Phase Behavior, Densities, and Isothermal Compressibility of CO_2 + Pentane and CO_2 + Acetone Systems in Various Phase Regions

Jiawei Chen, Weize Wu, Buxing Han,* Liang Gao, Tiancheng Mu, Zhimin Liu, Tao Jiang, and Jimin Du

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

The phase behavior and critical parameters of CO_2 (1) + pentane (2) and CO_2 (1) + acetone (2) were determined experimentally, and their densities were measured in both the subcritical and supercritical regions. The isothermal compressibility (K_T) was calculated using the density data. It is demonstrated that the density is sensitive to pressure as the pressure approaches the critical point of the mixtures, that is, K_T is large and increases sharply. K_T also increases significantly as the pressure approaches the dew point or the bubble point at other compositions close to the critical composition. However, K_T is very small and is not sensitive to pressure well above the dew point or the bubble point. When the composition is far from the critical one, K_T is fairly small and the effect of pressure on K_T is very limited, even near the phase separation point.

Introduction

In recent years, supercritical (SC) science and technology have received much attention.[1,2] Supercritical fluids (SCFs) have been used in many fields including extractions and separations,[1,3] chemical reactions,[4,5] and material processing.[2,6,7] SC CO_2 is very attractive because it is nonflammable, nontoxic, and low cost. However, the solubility of many solutes in SC CO_2 is very low, which can limit its wide application. The concept of adding cosolvents, which are also called modifiers or entrainers, to SC CO_2 has received much attention and thus partially overcomes this limitation. Many studies have demonstrated that cosolvents enhance the solubility of solutes[8−12] or improve reaction rates[13] and selectivities[14] in SCF media.

One of the features of SCFs is that their densities and density-dependent properties are very sensitive to pressure. Hence, the solvent properties can be adjusted effectively by changing pressure.[1,2] The phase behavior, critical parameters, and density of a mixture depend on its composition. Therefore, at a fixed temperature, SC CO_2 can change from a SC state to a subcritical mixture with addition of a cosolvent, and the properties of SC CO_2−cosolvent mixtures can be significantly different from those of pure SC CO_2.

Acetone and pentane are typical solvents. One is polar, and the other is nonpolar. They can be used as cosolvents of SC CO_2. The phase behaviors of CO_2 (1) + pentane (2) and CO_2 (1) + acetone (2) binary mixtures have been studied by different authors.[15−21] However, the effect of phase behavior on the properties of the mixtures is seldom studied. In this study, we have determined the phase behavior and critical parameters of CO_2 (1) + pentane (2) and CO_2 (1) + acetone (2) binary systems. The density and compressibility of the mixtures are then studied systematically in different phase regions. We focus on how the phase behavior, composition, and pressure affect the density and compressibility of the mixtures, especially in the critical region.

Experimental Section

Materials. CO_2 with a purity of 99.995% was supplied by the Beijing Analytical Instrument Factory. Acetone (>99.9%) and *n*-pentane (>99.8%) were A.R. grade produced by the Beijing Chemical Reagent Plant. The chemicals were used as received.

Apparatus and Procedures. The phase behavior and the densities of the mixtures were determined by the view-cell method, and the detailed measurements were shown in our previous work.[22] The accuracies of temperature and pressure measurements were ±0.05 K and ±0.025 MPa, respectively. In a typical experiment, the air in the view cell was removed by a vacuum, and a desired amount of the liquid chemical (pentane or acetone) was charged. CO_2 was then added from a sample bomb. The mass of CO_2 in the view cell was known from the mass difference of the sample bomb before and after charging the system. The cell was placed into a water bath at the desired temperature. After thermal equilibrium had been reached, the piston in the optical cell was moved up and down to change the volume and the pressure of the system. The volume of the system was ascertained from the position of the piston, which was calibrated accurately using water as a medium. At the critical point, very strong opalescence was observed and the meniscus appeared at half-volume after a slight pressure reduction.

It was estimated that the accuracy of determined density data was better than $\pm 0.001\ g{\cdot}cm^{-3}$. To calculated the compressibility (K_T), we used the 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%.

Results and Discussion

Critical Points and Phase Behavior of the Mixtures. The critical parameters of CO_2 were measured in this work

---

* To whom correspondence should be addressed. Tel: 86-10-62562821. Fax: 86-10-62559373. E-mail: Hanbx@iccas.ac.cn.

10.1021/je034087q CCC: $25.00

Table 1. Critical Parameters of CO_2 (1) + Pentane (2) and CO_2 (1) + Acetone (2) Binary Mixtures with Different Compositions

CO_2 (1) + pentane (2)				CO_2 (1) + acetone (2)			
χ_1	Tc/K	Pc/MPa	ρ_c/g·cm^{-3}	χ_1	Tc/K	Pc/MPa	ρ_c/g·cm^{-3}
0.901	326.15	8.52	0.456	0.902	336.35	9.94	0.524
0.916	323.15	8.21	0.451	0.909	335.15	9.79	0.530
0.947	315.55	7.92	0.463	0.933	326.65	9.15	0.525
0.960	312.35	7.75	0.473	0.948	323.15	8.94	0.531

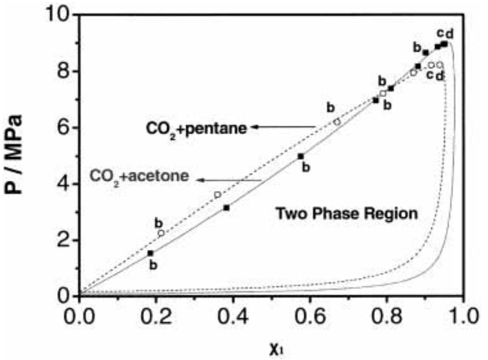

Figure 1. Phase diagram of CO_2 (1) + pentane (2) and CO_2 (1) + acetone (2) binary mixtures at 323.15 K: ○, CO_2 + pentane; ■, CO_2 + acetone; dashed line, PR-EOS for CO_2 + pentane; solid line, PR-EOS for CO_2 + acetone.

to verify the reliability of the apparatus. The results obtained of 304.25 K, 7.38 MPa, and 0.462 g·cm^{-3} agreed well with the literature data.[23]

The known critical parameters and phase behavior of the mixtures were the basis for selecting suitable experimental conditions. The critical parameters of the mixtures with different compositions are presented in Table 1. As expected, Tc and Pc increase with increasing cosolvent concentration.

The phase diagrams of the mixtures determined at 323.15 K are shown in Figure 1. The results calculated from the Peng−Robinson equation of state (PR-EOS)[24] are also illustrated in this figure and agree well with the experimental data. The binary interaction coefficients (k_{12}) of CO_2 (1) + pentane (2) and CO_2 (1) + acetone (2) systems used are 0.0510 and 0.0128, respectively.[25] In this paper, χ_1 stands for the mole fraction of CO_2, and labels b, c, and d stand for bubble point, critical point, and dew point, respectively. In Figure 1, a homogeneous mixture is vapor or supercritical fluid on the right-hand side of the critical composition. On the left-hand side of the critical composition, a mixture can be regarded as compressed liquid or homogeneous subcritical fluid when the pressure is higher than the bubble point pressure. The figure shows clearly

Table 2. Densities of CO_2 (1) + Pentane (2) Binary Mixtures at 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}	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}
$T = 323.15$ K				$T = 323.15$ K				$T = 323.15$ K				$T = 323.15$ K				$T = 323.15$ K			
$\chi_1 = 0.939^d$				$\chi_1 = 0.916^c$				$\chi_1 = 0.870^b$				$\chi_1 = 0.791^b$				$\chi_1 = 0.671^b$			
8.22^d	0.350^d	8.89	0.453	8.21^c	0.451^c	8.93	0.556	7.94^b	0.573^b	9.67	0.638	7.21^b	0.651^b	10.29	0.697	6.19^b	0.702^b	9.56	0.726
8.24	0.352	8.95	0.461	8.22	0.454	9.07	0.568	8.02	0.577	10.01	0.645	7.39	0.655	11.04	0.703	6.87	0.707	10.71	0.734
8.27	0.356	9.01	0.470	8.23	0.458	9.24	0.579	8.15	0.584	10.42	0.654	7.77	0.663	11.91	0.713	7.50	0.713	11.98	0.740
8.29	0.358	9.07	0.479	8.24	0.460	9.41	0.590	8.26	0.590	10.85	0.661	8.28	0.670	13.06	0.721	8.37	0.719	13.80	0.749
8.31	0.361	9.14	0.489	8.27	0.468	9.63	0.603	8.42	0.597	11.45	0.670	8.86	0.681	14.51	0.732				
8.33	0.363	9.21	0.500	8.32	0.475	9.94	0.615	8.55	0.602	11.97	0.678	9.55	0.688						
8.38	0.368	9.30	0.511	8.37	0.483	10.30	0.628	8.71	0.610	12.58	0.687	$T = 323.15$ K				$T = 323.15$ K			
8.42	0.375	9.40	0.522	8.41	0.491	10.73	0.642	8.92	0.619	13.29	0.695	$\chi_1 = 0.360^b$				$\chi_1 = 0.214^b$			
8.46	0.380	9.51	0.534	8.45	0.499	11.26	0.657	9.12	0.624	14.04	0.704	3.62^b	0.632^b	9.28	0.647	2.25^b	0.603^b	9.74	0.631
8.50	0.386	9.63	0.545	8.50	0.508	11.93	0.672	9.44	0.630	14.73	0.713	3.73	0.633	10.24	0.651	2.50	0.607	11.06	0.634
8.54	0.393	9.79	0.558	8.57	0.517	12.79	0.687					4.51	0.635	11.23	0.654	2.77	0.612	12.56	0.638
8.57	0.399	9.97	0.572	8.65	0.527	13.86	0.705					5.38	0.636	12.46	0.656	3.80	0.617	13.86	0.640
8.62	0.406	10.17	0.586	8.71	0.536	14.47	0.715					6.24	0.640	13.56	0.659	5.92	0.623	15.22	0.642
8.66	0.413	10.44	0.600	8.81	0.546							7.17	0.643	14.81	0.662	7.53	0.627		
8.70	0.420	10.79	0.616									8.15	0.645						
8.74	0.428	11.25	0.635																
8.81	0.436	11.32	0.639																
8.85	0.444																		
$T = 328.15$ K				$T = 326.15$ K				$T = 323.15$ K				$T = 318.15$ K				$T = 315.55$ K			
$\chi_1 = 0.901^d$				$\chi_1 = 0.901^c$				$\chi_1 = 0.901^b$				$\chi_1 = 0.901^b$				$\chi_1 = 0.947^c$			
8.63^d	0.428^d	10.35	0.584	8.52^c	0.456^c	9.56	0.567	8.35^b	0.511^b	10.00	0.622	7.92^b	0.585^b	10.56	0.680	7.92^c	0.463^c	8.39	0.566
8.65	0.431	10.38	0.586	8.54	0.461	9.68	0.573	8.39	0.515	10.08	0.626	7.98	0.590	10.68	0.683	7.94	0.466	8.49	0.578
8.69	0.436	10.49	0.590	8.56	0.465	9.76	0.579	8.43	0.520	10.16	0.628	8.07	0.594	10.88	0.685	7.96	0.472	8.61	0.592
8.72	0.442	10.58	0.594	8.58	0.469	9.87	0.583	8.46	0.524	10.27	0.633	8.17	0.600	11.07	0.689	7.97	0.475	8.76	0.605
8.76	0.448	10.75	0.601	8.61	0.472	9.99	0.590	8.50	0.529	10.42	0.637	8.28	0.606	11.29	0.694	8.01	0.484	8.97	0.620
8.83	0.459	10.88	0.606	8.63	0.476	10.13	0.595	8.53	0.533	10.62	0.642	8.38	0.613	11.49	0.697	8.04	0.492	9.20	0.635
8.88	0.465	11.06	0.612	8.67	0.481	10.25	0.601	8.57	0.538	10.76	0.647	8.52	0.619	11.65	0.698	8.07	0.502	9.52	0.650
8.93	0.473	11.14	0.614	8.70	0.486	10.41	0.608	8.62	0.542	10.95	0.652	8.66	0.625	11.89	0.702	8.11	0.512	9.94	0.666
8.97	0.475	11.50	0.625	8.74	0.491	10.72	0.618	8.67	0.548	11.22	0.656	8.81	0.631	12.11	0.705	8.15	0.522	10.20	0.676
9.03	0.483	11.67	0.629	8.78	0.496	10.92	0.625	8.71	0.552	11.44	0.661	8.98	0.638	12.38	0.710	8.20	0.532	10.49	0.684
9.10	0.491	11.80	0.634	8.84	0.503	11.15	0.631	8.76	0.558	11.61	0.666	9.18	0.644	12.60	0.713	8.25	0.543	10.84	0.695
9.16	0.499	11.97	0.639	8.87	0.509	11.38	0.638	8.83	0.562	11.89	0.672	9.40	0.651	12.94	0.716	8.32	0.555	11.48	0.711
9.23	0.507	12.18	0.642	8.92	0.516	11.66	0.645	8.89	0.568	12.08	0.675	9.44	0.654	13.28	0.722	$T = 312.35$ K			
9.32	0.517	12.34	0.646	8.97	0.520	11.95	0.652	8.98	0.573	12.44	0.681	9.55	0.656	13.69	0.727	$\chi_1 = 0.960^c$			
9.41	0.524	12.56	0.652	9.01	0.524	12.28	0.658	9.05	0.579	12.76	0.686	9.72	0.661	13.87	0.728	7.75^c	0.473^c	8.01	0.556
9.53	0.533	12.76	0.655	9.08	0.531	12.63	0.666	9.14	0.583	13.00	0.690	9.91	0.666	14.05	0.732	7.77	0.475	8.07	0.568
9.63	0.542	13.02	0.661	9.16	0.538	13.03	0.673	9.23	0.590	13.28	0.695	10.01	0.669	14.41	0.734	7.78	0.479	8.15	0.581
9.76	0.552	13.28	0.665	9.22	0.544	13.48	0.680	9.35	0.595	13.53	0.698	10.13	0.670	14.62	0.736	7.79	0.482	8.23	0.594
9.93	0.562	13.56	0.669	9.35	0.551	13.95	0.686	9.48	0.601	13.80	0.701	10.26	0.674	14.90	0.738	7.80	0.488	8.36	0.608
10.03	0.568	13.79	0.674	9.42	0.558	14.54	0.696	9.60	0.607	14.05	0.705	10.37	0.677			7.81	0.491	8.53	0.624
10.13	0.572	14.26	0.682	9.50	0.562	14.80	0.700	9.74	0.613	14.44	0.712					7.84	0.501	8.74	0.639
10.23	0.579	14.81	0.691					9.92	0.619	14.70	0.714					7.87	0.511	9.02	0.656
																7.89	0.522	9.40	0.674
																7.92	0.532	9.60	0.686
																7.97	0.544		

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

Table 3. Densities of CO$_2$ (1) + Acetone (2) Binary Mixtures at Different Conditions

P	ρ	P	ρ	P	ρ	P	ρ	P	ρ	P	ρ	P	ρ	P	ρ	P	ρ	P	ρ
MPa	g·cm^{-3}	MPa	g·cm^{-3}	MPa	g·cm^{-3}	MPa	g·cm^{-3}	MPa	g·cm^{-3}	MPa	g·cm^{-3}	MPa	g·cm^{-3}	MPa	g·cm^{-3}	MPa	g·cm^{-3}	MPa	g·cm^{-3}
	$T = 323.15$ K				$T = 323.15$ K				$T = 323.15$ K				$T = 323.15$ K				$T = 323.15$ K		
	$\chi_1 = 0.952$[d]				$\chi_1 = 0.948$[c]				$\chi_1 = 0.933$[b]				$\chi_1 = 0.902$[b]				$\chi_1 = 0.882$[b]		
8.96[d]	0.492[d]	9.52	0.571	8.94[c]	0.531[c]	10.03	0.638	8.85[b]	0.584[b]	10.05	0.669	8.65[b]	0.672[b]	11.00	0.736	8.16[b]	0.701[b]	10.29	0.748
8.98	0.495	9.56	0.578	9.00	0.540	10.29	0.651	8.86	0.586	10.22	0.678	8.75	0.678	11.26	0.740	8.25	0.703	10.63	0.754
9.00	0.497	9.62	0.582	9.06	0.549	10.60	0.666	8.88	0.590	10.42	0.684	8.92	0.683	11.50	0.744	8.50	0.712	10.95	0.761
9.03	0.502	9.68	0.588	9.12	0.559	10.98	0.679	8.93	0.594	10.64	0.693	9.02	0.687	11.76	0.751	8.63	0.716	11.44	0.764
9.06	0.505	9.75	0.594	9.20	0.568	11.48	0.696	8.99	0.601	10.88	0.699	9.16	0.690	12.03	0.754	8.79	0.719	11.87	0.769
9.09	0.510	9.85	0.603	9.30	0.579	12.09	0.711	9.04	0.606	11.16	0.707	9.27	0.694	12.30	0.757	8.93	0.721	12.26	0.779
9.12	0.514	9.94	0.611	9.41	0.590	12.75	0.727	9.10	0.613	11.46	0.714	9.40	0.699	12.62	0.762	9.11	0.728	12.97	0.785
9.14	0.519	10.10	0.623	9.54	0.602	13.64	0.744	9.18	0.618	11.80	0.724	9.52	0.702	12.96	0.769	9.38	0.732	13.56	0.791
9.17	0.523	10.32	0.636	9.66	0.613	14.73	0.762	9.24	0.624	12.20	0.731	9.71	0.707	13.24	0.771	9.65	0.736	14.55	0.800
9.19	0.527	10.59	0.649	9.84	0.625			9.33	0.630	12.62	0.740	9.87	0.711	13.45	0.775	9.90	0.743		
9.22	0.531	10.92	0.663		$T = 323.15$ K			9.41	0.637	13.13	0.748	10.02	0.715	13.77	0.776		$T = 323.15$ K		
9.25	0.537	11.28	0.678		$\chi_1 = 0.772$[b]			9.52	0.642	13.70	0.758	10.16	0.719	14.10	0.781		$\chi_1 = 0.383$[b]		
9.29	0.541	11.78	0.694	6.96[b]	0.779[b]	10.54	0.807	9.63	0.649	14.29	0.767	10.36	0.722	14.43	0.785	3.15[b]	0.787[b]	9.56	0.803
9.32	0.546	12.40	0.710	7.47	0.783	11.06	0.811	9.75	0.656	14.92	0.777	10.57	0.727	14.78	0.789	4.19	0.789	11.64	0.806
9.35	0.550	13.17	0.726	7.93	0.787	11.76	0.815	9.90	0.664			10.78	0.733	15.14	0.792	5.87	0.795	13.56	0.813
9.38	0.556	14.08	0.744	8.42	0.792	12.37	0.818									7.88	0.800	14.81	0.817
9.43	0.561	14.59	0.751	8.97	0.796	13.13	0.823												
9.48	0.567			9.45	0.798	13.79	0.827												
				9.96	0.803	14.55	0.831												
	$T = 323.15$ K				$T = 323.15$ K				$T = 323.15$ K				$T = 318.15$ K				$T = 328.15$ K		
	$\chi_1 = 0.811$[b]				$\chi_1 = 0.576$[b]				$\chi_1 = 0.186$[b]				$\chi_1 = 0.902$[b]				$\chi_1 = 0.902$[b]		
7.38[b]	0.758[b]	10.49	0.796	4.98[b]	0.795[b]	10.44	0.818	1.54[b]	0.760[b]	7.33	0.777	8.00[b]	0.709[b]	10.97	0.770	9.26[b]	0.626[b]	11.20	0.700
7.57	0.760	10.99	0.801	5.09	0.798	11.87	0.825	1.69	0.764	8.71	0.781	8.18	0.715	11.19	0.774	9.37	0.632	11.44	0.705
7.78	0.764	11.48	0.805	6.12	0.802	13.19	0.829	2.05	0.767	10.80	0.785	8.41	0.722	11.50	0.776	9.49	0.640	11.72	0.711
7.93	0.769	11.95	0.807	7.43	0.810	15.04	0.834	2.92	0.770	12.68	0.788	8.57	0.726	11.83	0.781	9.62	0.645	11.92	0.716
8.28	0.774	12.56	0.813	8.96	0.813			4.50	0.772	14.08	0.789	8.81	0.732	12.14	0.785	9.72	0.650	12.23	0.721
8.62	0.778	13.09	0.818					6.05	0.775	14.95	0.791	8.96	0.735	12.45	0.789	9.78	0.654	12.46	0.727
9.35	0.787	13.61	0.821									9.18	0.738	12.71	0.793	9.91	0.657	12.78	0.733
9.90	0.790	14.46	0.826									9.41	0.744	13.05	0.795	10.02	0.662	12.97	0.737
	$T = 333.15$ K				$T = 336.35$ K				$T = 338.15$ K			9.57	0.746	13.37	0.798	10.15	0.669	13.31	0.739
	$\chi_1 = 0.902$[b]				$\chi_1 = 0.902$[c]				$\chi_1 = 0.902$[d]			9.78	0.751	13.70	0.803	10.33	0.673	13.64	0.748
9.70[b]	0.570[b]	11.17	0.650	9.94[c]	0.524[c]	11.20	0.616	10.06[d]	0.508[d]	11.63	0.616	9.90	0.754	14.06	0.807	10.48	0.679	13.90	0.748
9.75	0.573	11.28	0.654	9.96	0.531	11.32	0.620	10.08	0.511	11.71	0.619	10.07	0.756	14.37	0.809	10.61	0.684	14.18	0.754
9.83	0.579	11.49	0.660	10.00	0.535	11.42	0.625	10.11	0.515	11.79	0.622	10.33	0.757	14.61	0.812	10.82	0.688	14.60	0.758
9.88	0.582	11.69	0.666	10.03	0.538	11.57	0.631	10.18	0.520	11.88	0.627	10.54	0.763	14.87	0.815	11.02	0.695	14.82	0.761
9.92	0.585	11.82	0.671	10.08	0.542	11.70	0.638	10.23	0.524	11.95	0.629	10.77	0.766						
9.99	0.590	12.00	0.676	10.11	0.545	11.79	0.641	10.28	0.529	12.04	0.632		$T = 335.15$ K				$T = 326.65$ K		
10.05	0.594	12.23	0.682	10.15	0.547	11.95	0.645	10.34	0.533	12.11	0.634		$\chi_1 = 0.909$[c]				$\chi_1 = 0.933$[c]		
10.10	0.599	12.39	0.687	10.19	0.551	12.08	0.649	10.38	0.538	12.24	0.640	9.79[c]	0.530[c]	10.78	0.611	9.15[c]	0.525[c]	10.01	0.617
10.18	0.603	12.56	0.690	10.23	0.555	12.21	0.654	10.43	0.542	12.33	0.642	9.80	0.532	10.89	0.616	9.16	0.528	10.11	0.625
10.25	0.607	12.84	0.697	10.26	0.558	12.40	0.659	10.50	0.548	12.46	0.646	9.82	0.535	11.02	0.623	9.18	0.531	10.21	0.630
10.32	0.610	13.01	0.700	10.31	0.561	12.57	0.663	10.56	0.552	12.57	0.651	9.86	0.539	11.15	0.628	9.20	0.535	10.34	0.637
10.38	0.614	13.28	0.705	10.36	0.566	12.71	0.668	10.64	0.558	12.70	0.654	9.90	0.543	11.28	0.635	9.24	0.540	10.47	0.643
10.50	0.619	13.63	0.711	10.39	0.569	12.94	0.673	10.71	0.563	12.88	0.659	9.94	0.548	11.44	0.640	9.27	0.544	10.59	0.650
10.61	0.626	13.80	0.716	10.45	0.573	13.14	0.678	10.78	0.569	13.01	0.663	10.00	0.551	11.60	0.648	9.31	0.549	10.75	0.656
10.75	0.631	13.98	0.719	10.54	0.579	13.32	0.684	10.86	0.573	13.20	0.668	10.05	0.558	11.79	0.653	9.34	0.553	10.92	0.663
10.85	0.636	14.28	0.723	10.61	0.583	13.58	0.688	10.91	0.581	13.32	0.671	10.10	0.562	12.01	0.661	9.37	0.559	11.10	0.670
10.92	0.641	14.46	0.726	10.71	0.590	13.90	0.694	10.98	0.584	13.48	0.675	10.16	0.567	12.24	0.667	9.41	0.563	11.32	0.677
11.08	0.646	14.83	0.733	10.81	0.595	14.18	0.701	11.08	0.590	13.71	0.680	10.22	0.572	12.46	0.675	9.46	0.569	11.54	0.684
				10.91	0.602	14.45	0.706	11.20	0.595	13.86	0.684	10.28	0.578	12.75	0.681	9.50	0.574	11.80	0.691
				11.02	0.606	14.70	0.710	11.28	0.600	14.08	0.689	10.35	0.583	13.08	0.691	9.55	0.579	12.06	0.699
				11.10	0.611	14.92	0.715	11.35	0.603	14.30	0.693	10.42	0.589	13.40	0.697	9.60	0.584	12.38	0.708
								11.42	0.606	14.56	0.699	10.50	0.593	13.77	0.706	9.66	0.590	12.73	0.715
								11.51	0.610	14.78	0.700	10.59	0.599	14.15	0.711	9.71	0.594	13.14	0.723
								11.59	0.615	15.01	0.705	10.68	0.604	14.60	0.721	9.79	0.601	13.58	0.731
																9.85	0.606	14.06	0.741
																9.93	0.612	14.60	0.749

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

that SC CO$_2$ changes into a subcritical fluid when the concentration of the cosolvents is high enough. In this work, besides phase separation points, all the experiments were carried out in the single-phase regions.

Densities of the Mixtures at Fixed Temperature. The densities of the mixtures were determined at 323.15 K up to 15 MPa in the SC and subcritical regions. Tables 2 and 3 list the densities of the CO$_2$ (1) + pentane (2) and CO$_2$ (1) + acetone (2) binary mixtures, respectively. The dependence of the densities on pressure and composition at 323.15 K is illustrated in Figures 2 and 3.

Figures 2 and 3 indicate that the sensitivity of density to system pressure depends on both composition and pressure at a fixed temperature. The isothermal compressibility (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.[26] K_T values of the mixtures have been calculated using the density data in Tables 2 and 3 by the following equation.

$$K_{\mathrm{T}} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \tag{1}$$

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

Figures 4 and 5 show the effect of pressure on K_T for the mixed fluids having different compositions. The variations of K_T with pressure and composition of the two mixtures show similar behaviors, despite pentane's nonpolar nature and acetone's stronger polarity. K_T is very large and sensitive to pressure as the pressure approaches the critical point of a mixture; that is, at the critical composition K_T increases sharply as the pressure ap-

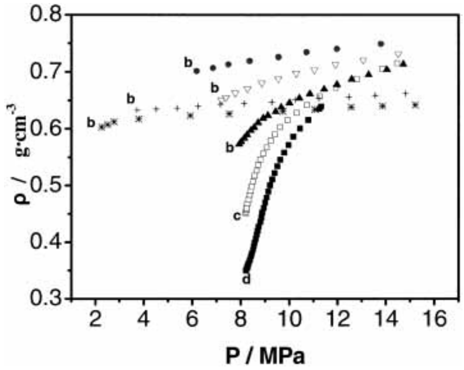

Figure 2. Dependence of the density of CO_2 (1) + pentane (2) binary mixtures on pressure at 323.15 K: ■, $\chi_1 = 0.939$; □, $\chi_1 = 0.916$; ▲, $\chi_1 = 0.870$; ▽, $\chi_1 = 0.791$; ●, $\chi_1 = 0.671$; +, $\chi_1 = 0.360$; ∗, $\chi_1 = 0.214$.

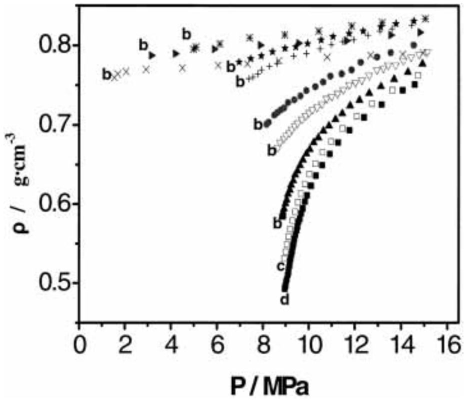

Figure 3. Dependence of the density of CO_2 (1) + acetone (2) binary mixtures on pressure at 323.15 K: ■, $\chi_1 = 0.952$; □, $\chi_1 = 0.948$; ▲, $\chi_1 = 0.933$; ▽, $\chi_1 = 0.902$; ●, $\chi_1 = 0.882$; +, $\chi_1 = 0.811$; ★, $\chi_1 = 0.772$; ∗, $\chi_1 = 0.576$; rightward-pointing triangle, $\chi_1 = 0.383$; ×, $\chi_1 = 0.186$.

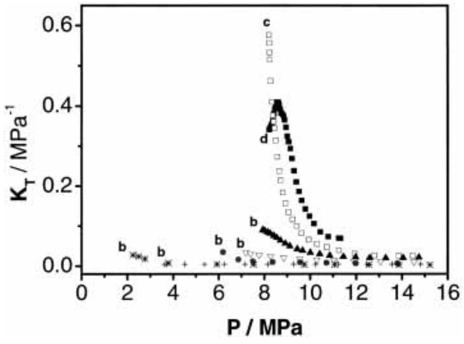

Figure 4. Isothermal compressibility K_T of CO_2 (1) + pentane (2) binary mixtures on pressure at 323.15 K: ■, $\chi_1 = 0.939$; □, $\chi_1 = 0.916$; ▲, $\chi_1 = 0.870$; ▽, $\chi_1 = 0.791$; ●, $\chi_1 = 0.671$; +, $\chi_1 = 0.360$; ∗, $\chi_1 = 0.214$.

proaches the phase separation pressure. K_T also increases significantly as the pressure approaches the dew point or the bubble point at other compositions close to the critical composition. However, K_T is very small and not sensitive to pressure when the pressure is well above the bubble point. The compressibility of CO_2 (1) + pentane (2) is larger than that of CO_2 (1) + acetone (2) under similar conditions.

The data in Figures 4 and 5 also illustrate that when the composition is far from the critical composition, the effect of pressure on K_T is very limited, even near the phase separation point.

Effect of Temperature and Pressure on the Density at a Fixed Composition. As discussed above, the critical parameters of mixtures change with composition. At a fixed composition, the effect of pressure on the density at different temperatures is interesting to note. This could have been quantified from Figures 6 and 7, which show the dependence of the densities of CO_2 (1) + pentane (2) and CO_2 (1) + acetone (2) mixtures at a fixed composition for a special pressure at different temperatures. The density is sensitive to pressure near the phase separation pressure. The phenomenon is more obvious at Tc or close to Tc. Similarly, the density of the fluids at pressures much higher than phase separation pressures is not sensitive to pressure.

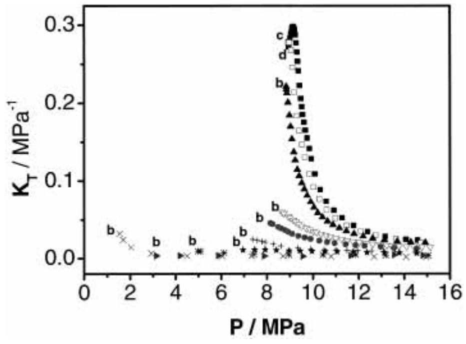

Figure 5. Isothermal compressibility K_T of CO_2 (1) + acetone (2) binary mixtures on pressure at 323.15 K: ■, $\chi_1 = 0.952$; □, $\chi_1 = 0.948$; ▲, $\chi_1 = 0.933$; ▽, $\chi_1 = 0.902$; ●, $\chi_1 = 0.882$; +, $\chi_1 = 0.811$; ★, $\chi_1 = 0.772$; ∗, $\chi_1 = 0.576$; rightward-pointing triangle, $\chi_1 = 0.383$; ×, $\chi_1 = 0.186$.

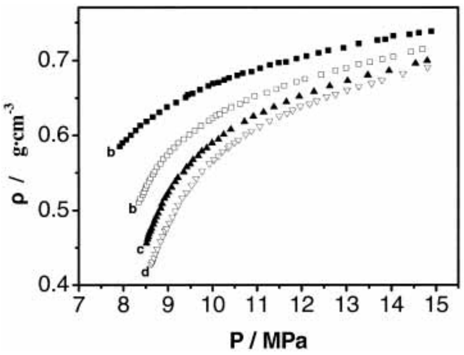

Figure 6. Dependence of the density of the CO_2 (1) + pentane (2) binary mixture with $\chi_1 = 0.901$ on temperature and pressure in the critical region: ■, $T = 318.15$ K; □, $T = 323.15$ K; ▲, $T = 326.15$ K; ▽, $T = 328.15$ K.

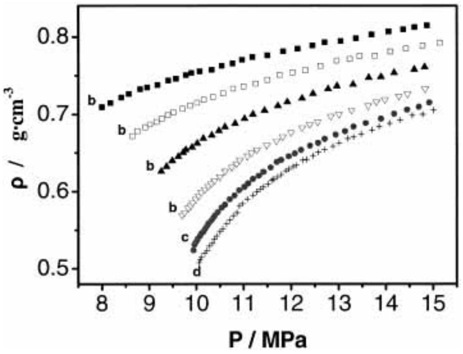

Figure 7. Dependence of the density of the CO_2 (1) + acetone (2) binary mixture with $\chi_1 = 0.902$ on temperature and pressure in the critical region: ■, $T = 318.15$ K; □, $T = 323.15$ K; ▲, $T = 328.15$ K; ▽, $T = 333.15$ K: ●, $T = 336.35$ K; +, $T = 338.15$ K.

Effect of Pressure on the Density of the Mixtures with Critical Composition. For a binary mixed system, Tc and Pc vary with composition. Figures 8 and 9 illustrate

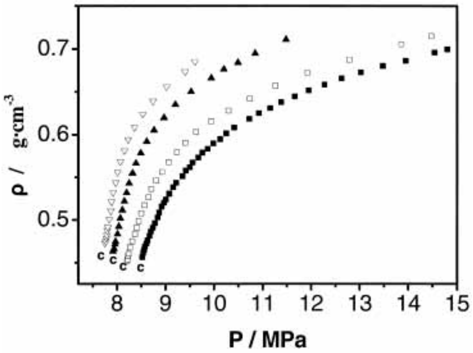

Figure 8. Effect of pressure on the density of CO_2 (1) + pentane (2) binary mixtures with critical compositions: ■, $\chi_1 = 0.901$, $T = 326.15$ K; □, $\chi_1 = 0.916$, $T = 323.15$ K; ▲, $\chi_1 = 0.947$, $T = 315.55$ K; ▽, $\chi_1 = 0.960$, $T = 312.35$ K.

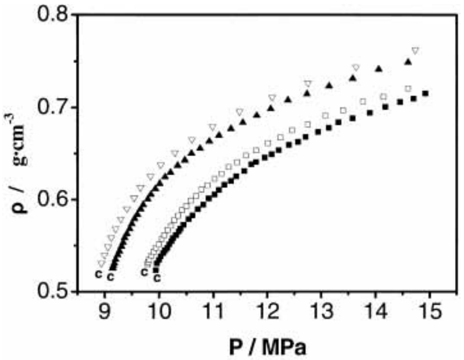

Figure 9. Effect of pressure on the density of CO_2 (1) + acetone (2) binary mixtures with critical compositions: ■, $\chi_1 = 0.902$, $T = 336.35$ K; □, $\chi_1 = 0.909$, $T = 335.15$ K; ▲, $\chi_1 = 0.933$, $T = 326.65$ K; ▽, $\chi_1 = 0.948$, $T = 323.15$ K.

the densities of the two mixed fluids with critical compositions at the experimental temperatures. At a fixed pressure, the density depends strongly on composition and temperature. However, the curves having different compositions are similar in that they change dramatically with pressure near the critical point, although their temperatures and composition are different. This is one of the features of fluids in the critical region.

Conclusion

Study on the densities and compressibility of CO_2 (1) + pentane (2) and CO_2 (1) + acetone (2) mixtures in different phase regions reveals that the density is sensitive to pressure near the critical points 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. To tune the properties of a mixed fluid effectively by changing pressure, both the composition and pressure should be close to the critical point of the mixture. Utilization of mixed solvents at conditions close to the critical point may become an effective way to broaden the applications of SCFs.

Literature Cited

(1) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice,* 2nd ed.; Butterworth-Heinmann: Boston, 1994.

(2) Eckert, C. A.; Knutson, B. L.; Debenedetti, P. G. Supercritical Fluids as Solvents for Chemical and Materials Processing. *Nature* **1996**, *383*, 313.

(3) King, J. W.; Sahle-Demessie, 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. *Chemical Synthesis Using Supercritical Fluids*; Wiley-VCH: Weinheim, 1999.

(5) Wittmann, K.; Wisniewski, W.; Mynott, R.; Leitner, W.; Kranemann, C. L.; Rische, T.; Eilbracht, P.; Kluwer, S.; Ernsting, J. M.; Elsevier, C. J. Rhodium-catalyzed Hydroaminomethylation using Supercritical Carbon Dioxide as Solvent and Temporary Protecting Group. *Chem.*—*Eur. J.* **2001**, *7*, 4584−4589.

(6) Cooper, A. I. Polymer Synthesis and Processing using Supercritical Carbon Dioxide. *J. Mater. Chem.* **2000**, *10*, 207−234.

(7) 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*, 4550−4560.

(8) Kurnik, R. T.; Reid, R. C. Solubility of Solid Mixtures in Supercritical Fluids. *Fluid Phase Equilib.* **1982**, *8*, 93−105.

(9) Chialvo, A. A. Solute−Solute and Solute−Solvent Correlations in Dilute Near-Critical Ternary Mixtures: Mixed-Solute and Entrainer Effects. *J. Phys. Chem.* **1993**, *97*, 2740−2744.

(10) Dobbs, J. M.; Wong, J. M.; Lahiere, R. J.; Johnston, K. P. Modification of Supercritical Fluid Phase Behavior Using Polar Cosolvents. *Ind. Eng. Chem. Res.* **1987**, *26*, 56−65.

(11) Koga, Y.; Iwai, Y.; Hata, Y.; Arai, Y. Influence of Cosolvent on Solubilities of Fatty Acids and Higher Alcohols in Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **1996**, *125*, 115−128.

(12) Tomasko, D. L.; Knutson, B. L.; Pouillot, F.; Liotta, C. L.; Eckert; C. A. Spectroscopic Study of Structure and Interactions in Cosolvent-Modified Supercritical Fluids. *J. Phys. Chem.* **1993**, *97*, 11823−11834.

(13) Ellington, J. B.; Park, K. M.; Brennecke, J. F. Effect of Local Composition Enhancements on the Esterification of Phthalic Anhydride with Methanol in Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **1994**, *33*, 965−974.

(14) Andrew, D.; Des Islet, B. T.; Margaritis, A.; Weedon, A. C. Photo-Fries Rearrangement of Naphthyl Acetate in Supercritical Carbon Dioxide: Chemical Evidence for Solvent−Solute Clustering. *J. Am. Chem. Soc.* **1995**, *117*, 6132−6133.

(15) Tochigi, K.; Hasegawa, K.; Asano, N.; Kojima, K. Vapor−Liquid Equilibria for the Carbon Dioxide + Pentane and Carbon Dioxide + Toluene Systems. *J. Chem. Eng. Data* **1998**, *43*, 954−956.

(16) Leu, A. H.; Robinson, D. B. Equilibrium Phase Properties of Selected Carbon Dioxide Binary Systems: *n*-Pentane−Carbon Dioxide and Isopentane−Carbon Dioxide. *J. Chem. Eng. Data* **1987**, *32*, 447−450.

(17) Besserer, G. J.; Robinson, D. B. Equilibrium-Phase Properties of *n*-Pentane−Carbon Dioxide System. *J. Chem. Eng. Data* **1973**, *18*, 416−419.

(18) Cheng, H.; Pozo de Fernandez, M. E.; Zollweg, J. A.; Streett, W. B. Vapor−Liquid Equilibrium in the System Carbon Dioxide + *n*-Pentane from 252 to 458 K at Pressures to 10 MPa. *J. Chem. Eng. Data* **1989**, *34*, 319−323.

(19) Kiran, E.; Pohler, H.; Xiong, Y. Volumetric Properties of Pentane + Carbon Dioxide at High Pressures. *J. Chem. Eng. Data* **1996**, *41*, 158−165.

(20) Pohler, H.; Kiran, E. Volumetric Properties of Carbon Dioxide + Acetone at High Pressures. *J. Chem. Eng. Data* **1997**, *42*, 379−383.

(21) Bamberger, A.; Maurer, G. High-Pressure (Vapour + Liquid) Equilibria in (Carbon Dioxide + Acetone or 2-Propanol) at Temperatures from 293 K to 333 K. *J. Chem. Thermodynamics* **2000**, *32*, 685−700.

(22) Zhang, H. F.; Han, B. X.; Hou, Z. S.; Liu, Z. M. Mesurement 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.

(23) *CRC Handbook of Chemistry and Physics*, 73rd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1992−1993.

(24) Peng, D. Y.; Robinson, D. B. A New-Two Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.

(25) Adrian, T.; Wendlanand, M.; Hasse, H.; Maurer, G. High-Pressure Multiphase Behavior of Ternary Systems Carbon Dioxide−Water−Polar Solvent: Review and Modeling with the Peng−Robinson Equation of State. *J. Supercrit. Fluids* **1998**, *12*, 185−221.

(26) Eckert, C. A.; Ziger, D. H.; Johnston, K. P.; Kim, S. Solute Partial Molal Volumes in Supercritical Fluids. *J. Phys. Chem.* **1986**, *90*, 2738−2746.

Received for review May 1, 2003. Accepted August 19, 2003. The authors are grateful to the National Natural Science Foundation of China (20133030) and the Ministry of Science and Technology for the financial support (G2000048010).

JE034087Q