	9.69	0.696	9.33	0.794
9.03	0.426	9.89	0.505	9.59	0.664	9.98	0.709	10.38	0.809
9.31	0.467	10.17	0.541	9.96	0.701	10.34	0.722	11.30	0.823
9.56	0.503	10.51	0.585	10.34	0.730	10.83	0.736	12.70	0.839
9.83	0.551	10.67	0.602	10.91	0.761	11.44	0.749	13.62	0.848
10.06	0.581	10.82	0.615	11.73	0.794	12.18	0.764	14.44	0.855
11.20	0.596	11.94	0.653	12.96	0.830	13.10	0.779	15.55	0.864
12.35	0.734	13.00	0.698	14.86	0.870	14.22	0.795	16.57	0.872
13.64	0.782	14.24	0.734						

[a] Bubble point. [b] Critical point. [c] Dew point.

The isothermal compressibility (K_T) of a fluid is a quantitative expression of the sensitivity of density to pressure, which is closely related to the structure of the fluids. K_T values of the mixture can be calculated by the equation

$$K_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \qquad (9)$$

where ρ is the density of the fluid and P is the pressure.

Figure 4 shows the effect of pressure on K_T for the mixed fluids with different compositions and the K_T data calculated from the PR EOS. As can be seen from Figure 4, K_T is large and sensitive to the pressure as the pressure approaches the critical point of a mixture; that is, K_T increases sharply as the pressure approachs the critical pressure. It also can be seen that K_T also increases significantly as the pressure approaches the dew point and bubble point. However, K_T is very small and not sensitive to the pressure when the pressure is far from the phase-separation pressure and/or the composition of the mixture is not close to the critical composition. Similarly, the agreement between the calculated data and the experimental data is not satisfactory.

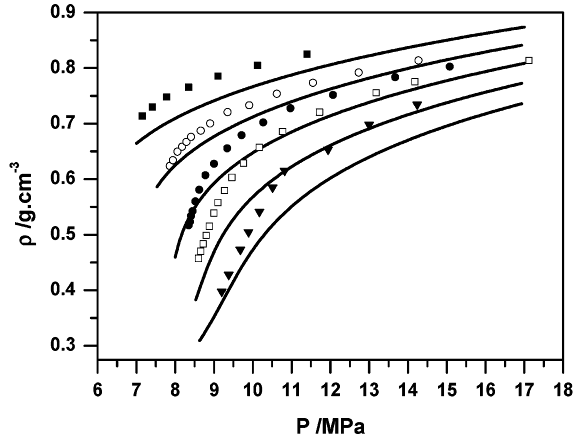

Figure 2. Dependence of the density of CO_2 (1) + ethanol (2) + dichloromethane (3) ternary mixtures ($x_2/x_3 = 1:1$, $x_1 = 0.952$) on pressure at different temperatures: ■, $T = 308.15$ K; ○, $T = 313.15$ K; ●, $T = 318.15$ K; □, $T = 323.15$ K; ▼, $T = 328.15$ K. Lines, calculated results; points, experimental data.

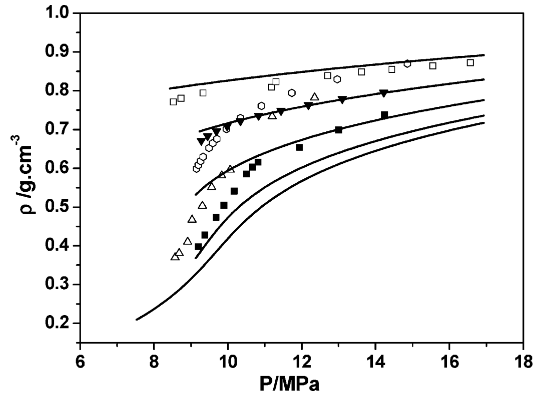

Figure 3. Dependence of the density of CO_2 (1) + ethanol (2) + dichloromethane (3) ternary mixtures ($x_2/x_3 = 1:1$) on pressure at 328.15 K: △, $x_1 = 0.965$; ■, $x_1 = 0.952$; ○, $x_1 = 0.921$; ▼, $x_1 = 0.871$; □, $x_1 = 0.790$. Lines, calculated results; points, experimental data.

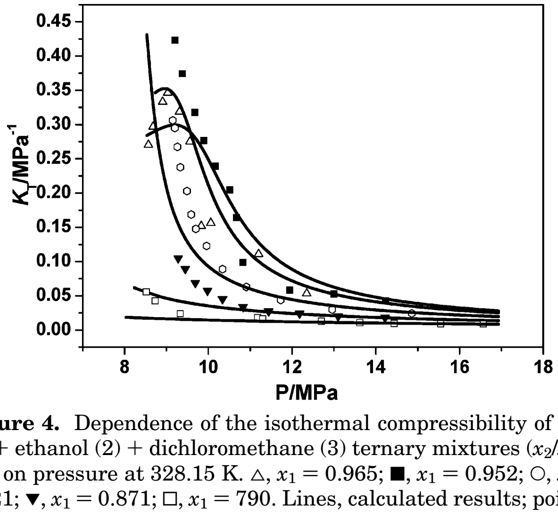

Figure 4. Dependence of the isothermal compressibility of CO_2 (1) + ethanol (2) + dichloromethane (3) ternary mixtures ($x_2/x_3 = 1:1$) on pressure at 328.15 K. △, $x_1 = 0.965$; ■, $x_1 = 0.952$; ○, $x_1 = 0.921$; ▼, $x_1 = 0.871$; □, $x_1 = 790$. Lines, calculated results; points, experimental data.

Conclusions

The phase behavior and density of the CO_2 + ethanol + dichloromethane ternary system were determined at different temperatures and pressures, and the K_T values of the mixed fluids were calculated. The results demonstrate that the density is sensitive to the pressure near the critical point of a mixture. When the pressure is much higher than the phase-separation pressure or the composition is far from the critical composition, then K_T is small, and the effect of pressure on K_T is very limited. The phase-separation pressures calculated from the PR EOS agree well with the experimental data, whereas the agreement between the calculated values and experimental results is relatively poor for the density.

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