Phase Behavior, Densities, and Isothermal Compressibility of Carbon Dioxide + 1-Bromobutane, Carbon Dioxide + 1-Chlorobutane, and Carbon Dioxide + 1-Methylimidazole

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The phase behavior and critical parameters of (carbon dioxide + 1-bromobutane), (carbon dioxide + 1-chlorobutane), and (carbon dioxide + 1-methylimidazole) have been determined using a high-pressure variable-volume view cell, and their densities have also been measured in sub- or supercritical regions. The isothermal compressibility (K_T) is calculated from the density of the binary mixtures. The transition points, bubble point, dew point, and critical point, have been measured with concentrations of organic solvent mole fractions from (0.0102 to 0.1495), temperatures from (308.2 to 337.4) K, and pressures from (6.21 to 19.04) MPa. It is demonstrated that the density is sensitive to the pressure as the pressure approaches the critical point of binary mixtures; that is, K_T is large and increases significantly. K_T also increases sharply when the pressure approaches the dew point or bubble point at other compositions near the critical composition. When the pressure is much higher than the phase transition pressure or the composition is far from the critical composition, K_T is rather small, and the effect of pressure on K_T is fairly limited. The phase boundary data of the binary mixtures can be correlated well by the Peng−Robinson equation of state (PR EoS) with two binary parameters.

Introduction

Supercritical carbon dioxide ($scCO_2$) has been considered as an environmentally benign solvent to replace the conventional toxic organic solvents which are used in many chemical processes because carbon dioxide is readily available, inexpensive, nontoxic, nonflammable, and environmentally benign and has a mild critical temperature (304.2 K) and critical pressure (7.38 MPa). Hence, up to now $scCO_2$ has been broadly employed in many fields including extractions and separations,[1−3] chemical reactions,[4] and material processing.[2,5,6]

1-Bromobutane, 1-chlorobutane, and 1-methylimidazole are important industrial materials that are used as intermediates for pharmaceuticals, agrochemicals, dyes, and other organic synthesis chemicals. Recently, they attracted much attention as common typical reactants for synthesizing room temperature ionic liquids (RTILs), one kind of environmentally benign solvents. Both 1-bromobutane and 1-chlorobutane can react with 1-methylimidazole to synthesize air and water stable imidazole-based RTILs. The synthesis processes usually use many volatile organic solvents, for example, acetonitrile, methanol, ethanol, benzene, ethyl acetate, dichloromethane, 1,1,1-trichloroethane, and so forth.[7−9] Recently, $scCO_2$ has been used as reaction and separation media to synthesize those 1-methylimidazole-based RTILs, in which processes $scCO_2$ can replace the volatile organic solvents. For instance, Zhou et al.[10] studied the preparation of 1-butyl-3-methylimidazolium chloride ([bmim]Cl) in $scCO_2$. Wu et al.[11] synthesized ILs, 1-butyl-3-methylimidazolium bromide ([bmim]Br), and 1,3-dimethylimidazolium trifluoromethanesulfonate ([Me_2Im]TfO) using $scCO_2$ as solvent. During the $scCO_2$ processes, the products and the excess reactants added could be in situ separated by $scCO_2$ extraction without any cross-contamination.

Phase behavior and critical parameters of fluid systems are crucial to the understanding of different chemical processes and separations that are conducted at high pressures and high temperatures, especially for supercritical fluid processes, where phase behavior can significantly influence the reaction rate, selectivity, mass transfer properties, and so forth.[12−14] It has been an interesting topic for years, and many related papers have been published, including the study of various carbon dioxide binary mixtures. However, the phase behavior of (carbon dioxide + 1-bromobutane), (carbon dioxide + 1-chlorobutane), and (carbon dioxide + 1-methylimidazole) mixtures are seldom reported in the literature. Chen et al.[15] studied the phase diagram and density of carbon dioxide + 1-methylimidazole binary system. Wang et al.[16] investigated the solubility of 1-chlorobutane, ethyl methacrylate, and trifluoroethyl acrylate in $scCO_2$ at temperatures of (50.0, 55.0, and 60.0) °C. Undoubtedly, such results can provide us with fundamental information about the density of the two-phase region of (carbon dioxide + 1-methylimidazole) and about the solubility of 1-chlorobutane in carbon dioxide at temperatures of (50.0, 55.0, and 60.0) °C. However, the knowledge of density is greatly important especially in the single-phase region and in more ranges of the temperature.

In this study, we have determined the phase behavior and critical parameters of (carbon dioxide + 1-bromobutane), (carbon dioxide + 1-chlorobutane), and (carbon dioxide + 1-methylimidazole). The density and compressibility of the mixtures were then studied systematically in different phase regions. We also investigated that the effect of phase behavior, composition, and pressure on the density and isothermal compressibility, especially in the critical region. The measured phase boundary data of the system were

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Table 1. Experimental Bubble Points, Critical Points, and Dew Points of Carbon Dioxide (1) + 1-Bromobutane (2) at Fixed Molar Compositions

T/K	P/MPa	phase transition[a]	T/K	P/MPa	phase transition[a]	T/K	P/MPa	phase transition[a]
	$x_2 = 0.0245$			$x_2 = 0.0461$			$x_2 = 0.0683$	
308.2	7.38	b	308.2	7.09	b	308.2	6.85	b
313.1	7.99	b	313.1	7.68	b	313.1	7.48	b
316.1	8.27	cp	317.9	8.33	b	317.9	8.23	b
317.9	8.45	d	322.7	8.86	b	322.7	8.81	b
322.7	8.82	d	327.6	9.36	cp	327.6	9.35	b
327.6	9.08	d	332.4	9.81	d	332.4	9.84	b
332.4	9.17	d	337.4	10.21	d	335.9	10.18	cp
337.4	9.12	d						
	$x_2 = 0.0989$			$x_2 = 0.1495$				
308.2	6.62	b	308.2	6.32	b			
313.1	7.23	b	313.1	6.90	b			
317.9	7.95	b	317.9	7.54	b			
322.7	8.50	b	322.7	8.26	b			
327.6	9.10	b	327.6	8.82	b			
332.4	9.67	b	332.4	9.35	b			
337.4	10.24	b	337.4	10.00	b			

[a] b: bubble point; cp: critical point; d: dew point.

Table 2. Experimental Bubble Points, Critical Points, and Dew Points of Carbon Dioxide (1) + 1-Chloromobutane (2) at Fixed Molar Compositions

T/K	P/MPa	phase transition[a]	T/K	P/MPa	phase transition[a]	T/K	P/MPa	phase transition[a]
	$x_2 = 0.0243$			$x_2 = 0.0483$			$x_2 = 0.0744$	
308.2	7.64	b	308.2	7.24	b	308.2	6.91	b
313.1	8.22	b	313.1	7.89	b	313.1	7.46	b
314.5	8.32	cp	317.9	8.53	b	317.9	8.05	b
317.9	8.56	d	324.0	9.11	cp	322.7	8.63	b
322.7	8.62	d	327.6	9.41	d	327.6	9.15	b
327.6	8.12	d	332.4	9.75	d	333.3	9.63	cp
			337.4	9.96	d	337.4	9.93	d
	$x_2 = 0.0981$			$x_2 = 0.1488$				
308.2	6.56	b	308.2	6.21	b			
313.1	7.13	b	313.1	6.76	b			
317.9	7.73	b	317.9	7.34	b			
322.7	8.33	b	322.7	7.90	b			
327.6	8.92	b	327.6	8.48	b			
332.4	9.43	b	332.4	9.07	b			
337.4	9.89	b	337.4	9.62	b			

[a] b: bubble point; cp: critical point; d: dew point.

modeled using the Peng−Robinson equation of state (PR EoS) with two binary parameters.

Experimental Section

Materials. Carbon dioxide with mass fraction purity of 0.99995 was purchased from the Beijing Haipu Company. 1-Bromobutane and 1-chlorobutane were analytical grade produced by the Beijing Yili Chemical Reagent International Co. 1-Methylimidazole was also analytical grade produced by the Beijing Chemical Reagent Plant and was further purified by vacuum distillation before used.

Apparatus and Procedures. The phase behavior and densities of the mixtures were determined using a high pressure variable-volume view-cell, and the detailed measurements were similar to those previously reported.[17] The volume of the view cell could be changed in the range of (25 to 55) cm^3 by moving the piston. The constant-temperature water bath was controlled by a temperature controller (A2, Beijing Changliu Scientific Instrument Company) with an accuracy of better than ± 0.1 K. The pressure gauge was composed of a pressure transducer and an indicator (Beijing Tianchen Instrument Company). Its uncertainty was ± 0.025 MPa in the pressure range of (0 to 20) MPa.

In a typical experiment, a desired amount of organic solvent (1-bromobutane, 1-chlorobutane, or 1-methylimidazole) was charged into the view cell, and the air in the system was slowly replaced with carbon dioxide. Carbon dioxide was then added using a sampling bomb. The mass of carbon dioxide in the view cell was calculated from the mass difference of the sampling bomb before and after charging the system. The cell was placed into the water bath at a desired temperature, and the system was stirred. It was supposed that equilibrium was reached when the system pressure and temperature were constant for at least half an hour. After thermal equilibration, the piston in the optical 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 ascertained from the position of the piston, which was calibrated accurately using water as a medium. The composition and density of the mixtures could easily be calculated from the masses of the components and the volume of the system.

Table 3. Experimental Bubble Points, Critical Points, and Dew Points of Carbon Dioxide (1) + 1-Methylimidazole (2) at Fixed Molar Compositions

T/K	P/MPa	phase transition[a]	T/K	P/MPa	phase transition[a]	T/K	P/MPa	phase transition[a]
	$x_2 = 0.0102$			$x_2 = 0.0247$			$x_2 = 0.0487$	
308.2	7.86	b	308.2	7.79	b	308.2	8.59	d
309.8	8.02	cp	313.1	8.90	d	313.1	10.07	d
313.1	8.75	d	317.9	10.18	d	317.9	11.51	d
317.9	9.73	d	322.7	11.46	d	322.7	12.99	d
322.7	10.72	d	327.6	12.51	d	327.6	14.19	d
327.6	11.61	d	332.4	13.55	d	332.4	15.45	d
332.4	12.41	d	337.4	14.49	d	337.4	16.64	d
337.4	13.05	d						
	$x_2 = 0.1024$							
308.2	9.85	d						
313.1	11.54	d						
317.9	13.15	d						
322.7	14.64	d						
327.6	16.08	d						
332.4	17.52	d						
337.4	18.72	d						

[a] b: bubble point; cp: critical point; d: dew point.

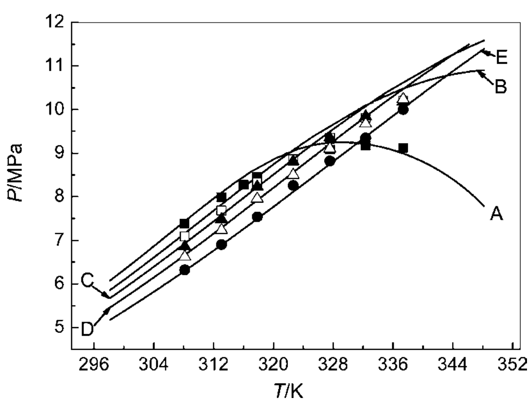

Figure 1. Phase boundary of carbon dioxide (1) + 1-bromobutane (2) with different compositions: (■, A), $x_2 = 0.0245$; (□, B), $x_2 = 0.0461$; (▲, C), $x_2 = 0.0683$; (△, D), $x_2 = 0.0989$; (●, E), $x_2 = 0.1495$; symbols, experimental data; lines, calculated results by PR EoS.

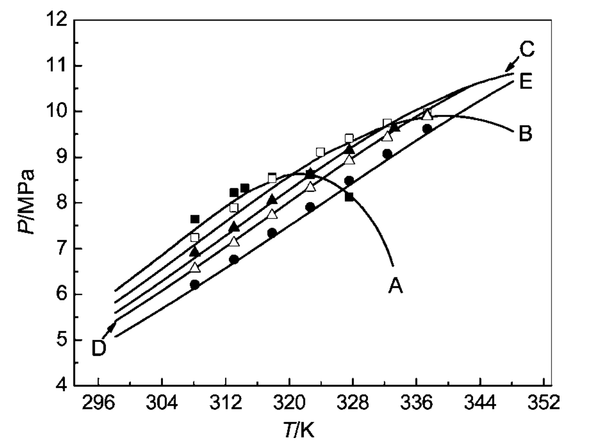

Figure 2. Phase boundary of carbon dioxide (1) + 1-chlorobutane (2) with different compositions: (■, A), $x_2 = 0.0243$; (□, B), $x_2 = 0.0483$; (▲, C), $x_2 = 0.0744$ (△, D), $x_2 = 0.0981$; (●, E), $x_2 = 0.1488$; symbols, experimental data; lines, calculated results by PR EoS.

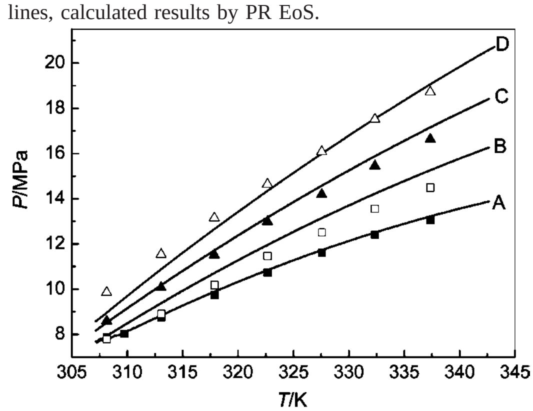

Figure 3. Phase boundary of carbon dioxide (1) + 1-methylimidazole (2) with different compositions: (■, A), $x_2 = 0.0102$; (□, B), $x_2 = 0.0247$; (▲, C), $x_2 = 0.0487$ (△, D), $x_2 = 0.1024$; symbols, experimental data; lines, calculated results by PR EoS.

It is estimated that the uncertainty of the density data is ± 0.001 g·cm^{-3}, and the uncertainty in the compositions of samples is better than ± 0.5 %. 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 uncertainty of the K_T data was better than ± 3 %.

Results and Discussion

Critical Points and Phase Behavior of the Mixtures. First, to verify the reliability of the apparatus, we measured the phase behavior of the carbon dioxide + acetone binary system at (303.13, 308.15, and 313.13) K with a carbon dioxide mole fraction of 0.8979, and the corresponding phase transition pressures are (6.03, 6.63, and 7.27) MPa, respectively, which show deviations of (0.4, 1.5, and 0.2) %, respectively, compared with literature results (interpolated).[18] Our results about the carbon dioxide + acetone binary system are also in good agreement with the data previously reported in literature.[19−21] Furthermore, the phase transition pressures for the carbon dioxide + 1-methylimidazole system have an average deviation of 1.3 % compared with the literature,[15] and the data for carbon dioxide + 1-chlorobutane have an average deviation of not more than 1.0 % compared with the literature,[16] which indicates that the present experimental data can be accorded well with the literature.

The bubble point, critical point, and dew point temperatures and pressures for the three binary systems (carbon dioxide + 1-bromobutane; carbon dioxide + 1-chlorobutane; carbon dioxide + 1-methylimidazole) at different compositions are listed in Tables 1, 2, and 3. As expected, at low concentrations of organic solvents from (0.0102 to 0.1495) mole fraction that

Table 4. Densities ρ of Carbon Dioxide (1) + 1-Bromobutane (2) 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 = 308.2 K, x_2 = 0.0245		T = 313.1 K, x_2 = 0.0245		T = 316.1 K, x_2 = 0.0245		T = 317.9 K, x_2 = 0.0245		T = 322.7 K, x_2 = 0.0245	
7.38^a	0.712^a	7.99^a	0.619^a	8.27^b	0.528^b	8.45^c	0.491^c	8.82^c	0.422^c
7.40	0.711	8.00	0.621	8.28	0.532	8.46	0.493	8.84	0.425
7.42	0.713	8.03	0.628	8.30	0.537	8.48	0.499	8.88	0.432
7.44	0.716	8.07	0.635	8.32	0.543	8.50	0.506	8.92	0.439
7.48	0.720	8.10	0.641	8.34	0.549	8.53	0.512	8.96	0.447
7.52	0.724	8.14	0.649	8.36	0.556	8.55	0.518	9.00	0.455
7.59	0.729	8.19	0.656	8.38	0.562	8.57	0.525	9.07	0.465
7.64	0.734	8.24	0.663	8.41	0.572	8.60	0.532	9.11	0.473
7.70	0.738	8.30	0.671	8.46	0.582	8.62	0.540	9.16	0.482
7.77	0.743	8.36	0.679	8.51	0.593	8.65	0.547	9.21	0.491
7.83	0.747	8.43	0.687	8.56	0.604	8.69	0.555	9.26	0.500
7.92	0.752	8.53	0.695	8.62	0.615	8.72	0.563	9.32	0.510
8.01	0.757	8.62	0.703	8.69	0.627	8.77	0.571	9.37	0.520
8.09	0.762	8.74	0.712	8.78	0.639	8.80	0.579	9.43	0.531
8.20	0.767	8.86	0.720	8.88	0.652	8.82	0.583	9.50	0.542
8.30	0.772	9.01	0.729	9.00	0.665	8.84	0.588	9.57	0.553
8.42	0.777	9.18	0.738	9.15	0.683	8.87	0.589	9.66	0.565
8.62	0.785	9.38	0.748	9.34	0.694	8.89	0.597	9.75	0.576
8.84	0.793	9.60	0.758	9.56	0.709	8.92	0.601	9.85	0.590
9.10	0.801	9.85	0.767	9.85	0.725	8.96	0.608	9.93	0.599
9.37	0.809	10.15	0.778	10.20	0.741			9.99	0.606
9.68	0.818	10.45	0.788	10.24	0.743			10.00	0.608
10.04	0.827	10.84	0.799	10.29	0.746				
10.42	0.835	11.28	0.810	10.35	0.750				
10.86	0.844	11.76	0.821						
11.35	0.853	12.32	0.833						
11.88	0.863	12.96	0.845						
12.48	0.873	13.70	0.857						
13.13	0.882	14.53	0.870						
13.59	0.889	14.98	0.876						
14.14	0.896	15.15	0.879						
14.29	0.899								
T = 327.6 K, x_2 = 0.0245		T = 332.4 K, x_2 = 0.0245		T = 337.9 K, x_2 = 0.0245		T = 308.2 K, x_2 = 0.0461		T = 313.1 K, x_2 = 0.0461	
9.08^c	0.359^c	9.17^c	0.317^c	9.12^c	0.280^c	7.09^a	0.805^a	7.68^a	0.756^a
9.11	0.362	9.20	0.319	9.15	0.283	7.23	0.811	7.73	0.758
9.17	0.369	9.25	0.323	9.22	0.288	7.39	0.817	7.82	0.764
9.22	0.375	9.30	0.328	9.29	0.292	7.55	0.823	7.91	0.769
9.27	0.382	9.35	0.332	9.37	0.297	7.66	0.827	8.01	0.775
9.33	0.389	9.40	0.336	9.44	0.303	7.75	0.830	8.10	0.780
9.38	0.396	9.44	0.340	9.52	0.308	7.85	0.833	8.24	0.786
9.42	0.401	9.49	0.345	9.60	0.314	7.95	0.836	8.36	0.791
9.46	0.406	9.54	0.349	9.68	0.320	8.06	0.839	8.50	0.797
9.52	0.414	9.58	0.354	9.75	0.325	8.19	0.843	8.65	0.802
9.58	0.423	9.64	0.359	9.83	0.331			8.84	0.808
9.65	0.431	9.69	0.364	9.92	0.338			9.04	0.814
9.72	0.440	9.74	0.369	10.00	0.345			9.24	0.820
9.79	0.449	9.79	0.375	10.08	0.352			9.47	0.826
9.86	0.459	9.84	0.380	10.18	0.359			9.71	0.833
9.95	0.469	9.90	0.386	10.27	0.367			9.99	0.840
10.03	0.480	9.95	0.392	10.36	0.375				
10.05	0.484	10.01	0.398	10.45	0.383				
10.06	0.486	10.02	0.399	10.56	0.391				
				10.62	0.397				
				10.63	0.399				
T = 317.9 K, x_2 = 0.0461		T = 322.7 K, x_2 = 0.0461		T = 327.6 K, x_2 = 0.0461		T = 332.4 K, x_2 = 0.0461		T = 337.4 K, x_2 = 0.0461	
8.33^a	0.703^a	8.86^a	0.629^a	9.36^b	0.555^b	9.81^c	0.512^c	10.21^c	0.479^c
8.37	0.705	8.90	0.632	9.38	0.559	9.83	0.516	10.26	0.482
8.45	0.712	8.94	0.639	9.39	0.563	9.89	0.521	10.34	0.492
8.55	0.721	8.99	0.647	9.43	0.569	9.93	0.527	10.43	0.502
8.68	0.731	9.06	0.655	9.47	0.577	9.97	0.533	10.54	0.513
8.84	0.741	9.12	0.662	9.49	0.584	10.02	0.539	10.66	0.524
8.96	0.748	9.19	0.671	9.56	0.591	10.06	0.546	10.79	0.537
9.10	0.756	9.27	0.679	9.65	0.599	10.12	0.552	10.91	0.549
9.27	0.764	9.38	0.687	9.71	0.606	10.18	0.559	11.06	0.563
9.53	0.774	9.48	0.696	9.76	0.615	10.24	0.566	11.23	0.577
9.81	0.785	9.61	0.705	9.83	0.623	10.30	0.573	11.37	0.588
10.16	0.796	9.81	0.718	9.92	0.631	10.37	0.580	11.51	0.599
10.59	0.809	10.09	0.733	10.01	0.640	10.44	0.587	11.68	0.611
11.06	0.821	10.42	0.748	10.12	0.649	10.52	0.595	11.86	0.623
11.60	0.833	10.82	0.764	10.24	0.658	10.59	0.603	12.08	0.636
11.89	0.839	11.29	0.779	10.36	0.668	10.72	0.615	12.32	0.649
		11.91	0.797	10.50	0.678	10.88	0.627	12.58	0.663
		12.64	0.814	10.66	0.688	11.07	0.640	12.91	0.674
		13.21	0.826	10.84	0.698	11.27	0.654	13.26	0.693
		13.83	0.838	10.99	0.706	11.51	0.668	13.53	0.703
						11.78	0.683		
						11.98	0.689		
						12.22	0.703		
						12.33	0.708		

Table 4. Continued

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 = 308.2 K		T = 313.1 K		T = 317.9 K		T = 322.7 K		T = 327.6 K	
x_2 = 0.0683		x_2 = 0.0683		x_2 = 0.0683		x_2 = 0.0683		x_2 = 0.0683	
6.85[a]	0.834[a]	7.48[a]	0.811[a]	8.23[a]	0.777[a]	8.81[a]	0.731[a]	9.35[a]	0.677[a]
6.93	0.836	7.59	0.814	8.34	0.780	8.88	0.735	9.38	0.680
6.98	0.838	7.67	0.817	8.49	0.786	8.97	0.740	9.47	0.688
7.05	0.842	7.76	0.820	8.63	0.791	9.07	0.745	9.57	0.696
7.09	0.845	7.86	0.823	8.79	0.797	9.16	0.750	9.70	0.705
7.16	0.848	7.95	0.826	8.94	0.802	9.25	0.755	9.83	0.714
7.24	0.850	8.06	0.829	9.13	0.808	9.36	0.759	10.00	0.723
7.35	0.854	8.17	0.832	9.33	0.814	9.48	0.765	10.19	0.733
7.45	0.858	8.29	0.835	9.54	0.820	9.60	0.770	10.38	0.742
7.54	0.861	8.39	0.838	9.77	0.826	9.73	0.775	10.63	0.752
7.66	0.864	8.54	0.842	10.03	0.832	9.87	0.780	10.92	0.762
7.78	0.867	8.66	0.845	10.31	0.838	10.05	0.786	11.24	0.773
		8.79	0.848	10.63	0.845	10.23	0.791	11.59	0.783
		8.93	0.851	10.94	0.850	10.42	0.797	11.99	0.794
		9.11	0.854	11.31	0.858	10.62	0.802	12.46	0.805
		9.26	0.858	11.69	0.863	10.84	0.808	13.04	0.817
		9.44	0.861	11.87	0.867	11.08	0.814	13.65	0.829
		9.58	0.864			11.34	0.820	13.99	0.835
		9.79	0.868			11.60	0.826	14.74	0.848
						11.91	0.832	14.96	0.851
						12.22	0.838		
						12.57	0.845		
						12.90	0.850		
						13.28	0.857		
						13.73	0.864		
						13.96	0.867		

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 = 332.4 K		T = 335.9 K		T = 308.2 K		T = 313.1 K		T = 317.9 K	
x_2 = 0.0683		x_2 = 0.0683		x_2 = 0.0989		x_2 = 0.0989		x_2 = 0.0989	
9.84[a]	0.622[a]	10.18[b]	0.589[b]	6.62[a]	0.890[a]	7.23[a]	0.875[a]	7.95[a]	0.850[a]
9.87	0.625	10.20	0.591	6.84	0.897	7.52	0.881	8.09	0.853
9.90	0.629	10.21	0.593	7.04	0.903	7.83	0.882	8.37	0.859
9.96	0.636	10.24	0.597	7.35	0.910	8.17	0.893	8.65	0.865
10.00	0.640	10.25	0.601	7.70	0.916	8.56	0.900	8.95	0.871
10.07	0.647	10.31	0.607	8.12	0.924	9.03	0.907	9.30	0.877
10.15	0.654	10.38	0.614	8.61	0.930	9.48	0.913	9.67	0.884
10.24	0.662	10.45	0.620	9.19	0.938	10.02	0.920	10.05	0.890
10.34	0.670	10.54	0.627	9.82	0.944	10.60	0.927	10.50	0.897
10.44	0.677	10.61	0.634	10.13	0.948	11.18	0.933	10.95	0.903
10.57	0.686	10.70	0.641			11.85	0.941	11.47	0.910
10.71	0.694	10.79	0.649			12.16	0.944	12.01	0.916
10.87	0.703	10.94	0.660			12.56	0.948	12.61	0.923
11.05	0.712	11.14	0.672					13.25	0.930
11.24	0.721	11.35	0.684					13.89	0.937
11.46	0.730	11.59	0.697					14.63	0.944
11.72	0.739	11.87	0.710					14.98	0.947
12.00	0.749	12.34	0.728						
12.33	0.759	12.93	0.747						
12.67	0.770	13.69	0.767						
13.08	0.780	14.35	0.783						
13.54	0.791	14.89	0.794						
14.05	0.802	14.99	0.797						
14.64	0.814	15.11	0.800						
14.96	0.820								

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 = 322.7 K		T = 327.6 K		T = 332.4 K		T = 337.4 K		T = 308.2 K	
x_2 = 0.0989		x_2 = 0.0989		x_2 = 0.0989		x_2 = 0.0989		x_2 = 0.1495	
8.50[a]	0.818[a]	9.10[a]	0.786[a]	9.67[a]	0.750[a]	10.24[a]	0.714[a]	6.32[a]	1.011[a]
8.72	0.825	9.23	0.791	9.78	0.755	10.29	0.717	7.40	1.018
8.92	0.830	9.39	0.796	9.89	0.759	10.36	0.722	8.19	1.026
9.16	0.836	9.54	0.801	10.00	0.764	10.44	0.726	9.04	1.033
9.40	0.841	9.70	0.806	10.11	0.769	10.52	0.730	9.96	1.041
9.65	0.847	9.89	0.811	10.24	0.774	10.59	0.735	10.92	1.048
9.93	0.853	10.08	0.817	10.37	0.778	10.69	0.739	11.37	1.051
10.24	0.859	10.29	0.822	10.51	0.783	10.79	0.743	11.91	1.055
10.55	0.870	10.51	0.828	10.65	0.788	10.89	0.748	12.51	1.060
10.91	0.872	10.73	0.833	10.82	0.793	10.99	0.752	13.08	1.063
11.27	0.877	11.06	0.839	10.99	0.798	11.13	0.757	13.64	1.067
11.68	0.884	11.31	0.845	11.18	0.804	11.24	0.762	14.21	1.071
12.13	0.890	11.62	0.851	11.39	0.808	11.37	0.766	14.85	1.075
12.61	0.897	11.96	0.857	11.60	0.814	11.52	0.771	15.15	1.077
13.11	0.903	12.31	0.862	11.83	0.819	11.68	0.776		
13.64	0.910	12.71	0.869	12.06	0.825	11.83	0.781		
14.21	0.916	13.11	0.875	12.33	0.830	12.01	0.786		
14.88	0.924	13.52	0.880	12.62	0.836	12.20	0.791		
15.16	0.926	13.98	0.887	12.93	0.842	12.39	0.796		
		14.47	0.893	13.25	0.847	12.62	0.801		
		15.00	0.900	13.60	0.853	12.85	0.806		
				13.98	0.859	13.11	0.812		
				14.36	0.865	13.36	0.817		
				14.81	0.871	13.65	0.822		
						13.92	0.828		
						14.22	0.833		
						14.57	0.839		
						14.88	0.844		
						15.22	0.850		

Table 4. Continued

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 = 313.1 K, x_2 = 0.1495		T = 317.9 K, x_2 = 0.1495		T = 322.7 K, x_2 = 0.1495		T = 327.6 K, x_2 = 0.1495		T = 332.4 K, x_2 = 0.1495	
6.90[a]	0.986[a]	7.54[a]	0.964[a]	8.26[a]	0.946[a]	8.82[a]	0.922[a]	9.35[a]	0.896[a]
7.25	0.991	7.77	0.967	8.47	0.948	8.95	0.924	9.58	0.900
7.51	0.994	7.99	0.970	8.71	0.952	9.14	0.927	9.76	0.903
7.77	0.997	8.23	0.974	8.92	0.954	9.34	0.930	9.89	0.906
8.09	1.001	8.45	0.977	9.16	0.958	9.52	0.933	10.04	0.909
8.46	1.004	8.66	0.980	9.38	0.961	9.71	0.936	10.19	0.912
8.79	1.008	8.99	0.984	9.67	0.964	9.89	0.939	10.37	0.915
9.54	1.015	9.25	0.987	9.91	0.968	10.07	0.942	10.56	0.918
9.95	1.018	9.58	0.990	10.16	0.971	10.31	0.945	10.75	0.921
10.33	1.022	9.86	0.993	10.44	0.974	10.56	0.949	10.94	0.924
10.77	1.026	10.24	0.997	10.76	0.977	10.78	0.951	11.12	0.927
11.24	1.030	10.56	1.000	10.98	0.980	11.00	0.954	11.31	0.930
11.69	1.033	10.93	1.004	11.37	0.984	11.28	0.958	11.53	0.933
12.12	1.036	11.27	1.007	11.64	0.987	11.52	0.961	11.73	0.936
12.60	1.040	11.70	1.011	11.99	0.990	11.79	0.964	11.97	0.939
13.09	1.044	12.06	1.014	12.29	0.994	12.05	0.967	12.19	0.942
13.64	1.047	12.52	1.018	12.66	0.997	12.37	0.970	12.45	0.945
14.17	1.051	12.97	1.022	13.01	1.000	12.67	0.974	12.65	0.948
14.74	1.056	13.43	1.026	13.49	1.004	13.00	0.977	12.92	0.951
15.07	1.058	13.86	1.029	13.82	1.008	13.35	0.981	13.17	0.954
15.32	1.060	14.38	1.033	14.23	1.011	13.66	0.984	13.47	0.958
		14.80	1.036	14.62	1.015	13.96	0.987	13.75	0.961
		15.02	1.038	15.12	1.018	14.32	0.990	14.04	0.964
						14.69	0.993	14.32	0.967
						15.09	0.997	14.63	0.970
								14.91	0.973
								15.09	0.975
T = 337.4 K, x_2 = 0.1495									
10.00[a]	0.872[a]								
10.19	0.876								
10.31	0.879								
10.43	0.881								
10.58	0.884								
10.69	0.887								
10.81	0.889								
10.97	0.893								
11.10	0.895								
11.25	0.898								
11.42	0.901								
11.58	0.904								
11.74	0.906								
11.92	0.909								
12.07	0.912								
12.28	0.915								
12.49	0.918								
12.68	0.921								
12.89	0.924								
13.13	0.927								
13.32	0.930								
13.55	0.933								
13.77	0.936								
14.02	0.939								
14.30	0.942								
14.53	0.945								
14.75	0.948								
15.05	0.951								

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

we investigated, T_C and P_C increase with the increase of the concentration of organic solvents. Figures 1, 2, and 3 give graphical representations of the experimentally determined phase boundaries for the three binary systems. There is a two-phase region below or inside lines of fixed composition, while the one-phase region is above or outside these lines. In this work, besides phase separation points, all of the experiments were carried out in the single-phase regions, that is, above the phase transition lines.

Density and Isothermal Compressibility. The densities of the mixtures were measured at temperatures up to 337.4 K and pressures up to 19.04 MPa in the supercritical and subcritical regions. Tables 4, 5, and 6 summarize the densities of the (carbon dioxide + 1-bromobutane), (carbon dioxide + 1-chlorobutane), and (carbon dioxide + 1-methylimidazole), respectively. Figures 4 and 5 illustrate the dependence of the densities of (carbon dioxide + 1-bromobutane) and (carbon dioxide + 1-methylimidazole) on pressure and temperature at different compositions. The dependence of the density of (carbon dioxide + 1-chlorobutane) has a similar tendency to that of the binary mixture of (carbon dioxide + 1-bromobutane) because 1-chlorobutane and 1-bromobutane are homologous. It can be seen from Figures 4 and 5 that a similar tendency was observed for different compositions and different materials. Obviously, at fixed composition and fixed temperature, the density increases with increasing pressure,

Table 5. Densities ρ of Carbon Dioxide (1) + 1-Chlorobutane (2) 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 = 308.2 K, x_2 = 0.0243		T = 313.1 K, x_2 = 0.0243		T = 314.5 K, x_2 = 0.0243		T = 317.9 K, x_2 = 0.0243		T = 322.7 K, x_2 = 0.0243	
7.64^a	0.670^a	8.22^a	0.545^a	8.32^b	0.495^b	8.56^c	0.417^c	8.62^c	0.328^c
7.67	0.674	8.23	0.549	8.33	0.501	8.59	0.423	8.69	0.336
7.71	0.678	8.25	0.555	8.36	0.510	8.63	0.433	8.75	0.343
7.74	0.682	8.28	0.563	8.39	0.522	8.67	0.443	8.81	0.351
7.78	0.686	8.30	0.571	8.43	0.531	8.72	0.453	8.86	0.360
7.82	0.690	8.33	0.580	8.46	0.541	8.75	0.464	8.92	0.368
7.86	0.694	8.36	0.588	8.49	0.552	8.79	0.473	8.98	0.377
7.94	0.701	8.40	0.597	8.53	0.562	8.85	0.484	9.05	0.387
8.03	0.707	8.47	0.610	8.59	0.575	8.89	0.496	9.11	0.397
8.12	0.713	8.55	0.623	8.65	0.588	8.94	0.507	9.17	0.407
8.23	0.720	8.65	0.637	8.72	0.602	8.99	0.520	9.24	0.418
8.35	0.727	8.77	0.651	8.82	0.617	9.06	0.534	9.32	0.430
8.48	0.734	8.93	0.666	8.93	0.632	9.14	0.549	9.39	0.443
8.57	0.738	9.13	0.682	9.08	0.648	9.23	0.565	9.47	0.456
8.80	0.748	9.39	0.698	9.27	0.664	9.34	0.582	9.56	0.470
8.91	0.753	9.71	0.716	9.48	0.680	9.46	0.599	9.63	0.482
9.05	0.758	10.02	0.729	9.79	0.698	9.58	0.615	9.70	0.494
9.19	0.763	10.28	0.738	10.15	0.715	9.74	0.630	9.74	0.501
		10.55	0.748	10.48	0.729	9.84	0.639	9.79	0.507
		10.70	0.753	10.73	0.738	9.95	0.647	9.81	0.510
		10.85	0.758	11.03	0.748	10.03	0.654		
		11.03	0.763	11.37	0.758				
				11.74	0.767				

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 = 327.6 K, x_2 = 0.0243		T = 308.2 K, x_2 = 0.0483		T = 313.1 K, x_2 = 0.0483		T = 317.9 K, x_2 = 0.0483		T = 324.0 K, x_2 = 0.0483	
8.12^c	0.244^c	7.24^a	0.742^a	7.89^a	0.693^a	8.53^a	0.630^a	9.11^b	0.519^b
8.18	0.249	7.33	0.747	7.94	0.697	8.59	0.636	9.14	0.527
8.25	0.253	7.43	0.752	8.00	0.701	8.69	0.646	9.19	0.537
8.32	0.258	7.53	0.757	8.10	0.707	8.81	0.656	9.25	0.546
8.39	0.263	7.66	0.761	8.21	0.713	8.94	0.667	9.31	0.556
8.46	0.268	7.79	0.766	8.34	0.719	9.08	0.678	9.37	0.566
8.52	0.274	7.94	0.770	8.45	0.725	9.20	0.689	9.45	0.576
8.59	0.279	8.11	0.776	8.60	0.732	9.49	0.701	9.54	0.587
8.67	0.285	8.28	0.780	8.76	0.738	9.77	0.713	9.63	0.599
8.75	0.291	8.47	0.785	8.94	0.745	10.09	0.725	9.75	0.611
8.82	0.298	8.56	0.788	9.15	0.751	10.35	0.734	9.85	0.620
8.88	0.304	8.67	0.790	9.37	0.759	10.65	0.742	10.01	0.633
8.95	0.311	8.77	0.793	9.62	0.765	10.97	0.752	10.20	0.646
9.04	0.318	8.89	0.795	9.81	0.770	11.34	0.761	10.42	0.660
9.11	0.326	9.00	0.798	10.00	0.775	11.74	0.770	10.69	0.674
9.18	0.334	9.12	0.800	10.22	0.780	12.22	0.780	11.03	0.689
9.27	0.343	9.23	0.803	10.46	0.785	12.74	0.790	11.44	0.705
9.35	0.352	9.35	0.805	10.68	0.790	13.32	0.800	11.96	0.721
9.41	0.359	9.49	0.808	10.95	0.795	13.62	0.805	12.55	0.738
9.46	0.364	9.64	0.811	11.22	0.800	13.95	0.811	13.03	0.749
		9.78	0.813	11.51	0.806	14.30	0.816	13.45	0.758
		9.91	0.815	11.81	0.811			13.95	0.768
				12.11	0.816			14.45	0.778
								15.02	0.788

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 = 327.6 K, x_2 = 0.0483		T = 332.4 K, x_2 = 0.0483		T = 337.4 K, x_2 = 0.0483		T = 308.2 K, x_2 = 0.0744		T = 313.1 K, x_2 = 0.0744	
9.41^c	0.469^c	9.75^c	0.421^c	9.96^c	0.378^c	6.91^a	0.786^a	7.46^a	0.754^a
9.43	0.473	9.80	0.426	10.04	0.384	7.08	0.791	7.64	0.759
9.47	0.480	9.86	0.433	10.09	0.390	7.47	0.801	7.77	0.764
9.52	0.487	9.91	0.441	10.16	0.396	7.70	0.807	7.94	0.769
9.57	0.494	9.97	0.449	10.23	0.402	7.95	0.812	8.09	0.773
9.62	0.502	10.05	0.458	10.29	0.409	8.07	0.814	8.27	0.778
9.67	0.510	10.15	0.469	10.36	0.415	8.23	0.817	8.47	0.782
9.73	0.518	10.20	0.478	10.42	0.422	8.35	0.820	8.68	0.787
9.79	0.526	10.28	0.487	10.49	0.429	8.50	0.822	8.90	0.792
9.86	0.535	10.39	0.497	10.57	0.436	8.64	0.825	9.15	0.797
9.93	0.544	10.49	0.507	10.65	0.444	8.83	0.828	9.41	0.802
10.01	0.553	10.59	0.518	10.73	0.452	8.97	0.830	9.67	0.807
10.09	0.562	10.70	0.529	10.82	0.459	9.16	0.833	9.96	0.812
10.19	0.572	10.83	0.541	10.90	0.468	9.33	0.836	10.29	0.817
10.29	0.582	10.97	0.554	10.99	0.477	9.53	0.838	10.62	0.823
10.41	0.593	11.14	0.569	11.09	0.485	9.70	0.841	10.97	0.828
10.54	0.604	11.35	0.584	11.19	0.495	9.94	0.844	11.35	0.833
10.69	0.615	11.56	0.598	11.27	0.501	10.11	0.846	11.78	0.839
10.81	0.623	11.83	0.613	11.34	0.508			12.22	0.844
10.91	0.629	12.12	0.629	11.44	0.516			12.43	0.847
11.00	0.635	12.30	0.637	11.51	0.521				
11.06	0.639	12.53	0.648						
11.14	0.644	12.61	0.652						
11.22	0.648								

Table 5. Continued

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 = 317.9 K		T = 322.7 K		T = 327.6 K		T = 333.3 K		T = 337.4 K	
x_2 = 0.0744		x_2 = 0.0744		x_2 = 0.0744		x_2 = 0.0744		x_2 = 0.0744	
8.05^a	0.713^a	8.63^a	0.669^a	9.15^a	0.616^a	9.63^b	0.545^b	9.93^c	0.509^c
8.23	0.720	8.74	0.675	9.19	0.620	9.66	0.551	9.96	0.513
8.36	0.727	8.86	0.683	9.26	0.626	9.69	0.556	10.01	0.520
8.52	0.733	8.99	0.690	9.38	0.635	9.74	0.563	10.08	0.527
8.69	0.740	9.14	0.698	9.50	0.645	9.81	0.571	10.18	0.536
8.88	0.746	9.29	0.705	9.64	0.655	9.90	0.578	10.28	0.547
9.11	0.753	9.47	0.713	9.81	0.665	9.98	0.586	10.42	0.560
9.36	0.760	9.70	0.721	10.01	0.675	10.10	0.597	10.55	0.571
9.60	0.766	9.94	0.729	10.24	0.686	10.25	0.608	10.70	0.583
9.89	0.773	10.21	0.738	10.51	0.697	10.41	0.620	10.87	0.595
10.22	0.780	10.52	0.746	10.70	0.705	10.60	0.632	11.06	0.607
10.56	0.787	10.87	0.755	10.94	0.713	10.84	0.645	11.27	0.620
10.94	0.794	11.23	0.764	11.20	0.721	11.11	0.658	11.52	0.634
11.37	0.802	11.68	0.773	11.48	0.729	11.42	0.672	11.83	0.648
11.86	0.810	12.17	0.782	11.80	0.738	11.80	0.686	12.20	0.663
12.37	0.817	12.72	0.792	12.35	0.750	12.26	0.701	12.63	0.679
12.93	0.825	13.32	0.802	12.97	0.763	12.81	0.717	13.16	0.695
13.51	0.833	14.02	0.812	13.46	0.773	13.47	0.733	13.80	0.713
14.18	0.841	14.60	0.820	14.01	0.782	14.29	0.750	14.58	0.731
14.91	0.849	14.96	0.824	14.60	0.792	14.75	0.759	15.14	0.742
		15.19	0.828	15.27	0.802	15.24	0.768		
T = 308.2 K		T = 313.1 K		T = 317.9 K		T = 322.7 K		T = 327.6 K	
x_2 = 0.0981		x_2 = 0.0981		x_2 = 0.0981		x_2 = 0.0981		x_2 = 0.0981	
6.56^a	0.819^a	7.13^a	0.791^a	7.73^a	0.761^a	8.33^a	0.728^a	8.92^a	0.692^a
6.79	0.825	7.31	0.795	7.90	0.766	8.51	0.734	9.05	0.698
6.98	0.827	7.57	0.802	8.09	0.771	8.62	0.739	9.20	0.704
7.14	0.831	7.86	0.807	8.31	0.777	8.78	0.744	9.36	0.711
7.32	0.834	8.18	0.813	8.53	0.782	8.94	0.749	9.53	0.718
7.50	0.837	8.51	0.819	8.77	0.787	9.12	0.754	9.73	0.725
7.73	0.840	8.89	0.825	9.05	0.793	9.30	0.759	9.94	0.731
7.94	0.843	9.26	0.830	9.35	0.799	9.50	0.764	10.20	0.739
8.17	0.846	9.72	0.837	9.65	0.804	9.72	0.769	10.45	0.746
8.39	0.849	10.19	0.843	10.01	0.810	10.08	0.777	10.77	0.754
8.63	0.852	10.69	0.849	10.35	0.815	10.48	0.785	11.11	0.761
8.90	0.856	11.23	0.855	10.75	0.822	10.92	0.792	11.46	0.769
9.16	0.859	11.82	0.862	11.18	0.827	11.44	0.802	11.88	0.777
9.45	0.862	12.44	0.869	11.67	0.834	12.00	0.810	12.33	0.785
9.78	0.865	12.78	0.872	12.14	0.839	12.60	0.818	12.83	0.792
10.03	0.869	13.00	0.874	12.69	0.846	13.03	0.824	13.41	0.802
10.38	0.872			13.25	0.852	13.53	0.830	14.22	0.813
10.51	0.874			13.83	0.859	14.03	0.836	14.94	0.822
				14.53	0.865	14.59	0.843	15.14	0.825
				15.22	0.872	15.17	0.849		
T = 332.4 K		T = 337.4 K		T = 308.2 K		T = 313.1 K		T = 317.9 K	
x_2 = 0.0981		x_2 = 0.0981		x_2 = 0.1488		x_2 = 0.1488		x_2 = 0.1488	
9.43^a	0.649^a	9.89^a	0.605^a	6.21^a	0.843^a	6.76^a	0.825^a	7.34^a	0.805^a
9.51	0.654	9.98	0.612	6.56	0.848	6.98	0.828	7.74	0.811
9.56	0.657	10.07	0.619	6.85	0.853	7.31	0.832	8.06	0.815
9.66	0.663	10.15	0.625	7.25	0.858	7.74	0.837	8.45	0.820
9.76	0.669	10.25	0.632	7.74	0.863	8.19	0.841	8.83	0.823
9.87	0.675	10.36	0.639	8.29	0.868	8.91	0.849	9.24	0.828
10.00	0.682	10.50	0.647	8.84	0.873	9.45	0.853	9.66	0.832
10.13	0.687	10.63	0.654	9.48	0.878	10.27	0.860	10.09	0.836
10.29	0.694	10.79	0.662	10.15	0.883	10.86	0.865	10.58	0.841
10.47	0.700	10.96	0.670	10.85	0.888	11.50	0.870	11.09	0.847
10.65	0.707	11.17	0.678	11.62	0.893	12.17	0.875	11.62	0.851
10.85	0.713	11.38	0.686	12.43	0.898	12.54	0.878	11.94	0.853
11.08	0.720	11.64	0.694	13.27	0.904	12.89	0.880	12.24	0.856
11.33	0.727	11.93	0.703	13.66	0.906	13.24	0.883	12.52	0.858
11.59	0.734	12.24	0.711	14.09	0.909	13.66	0.885	12.85	0.861
11.98	0.743	12.58	0.721	14.42	0.911	14.02	0.888	13.14	0.863
12.43	0.753	12.95	0.729	14.87	0.914	14.46	0.890	13.44	0.865
12.96	0.763	13.38	0.739			14.83	0.893	13.80	0.868
13.54	0.774	14.11	0.753					14.19	0.871
14.19	0.785	14.97	0.768					14.48	0.873
14.90	0.795	15.30	0.774					14.86	0.875
15.11	0.798								

and at fixed composition and fixed pressure, the density decreases with increasing temperature.

As pressures approach the phase boundary, especially close to the critical point, the density of the mixture is sensitive to the pressure; that is, the density of the mixture decreases greatly when the pressure decreases close to the critical point. However, when the pressure is far away from the phase separation pressure, the density of these fluids has no obvious change.

The results in Figures 4 and 5 indicate that the sensitivity of density to system pressure depends on both the composition and the pressure at fixed temperatures. The isothermal com-

Table 5. Continued

$\frac{P}{\text{MPa}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{P}{\text{MPa}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{P}{\text{MPa}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{P}{\text{MPa}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{P}{\text{MPa}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$
$T = 322.7$ K, $x_2 = 0.1488$		$T = 327.6$ K, $x_2 = 0.1488$		$T = 332.4$ K, $x_2 = 0.1488$		$T = 337.4$ K, $x_2 = 0.1488$			
7.90[a]	0.782[a]	8.48[a]	0.758[a]	9.07[a]	0.732[a]	9.62[a]	0.705[a]		
8.14	0.786	8.71	0.762	9.26	0.737	9.77	0.709		
8.38	0.789	8.92	0.766	9.42	0.740	9.95	0.714		
8.67	0.794	9.14	0.770	9.59	0.744	10.15	0.719		
8.97	0.798	9.37	0.774	9.76	0.748	10.36	0.724		
9.28	0.802	9.60	0.778	9.94	0.751	10.58	0.729		
9.60	0.807	9.85	0.781	10.13	0.755	10.84	0.735		
9.95	0.811	10.11	0.785	10.34	0.758	11.09	0.740		
10.31	0.815	10.41	0.790	10.57	0.762	11.38	0.746		
10.73	0.820	10.72	0.794	10.80	0.766	11.68	0.751		
11.11	0.823	11.05	0.798	11.03	0.770	12.03	0.757		
11.54	0.828	11.38	0.802	11.28	0.774	12.38	0.762		
12.02	0.832	11.77	0.806	11.57	0.778	12.75	0.768		
12.27	0.835	12.15	0.811	11.84	0.782	13.18	0.774		
12.52	0.837	12.53	0.815	12.33	0.788	13.45	0.778		
12.78	0.839	12.95	0.819	12.82	0.794	13.78	0.781		
13.27	0.844	13.40	0.823	13.36	0.800	14.12	0.786		
13.57	0.846	13.89	0.828	13.94	0.806	14.48	0.790		
13.85	0.849	14.35	0.832	14.57	0.813	14.83	0.794		
14.17	0.851	14.90	0.837	14.84	0.816				
14.47	0.853								
14.74	0.856								

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

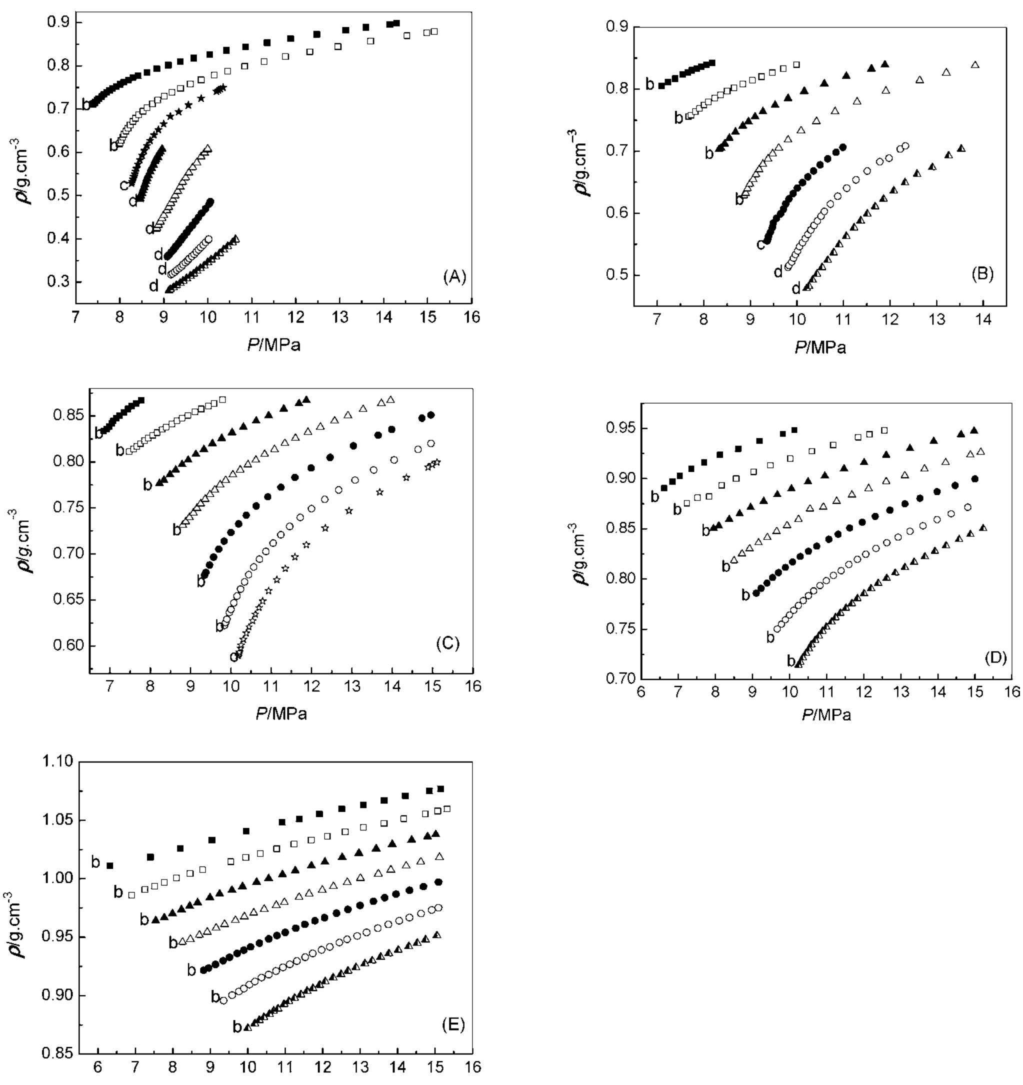

Figure 4. Dependence of the density ρ of the carbon dioxide (1) + 1-bromobutane (2) binary mixture on temperature and pressure in the critical region with different compositions: A, $x_2 = 0.0245$; B, $x_2 = 0.0461$; C, $x_2 = 0.0683$; D, $x_2 = 0.0989$; E, $x_2 = 0.1495$. Temperatures are labeled as follows: ■, $T = 308.2$ K; □, $T = 313.1$ K; ★, $T = 316.1$ K; ▲, $T = 317.9$ K; △, $T = 322.7$ K; ●, $T = 327.6$ K; ○, $T = 332.4$ K; ☆, $T = 335.9$ K.; ◭, $T = 337.9$ K. b, bubble point; c, critical point; d, dew point.

Table 6. Densities ρ of Carbon Dioxide (1) + 1-Methylimidazole (2) 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 = 308.2 K, x_2 = 0.0102		T = 309.8 K, x_2 = 0.0102		T = 313.1 K, x_2 = 0.0102		T = 317.9 K, x_2 = 0.0102		T = 322.7 K, x_2 = 0.0102	
7.86[a]	0.638[a]	8.02[b]	0.543[b]	8.75[c]	0.576[c]	9.73[c]	0.555[c]	10.72[c]	0.558[c]
7.87	0.640	8.03	0.551	8.77	0.581	9.78	0.563	10.82	0.568
7.90	0.646	8.04	0.560	8.81	0.589	9.85	0.573	10.93	0.578
7.94	0.652	8.06	0.571	8.85	0.597	9.91	0.583	11.04	0.589
7.95	0.655	8.07	0.581	8.89	0.606	9.99	0.594	11.14	0.600
7.98	0.661	8.09	0.589	8.94	0.615	10.08	0.606	11.27	0.612
8.02	0.667	8.11	0.600	8.99	0.624	10.18	0.618	11.43	0.624
8.08	0.676	8.14	0.612	9.04	0.633	10.30	0.630	11.61	0.636
8.16	0.686	8.18	0.624	9.12	0.643	10.44	0.643	11.81	0.649
8.26	0.696	8.23	0.636	9.20	0.653	10.62	0.656	12.03	0.663
8.38	0.706	8.30	0.649	9.30	0.663	10.81	0.670	12.30	0.677
8.52	0.716	8.39	0.663	9.42	0.673	11.05	0.684	12.64	0.692
8.69	0.727	8.50	0.677	9.55	0.684	11.33	0.699	13.03	0.707
8.91	0.738	8.65	0.691	9.70	0.695	11.68	0.715	13.48	0.723
9.15	0.750	8.83	0.707	9.90	0.707	12.10	0.731	14.04	0.740
9.44	0.761	9.09	0.723	10.13	0.719	12.64	0.749	14.51	0.753
9.80	0.773	9.42	0.740	10.38	0.731	13.26	0.766	15.26	0.771
10.20	0.786	9.83	0.758	10.70	0.744	14.06	0.785	16.21	0.790
10.70	0.799	10.21	0.772	11.08	0.758	15.05	0.806	17.02	0.805
11.25	0.812	10.88	0.790	11.54	0.771	15.89	0.821	17.96	0.821
11.92	0.826	11.97	0.816	12.07	0.786	16.91	0.837	18.15	0.824
12.61	0.840	12.53	0.826	12.70	0.800				
13.44	0.859	13.14	0.836	13.46	0.816				
14.56	0.875	13.68	0.846	14.34	0.832				
14.99	0.880			15.01	0.842				
15.43	0.886								
T = 327.6 K, x_2 = 0.0102		T = 332.4 K, x_2 = 0.0102		T = 337.4K, x_2 = 0.0102		T = 308.2 K, x_2 = 0.0247		T = 313.1 K, x_2 = 0.0247	
11.61[c]	0.548[c]	12.41[c]	0.539[c]	13.05[c]	0.568[c]	7.79[a]	0.745[a]	8.90[c]	0.717[c]
11.72	0.558	12.55	0.548	13.15	0.576	7.97	0.755	9.00	0.723
11.84	0.568	12.67	0.558	13.27	0.584	8.20	0.766	9.12	0.729
11.97	0.578	12.82	0.568	13.37	0.593	8.47	0.777	9.26	0.737
12.11	0.589	12.98	0.578	13.49	0.601	8.82	0.790	9.40	0.744
12.27	0.600	13.16	0.589	13.62	0.610	9.25	0.802	9.56	0.751
12.44	0.612	13.35	0.600	13.77	0.619	9.75	0.815	9.73	0.759
12.63	0.624	13.56	0.612	13.91	0.628	10.13	0.824	9.94	0.766
12.85	0.636	13.79	0.623	14.08	0.638	10.56	0.833	10.17	0.774
13.11	0.649	14.04	0.636	14.24	0.648	11.07	0.842	10.57	0.786
13.40	0.663	14.32	0.649	14.43	0.658	11.62	0.851	10.87	0.794
13.73	0.677	14.64	0.663	14.63	0.669	12.24	0.860	11.20	0.802
14.11	0.692	15.03	0.677	14.85	0.680	12.59	0.865	11.58	0.811
14.56	0.707	15.48	0.692	15.08	0.691	12.94	0.870	12.00	0.819
15.10	0.723	15.97	0.707	15.35	0.703	13.31	0.875	12.49	0.828
15.73	0.740	16.57	0.723	15.74	0.719	13.72	0.880	13.01	0.837
16.46	0.758	17.26	0.740	16.08	0.732	14.14	0.885	13.60	0.846
17.13	0.771	18.06	0.757	16.45	0.745	14.61	0.890	14.28	0.855
17.85	0.786	18.62	0.769	16.84	0.759	15.06	0.895	14.97	0.865
18.38	0.795	18.86	0.773	17.30	0.773	15.60	0.901	15.36	0.870
18.84	0.802			17.82	0.788			15.79	0.875
				18.20	0.798			16.22	0.880
				18.61	0.808			16.69	0.885
				18.81	0.813				
T = 317.9 K, x_2 = 0.0247		T = 322.7 K, x_2 = 0.0247		T = 327.6 K, x_2 = 0.0247		T = 332.4 K, x_2 = 0.0247		T = 337.4 K, x_2 = 0.0247	
10.18[c]	0.708[c]	11.46[c]	0.701[c]	12.51[c]	0.682[c]	13.55[c]	0.668[c]	14.49[c]	0.650[c]
10.34	0.716	11.57	0.706	12.63	0.687	13.73	0.675	14.56	0.653
10.49	0.723	11.73	0.712	12.72	0.691	13.89	0.681	14.66	0.658
10.64	0.730	11.91	0.719	12.89	0.698	13.96	0.684	14.78	0.662
10.81	0.737	12.09	0.726	13.06	0.704	14.14	0.690	14.90	0.666
11.00	0.744	12.30	0.733	13.25	0.711	14.33	0.696	15.02	0.671
11.22	0.751	12.52	0.740	13.46	0.718	14.52	0.703	15.14	0.675
11.46	0.758	12.75	0.747	13.67	0.724	14.74	0.709	15.27	0.680
11.71	0.766	13.02	0.755	13.90	0.731	14.97	0.716	15.42	0.684
11.96	0.774	13.31	0.762	14.14	0.738	15.22	0.723	15.56	0.689
12.29	0.781	13.62	0.770	14.41	0.745	15.48	0.730	15.73	0.693
12.82	0.793	13.95	0.777	14.71	0.753	15.75	0.737	15.88	0.698
13.44	0.806	14.34	0.786	15.01	0.760	15.96	0.742	16.05	0.703
14.14	0.819	14.75	0.794	15.27	0.766	16.19	0.747	16.23	0.708
14.67	0.828	15.20	0.802	15.55	0.772	16.43	0.752	16.41	0.713
15.28	0.837	15.69	0.810	15.97	0.779	16.72	0.758	16.61	0.717
15.57	0.841	16.07	0.816	16.40	0.787	16.91	0.762	16.89	0.724
15.92	0.846	16.54	0.824	16.64	0.791	17.09	0.766	17.19	0.731
16.26	0.851	16.83	0.828	16.98	0.798	17.30	0.770	17.45	0.737
16.62	0.855	17.16	0.833	17.21	0.802	17.51	0.774	17.68	0.742
17.01	0.860	17.49	0.837	17.60	0.808	17.80	0.779	18.06	0.749
		17.83	0.842	17.87	0.813				

Table 6. Continued

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}
$T = 308.2$ K, $x_2 = 0.0487$		$T = 313.1$ K, $x_2 = 0.0487$		$T = 317.9$ K, $x_2 = 0.0487$		$T = 322.7$ K, $x_2 = 0.0487$		$T = 327.6$ K, $x_2 = 0.0487$	
8.59^c	0.838^c	10.07^c	0.827^c	11.51^c	0.815^c	12.99^c	0.807^c	14.19^c	0.791^c
8.68	0.841	10.19	0.830	11.59	0.817	13.12	0.809	14.34	0.795
8.79	0.844	10.32	0.833	11.70	0.820	13.25	0.812	14.57	0.799
8.91	0.847	10.44	0.835	11.82	0.822	13.50	0.817	14.83	0.804
9.04	0.849	10.56	0.838	11.97	0.825	13.79	0.822	15.08	0.809
9.15	0.852	10.69	0.841	12.08	0.827	14.08	0.827	15.37	0.814
9.29	0.853	10.83	0.843	12.21	0.830	14.37	0.832	15.66	0.819
9.45	0.858	10.99	0.846	12.35	0.833	14.71	0.838	15.94	0.825
9.60	0.860	11.13	0.849	12.48	0.836	15.07	0.843	16.28	0.829
9.75	0.863	11.28	0.852	12.64	0.838	15.43	0.849	16.65	0.836
9.92	0.866	11.44	0.855	12.93	0.843	15.86	0.855	17.33	0.846
		11.62	0.858	13.30	0.849	16.28	0.860	17.74	0.851
		11.79	0.860	13.66	0.854	16.70	0.866	18.20	0.857
		11.98	0.862	14.03	0.860			18.69	0.863
		12.18	0.865	14.45	0.866				
$T = 332.4$ K, $x_2 = 0.0487$		$T = 337.4$ K, $x_2 = 0.0487$		$T = 308.2$ K, $x_2 = 0.1024$		$T = 313.1$ K, $x_2 = 0.1024$		$T = 317.9$ K, $x_2 = 0.1024$	
15.45^c	0.779^c	16.64^c	0.769^c	9.85^c	0.937^c	11.54^c	0.928^c	13.15^c	0.919^c
15.71	0.784	16.60	0.768	10.03	0.939	11.74	0.930	13.40	0.922
15.92	0.789	16.73	0.770	10.36	0.942	11.99	0.933	13.72	0.925
16.13	0.794	16.85	0.773	10.63	0.945	12.32	0.936	13.98	0.927
16.26	0.797	16.96	0.775	11.00	0.948	12.62	0.939	14.31	0.930
16.39	0.799	17.07	0.777	11.31	0.951	12.97	0.942	14.56	0.933
16.52	0.801	17.17	0.780	11.71	0.954	13.28	0.944	14.71	0.934
16.65	0.804	17.29	0.782	12.01	0.956	13.66	0.947	14.88	0.936
16.83	0.806	17.41	0.784	12.46	0.960	14.02	0.950	15.13	0.938
16.97	0.809	17.56	0.787	12.82	0.963	14.43	0.954	15.33	0.939
17.13	0.811	17.68	0.789	13.25	0.966	14.78	0.956	15.48	0.941
17.26	0.814	17.81	0.791	13.69	0.969	15.21	0.959	15.63	0.942
17.44	0.817	17.94	0.794	14.14	0.972	15.65	0.963	15.95	0.944
17.59	0.819	18.09	0.797	14.57	0.975	16.15	0.966	16.38	0.947
17.75	0.821	18.21	0.799	15.08	0.978	16.56	0.969	16.80	0.950
17.92	0.824	18.35	0.800	15.54	0.981	17.10	0.972	17.18	0.953
18.12	0.827	18.51	0.804	16.08	0.984	17.54	0.975	17.60	0.956
18.28	0.829	18.67	0.806	16.57	0.987	18.15	0.979	18.05	0.959
18.48	0.832	18.82	0.809	17.25	0.991	18.57	0.981	18.37	0.962
18.67	0.835	18.99	0.811	17.65	0.994	18.94	0.983	18.75	0.964
18.86	0.837			18.34	0.998			18.99	0.965
19.04	0.840			18.88	1.001				
$T = 322.7$ K, $x_2 = 0.1024$		$T = 327.6$ K, $x_2 = 0.1024$		$T = 332.4$ K, $x_2 = 0.1024$					
14.64^c	0.909^c	16.08^c	0.899^c	17.52^c	0.890^c				
14.78	0.911	16.17	0.900	17.68	0.892				
14.92	0.912	16.30	0.901	17.73	0.892				
15.03	0.913	16.42	0.903	17.80	0.893				
15.18	0.915	16.54	0.904	17.89	0.894				
15.29	0.916	16.65	0.905	17.96	0.895				
15.47	0.917	16.78	0.906	18.04	0.896				
15.59	0.918	16.93	0.908	18.09	0.896				
15.90	0.922	17.06	0.909	18.15	0.897				
16.23	0.924	17.21	0.911	18.20	0.897				
16.53	0.927	17.39	0.912	18.25	0.898				
16.88	0.929	17.49	0.913	18.31	0.899				
17.18	0.933	17.62	0.914	18.40	0.900				
17.34	0.934	17.75	0.916	18.47	0.900				
17.57	0.936	17.96	0.918	18.53	0.901				
17.75	0.937	18.08	0.919	18.58	0.901				
17.92	0.939	18.23	0.920	18.62	0.902				
18.12	0.940	18.38	0.922	18.69	0.902				
18.33	0.942	18.58	0.923	18.75	0.903				
18.57	0.943	18.77	0.924	18.86	0.904				
18.77	0.945	18.94	0.925	18.94	0.905				
18.99	0.946								

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

pressibility (K_T) of a fluid is a quantitative expression of the sensitivity of density to pressure, which is closely related with the structure of fluids.[22] K_T values of the mixture can be calculated by the following equation:

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

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

Figures 6 and 7 show the effect of the pressure on K_T for mixed fluids having the different compositions. The variations of K_T with pressure and composition of the three mixtures show similar behavior. As can be seen from the figures, K_T is very large and sensitive to the pressure as the pressure approaches to the critical point of mixture; that is, K_T increases sharply as the pressure approaches to the crit-

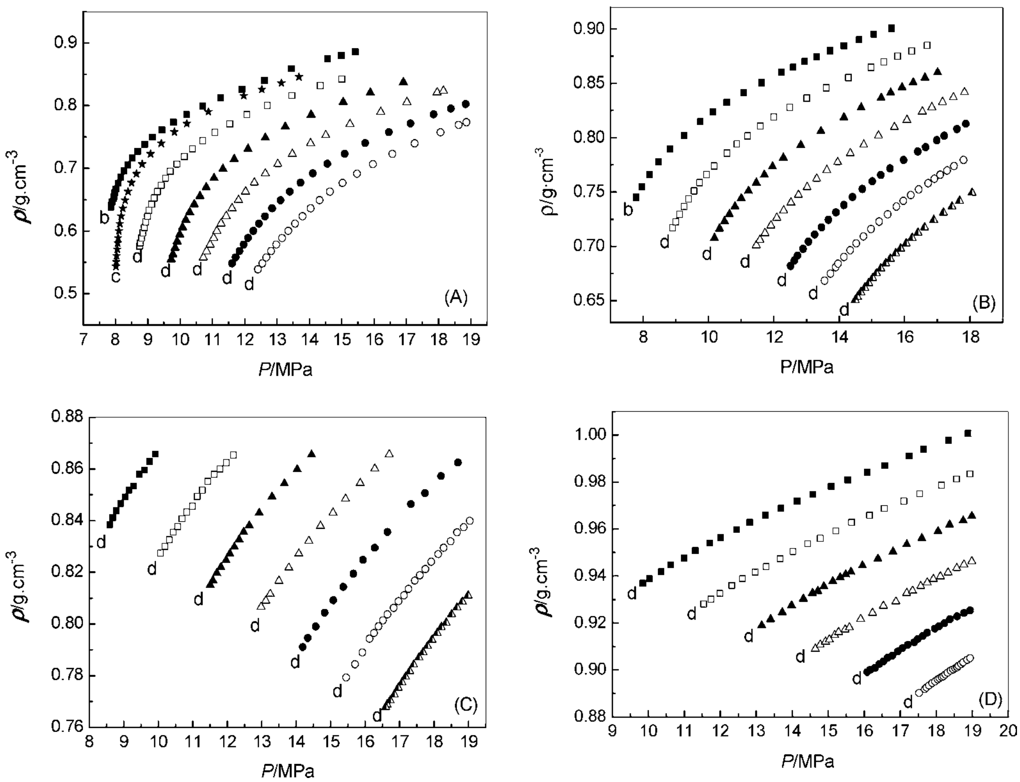

Figure 5. Dependence of the density ρ of the carbon dioxide (1) + 1-methylimidazole (2) binary mixture on temperature and pressure in the critical region with different compositions: A, $x_2 = 0.0102$; B, $x_2 = 0.0247$; C, $x_2 = 0.0487$; D, $x_2 = 0.1024$; Temperatures are labeled as follows: ■, $T = 308.2$ K; ★, $T = 309.8$ K; □, $T = 313.1$ K; ▲, $T = 317.9$ K; △, $T = 322.7$ K; ●, $T = 327.6$ K; ○, $T = 332.4$ K; ◭, $T = 337.4$ K. b, bubble point; c, critical point; d, dew point.

Table 7. Pure Component Parameters and Binary Parameters Used in the PR EoS and Corresponding Values of the Average Absolute Relative Deviation (AARD) for Carbon Dioxide + 1-Bromobutane, Carbon Dioxide + 1-Chlorobutane, and Carbon Dioxide + 1-Methylimidozole Binary Systems

	T_c	P_c				AARD
component	K	MPa	ω	k_{12}[a]	l_{12}[a]	%
carbon dioxide	304.3	7.38	0.225			
1-bromobutane	568.6[b]	4.26[b]	0.331[b]	0.024	−0.10	3.53
1-chlorobutane	539.2[c]	3.77[b]	0.274[b]	0.041	−0.02	1.89
1-methylimidazole	742.5[b]	5.56[b]	0.284[b]	0.020	−0.01	3.63

[a] 1 for carbon dioxide and 2 for the corresponding organic solvent. [b] Calculated using the method reported by Joback and Reid.[28] [c] Reported by Morton et al.[27]

ical pressure. It also can be seen that K_T increases significantly as the pressure nears the phase separation pressure. However, K_T is very small and not sensitive to pressure when the pressure is well above the phase separation pressure.

The data in Figures 6 and 7 also illustrate that, when the temperature is far from the critical points, the effect of pressure on K_T is limited, even near the phase separation point, especially in the Figure 6D,E.

Correlation. High pressure phase behaviors of carbon dioxide containing mixtures have been modeled successfully with cubic EoS's, such as PR EoS and Redlich-Kwong EoS.[23−25] In this work, the PR EoS with the van der Waals mixing rules[26] was selected to correlate the vapor−liquid equilibrium data and the critical points of the three mixtures. The explicit form for this equation is expressed as follows.

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \tag{2}$$

The constants a and b can be obtained from the related parameters of pure components. For a mixture, the van der Waals mixing rules are presented:

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i b_j}(1 - k_{ij}) \tag{3}$$

$$b = \sum_i \sum_j 0.5 x_i x_j (b_i + b_j)(1 - l_{ij}) \tag{4}$$

where a_i and b_i are parameters of pure components, k_{ij} and l_{ij} are the binary interaction parameters for the (i, j) pair, and x_i is the mole fraction of the ith component.

The physical property information (T_c, P_c, and ω) used for the pure component carbon dioxide is taken from NIST (see Table 7). The critical temperature of 1-chlorobutane is reported by Morton et al.[27] The physical properties of the other organic solvents (1-bromobutane, 1-chlorobutane, and 1-methylimidazole) are calculated using the method reported by Joback and Reid,[28] and the results are also listed in Table 7.

Binary parameters are empirical parameters that can be regressed from the binary data by minimizing the average absolute deviation for bubble and dew point pressures. The k_{ij} and l_{ij} values for these binary mixtures involved in this work are shown in Table 7; they were obtained by minimizing the following objective function (OF).

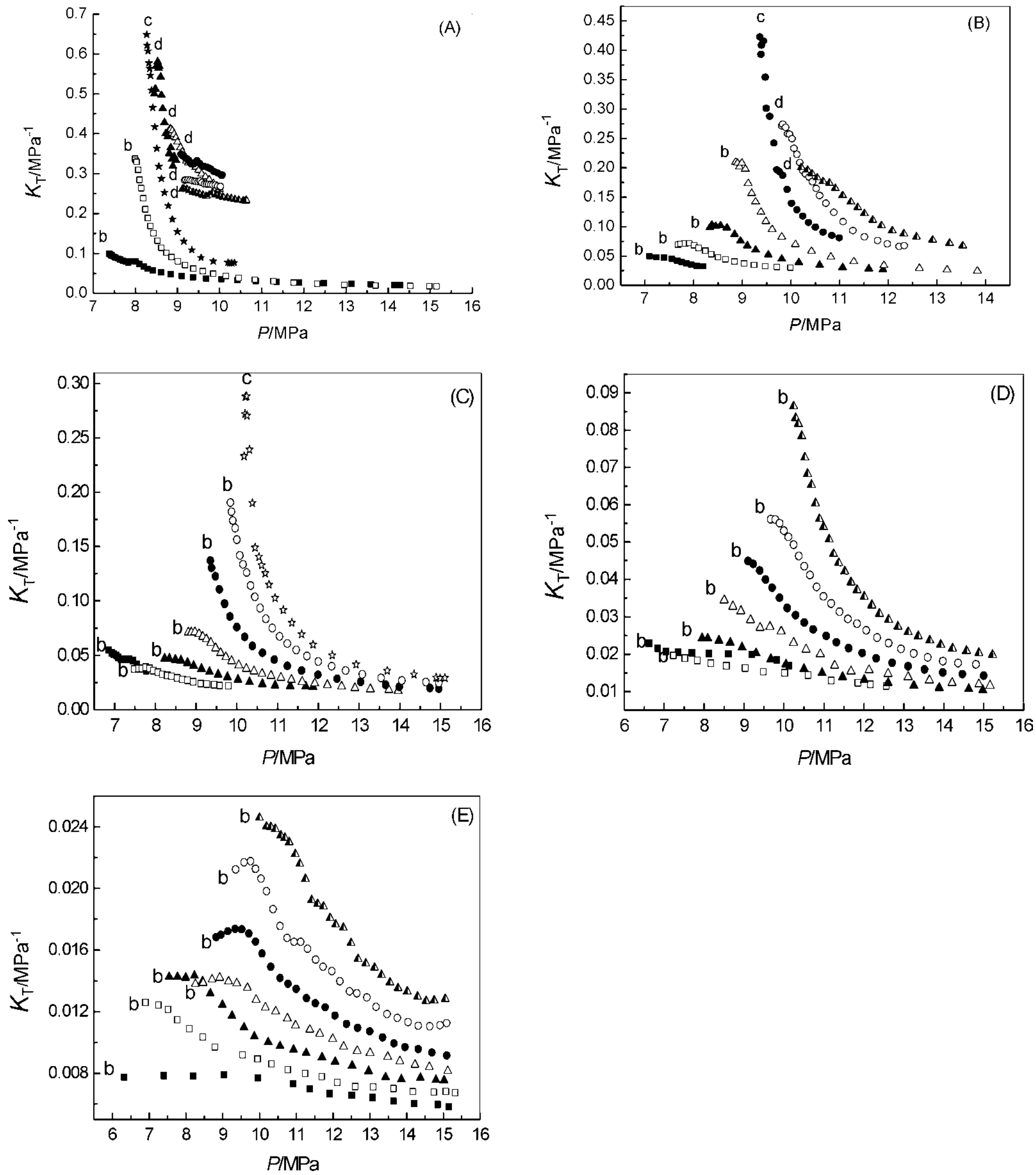

Figure 6. Dependence of the isothermal compressibility K_T of the carbon dioxide (1) + 1-bromobutane (2) binary mixture on temperature and pressure with different compositions: A, $x_2 = 0.0245$; B, $x_2 = 0.0461$; C, $x_2 = 0.0683$; D, $x_2 = 0.0989$; E, $x_2 = 0.1495$. Temperatures are labeled as follows: ■, $T = 308.2$ K; □, $T = 313.1$ K; ★, $T = 316.1$ K; ▲, $T = 317.9$ K; △, $T = 322.7$ K; ●, $T = 327.6$ K; ○, $T = 332.4$ K; ☆, $T = 335.9$ K.; ◭, $T = 337.9$ K. b, bubble point; c, critical point; d, dew point.

$$\mathrm{OF} = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{\xi^{\mathrm{exptl}} - \xi^{\mathrm{calcd}}}{\xi^{\mathrm{exptl}}}\right| \qquad (5)$$

where n is the number of experimental points and ξ^{exptl} and ξ^{calcd} are the experimental and the calculated pressure at each phase transition point, respectively.

The average absolute relative deviation (AARD) of this calculation was defined as follows:

$$\mathrm{AARD} = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{\xi^{\mathrm{exptl}} - \xi^{\mathrm{calcd}}}{\xi^{\mathrm{exptl}}}\right|\cdot 100\ \% \qquad (6)$$

The corresponding values of AARD are also shown in Table 7.

On the basis of the physical properties and the two binary parameters, the PR EoS was used to correlate the phase behavior of the (carbon dioxide + 1-bromobutane), (carbon dioxide + 1-chlorobutane), and (carbon dioxide + 1-methylimidazole). The correlation results are also shown in Figures 1 to 3. It can be seen from the figures that the PR EoS can correlate the phase boundary of three binary systems to a satisfactory degree from (308.2 to 337.4) K.

Conclusion

The phase behavior and densities of (carbon dioxide + 1-bromobutane), (carbon dioxide + 1-chlorobutane), and (carbon dioxide + 1-methylimidazole) were determined at different temperatures and pressures, and the isothermal compressibility K_T was calculated from the densities of these binary mixtures. The PR EoS was used to correlate the experimental data. The results demonstrate that the density is sensitive to the pressure near the critical point of the mixtures. When the pressure is much higher than the phase separation pressure or the composition is far from the critical composition, K_T is very small, and the effect of pressure on K_T is very limited. The phase boundary pressures

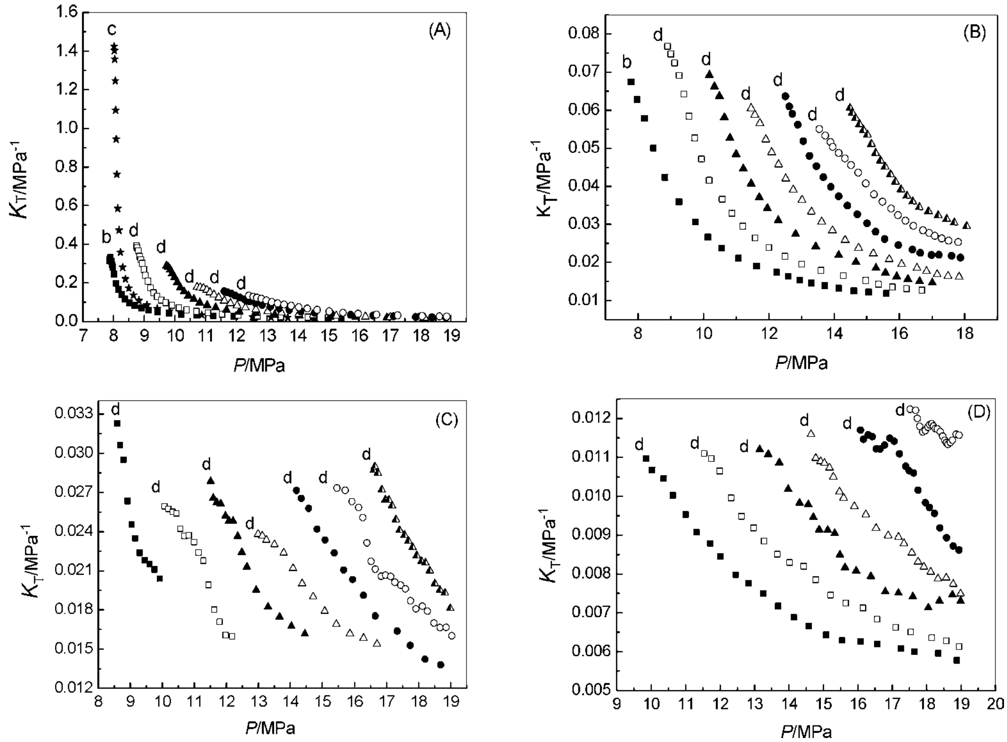

Figure 7. Dependence of the isothermal compressibility K_T of the carbon dioxide (1) + 1-methylimidazole (2) binary mixture on temperature and pressure with different compositions: A, $x_2 = 0.0102$; B, $x_2 = 0.0247$; C, $x_2 = 0.0487$; D, $x_2 = 0.1024$. Temperatures are labeled as follows: ■, $T = 308.2$ K; ★, $T = 309.8$ K; □, $T = 313.1$ K; ▲, $T = 317.9$ K; △, $T = 322.7$ K; ●, $T = 327.6$ K; ○, $T = 332.4$ K; ◭, $T = 337.4$ K. b, bubble point; c, critical point; d, dew point.

and temperatures which were calculated from the PR EoS with two binary parameters agree well with the experimental data.

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Literature Cited

(1) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice*, 2nd ed.; Butterworth-Heinemann: Boston, 1994.
(2) Eckert, C. A.; Knutson, B. L.; Debenedetti, P. G. Supercritical Fluids as Solvents for Chemical and Material Processing. *Nature* **1996**, *383*, 313.
(3) King, J. W.; Sahle-Demessle, E.; Temelli, F.; Teel, J. A. Thermal Gradient Fractionation of Glyceride Mixtures under Supercritical Fluid Conditions. *J. Supercrit. Fluids* **1997**, *10*, 127–137.
(4) Jessop, P. G.; Leitner, W., Eds. *Chemical Synthesis Using Supercritical fluids*; Wiley-VCH: Weinheim, Germany, 1999; pp 676−688.
(5) Cooper, A. I. Polymer Synthesis and Processing Using Supercritical Carbon Dioxide. *J. Mater. Chem.* **2000**, *10*, 207–234.
(6) Li, D.; Han, B. X. Phase Behavior of Supercritical CO_2/Styrene/Poly(vinyl chloride) System and Synthesis of Polystyrene/Poly (vinyl chloride) Composites. *Macromolecules* **2000**, *33*, 4555–4560.
(7) Bonhôte, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. Hydrophobic, Highly Conductive Ambient - Temperature Molten Salts. *Inorg. Chem.* **1996**, *35*, 1168–1178.
(8) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. Dialkylimidazolium Chloroaluminate Melts: A New Class of Room-Temperature Ionic Liquids for Electrochemistry, Spectroscopy, and Synthesis. *Inorg. Chem.* **1982**, *21*, 1263–1264.
(9) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. Room Temperature Ionic Liquids as Novel Media for 'Clean' Liquid-Liquid Extraction. *Chem. Commun.* **1998**, *998*, 1765–1766.
(10) Zhou, Z. H.; Wang, T.; Xing, H. B. Butyl-3-methylimidazolium Chloride Preparation in Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **2006**, *45*, 525–529.
(11) Wu, W. Z.; Li, W. J.; Han, B. X.; Zhang, Z.; Jiang, T.; Liu, Z. M. A Green and Effective Method to Synthesize Ionic Liquids: Supercritical CO_2 Route. *Green Chem.* **2005**, *7*, 701–704.
(12) Brennecke, J. F.; Chateauneuf, J. E. Homogeneous Organic Reactions as Mechanistic Probes in Supercritical Fluids. *Chem. Rev.* **1999**, *99*, 433–452.
(13) Chouchi, D.; Gourgouillon, D.; Courel, M.; Vital, J.; Nunes da Ponte, M. The Influence of Phase Behavior on Reaction at Supercritical Conditions: The Hydrogenation of α-Pinene. *Ind. Eng. Chem. Res.* **2001**, *40*, 2551–2554.
(14) Pereda, S.; Bottini, S. B.; Brignole, E. A. Supercritical Fluids and Phase Behavior in Heterogeneous Gas-Liquid Catalytic Reactions. *Appl. Catal., A* **2005**, *281*, 129–137.
(15) Chen, X. T.; Hou, Y. C.; Wu, W. Z.; Ren, S. H.; Zhang, J. W.; Fan, J. L. High Pressure Phase Behavior and Density of the Carbon Dioxide + 1-Methylimidazole Binary System. *J. Supercrit. Fluids* **2009**, *49*, 310–314.
(16) Wang, B.; He, J.; Sun, D. H.; Zhang, R.; Han, B. X. Solubility of Chlorobutane, Ethyl Methacrylate and Trifluoroethyl Acrylate in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2006**, *239*, 63–68.
(17) Zhang, H. F.; Han, B. X.; Hou, Z. S.; Liu, Z. M. Measurement of Critical Points of the Methylcyclohexane (MCH)-H_2-CO_2 System in the CO_2-Rich Region. *Fluid Phase Equilib.* **2001**, *179*, 131–138.
(18) Chany-Yih, D.; Chiehming, J. C.; Chiu-Yang, C. Phase Equilibrium of Ethanol + CO_2 and Acetone + CO_2 at Elevated Pressures. *J. Chem. Eng. Data* **1999**, *44*, 365.
(19) Wu, J. L.; Pan, Q. M.; Rempel, G. L. Pressure-Density-Temperature Behavior of CO_2/Acetone, CO_2/Toluene, and CO_2/Monochlorobenzene Mixtures in the Near-Critical Region. *J. Chem. Eng. Data* **2004**, *49*, 976–979.
(20) Adrian, T.; Maurer, G. Solubility of Carbon Dioxide in Acetone and Propionic Acid at Temperatures between 298 K and 333 K. *J. Chem. Eng. Data* **1997**, *42*, 668–672.
(21) Pöhler, H.; Kiran, E. Volumetric Properties of Carbon Dioxide + Acetone at High Pressures. *J. Chem. Eng. Data* **1997**, *42*, 379–383.
(22) Stradi, B. A.; Kohn, J. P.; Stadtherr, M. A.; Brennecke, J. F. Phase Behavior of the Reactants, Products and Catalysts Involved in the Allylic Epoxidation of Trans-2-Hexen-1-ol to (2R,3R)-(+)-3-Propyloxiranemethanol in High Pressure Carbon Dioxide. *J. Supercrit. Fluids* **1998**, *12*, 109–122.
(23) Shiflett, M. B.; Yokozeki, A. Solubilities and Diffusivities of Carbon Dioxide in Ionic Liquids: [bmim][PF_6] and [bmim][BF_4]. *Ind. Eng. Chem. Res.* **2005**, *12*, 4453–4464.

(24) Shiflett, M. B.; Yokozeki, A. Solubility of CO_2 in Room Temperature Ionic Liquid [hmim][Tf_2N]. *J. Phys. Chem. B* **2007**, *111*, 2070–2074.
(25) Shariati, A.; Peters, C. J. High-Pressure Phase Behavior of Systems with Ionic Liquids: Measurements and Modeling of the Binary System Fluoroform + 1-Ethyl-3-methylimidazolium Hexafluorophosphate. *J. Supercrit. Fluids* **2003**, *28*, 109–117.
(26) Peng, D. Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Res.* **1976**, *15*, 59–64.
(27) Morton, D. W.; Lui, M. P. W.; Tran, C. A.; Young, C. L. The Gas-Liquid Critical Temperature of Some Chlorinated Alkanes and Halogenated Aromatic Hydrocarbons. *J. Chem. Eng. Data* **2000**, *45*, 437–439.
(28) Joback, K. G.; Reid, R. C. Estimation of Pure-Component Properties from Group-Contribution. *Chem. Eng. Commun.* **1987**, *57*, 233–243.

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