Volumetric Properties of Carbon Dioxide + Toluene at High Pressures

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Volumetric behavior of carbon dioxide + toluene has been investigated at (323, 348, 373, 398, and 423) K at pressures up to 70 MPa. Densities for pure components and mixtures containing (58, 68, 80, and 88) mass % carbon dioxide are determined as a function of pressure at each temperature. It is shown that with increasing pressure the density of carbon dioxide becomes greater than that of toluene. Mixture densities also show a density crossover at different pressures depending upon the composition. In the composition range evaluated, the excess volume of the mixtures is observed to be mostly negative. It becomes more negative with increasing temperature, but less negative with increasing pressure.

Introduction

Volumetric behavior of the binary mixtures of carbon dioxide with conventional organic solvents at high pressures is of particular importance for the development of new, environmentally desirable supercritical fluid processing technologies. The mixture composition is an important tuning parameter which influences the suitability of a mixture as a process or processing fluid with respect to (a) the operational temperatures and pressures and (b) the process selectivity or reactivity. Carbon dioxide is especially desirable in reducing the use of undesirable solvents. At the University of Maine, we utilize binary near critical and supercritical fluids as solvents in the formation, modification, and processing of polymeric materials (Kiran, 1994). We have already reported on the miscibility and phase separation of selected polymers and their polymerizations or extractions in binary mixtures of carbon dioxide and alkanes, or other solvents such as toluene, cyclohexane, alcohols, and acetic acid (Kiran, 1994; Kiran et al., 1993; Xiong and Kiran, 1994a,b; Kiran and Gokmenoglu, 1994, 1995; Kiran and Balkan, 1994; Kiran, 1995).

Even though there is considerable information on phase equilibria, and the data base on the critical properties of mixtures is expanding, detailed volumetric information, especially information on the densities of fluid mixtures at high pressures, appears to be essentially nonexistent. Density being an extremely important quantity in many supercritical fluid-based processes, we have initiated a program to systematically explore the volumetric properties of fluid mixtures, especially those in which carbon dioxide constitutes one of the components. We have already reported on the volumetric properties of carbon dioxide + pentane (Kiran *et al.*, 1996) and carbon dioxide + sulfur hexafluoride (Gokmenoglu *et al.*, 1996). We now report on the volumetric behavior of binary mixtures of carbon dioxide and toluene at pressures up to 70 MPa. Pressure−density data are reported for the mixtures containing 0, 58, 68, 80, 88, and 100 mass % carbon dioxide at (323, 348, 373, 398, and 423) K. The excess volumes for these mixtures and their variation with composition, temperature, and pressure are also reported.

Experimental Section

All experiments were carried out in a specially designed variable-volume view cell. The details of the system and the high-pressure cell and the operational procedures with respect to loading and determination of the cell volume have been described in detail in our previous publications (Kiran *et al.*, 1995; Gokmenoglu *et al.*, 1996). Figure 1 is a schematic diagram of the overall system which is operable up to 70 MPa and 473 K. Briefly, the cell is loaded sequentially with each fluid from small fluid-transfer vessels (TV) while monitoring the change in weight of the transfer vessel with a sensitive balance (Mettler 6100, with ±0.01 g accuracy). After loading, the cell is heated to a desired temperature, and the pressure is changed by applying pressure from the pressure generation line (PGN) to move a piston inside the variable-volume attachment (VVP) of the cell. The unique feature of this view cell is that its internal volume is monitored at all temperatures and pressures by precisely determining the position of the piston. This is achieved with the aid of a linear variable differential transformer (LVDT) and a position readout unit (PRU). The LVDT helps locate the position of a ferromagnetic core which is attached to an extension rod connected to the piston. At each temperature, cell volumes and hence the fluid densities corresponding to different pressures are determined. As demonstrated by comparisons with literature data in our previous publications (Kiran *et al.*, 1996), with this system, the densities are determined with an accuracy of ±1.2%. The maximum internal volume of the cell is 22.43 cm^3. Volume changes are determined with an accuracy of ±0.0025 cm^3.

Materials. Carbon dioxide was bone-dry grade with a purity of 99.8% (Airco; supplied with an eductor tube). Toluene (99.8% purity) was obtained from Fisher Chemicals.

Results and Discussion

Density. Densities of pure carbon dioxide and toluene and of their binary mixtures containing (58, 68, 80, and 88) mass % carbon dioxide have been determined at (323, 348, 373, 398, and 423) K over a wide pressure range. They are shown in Table 1. At these conditions, the mixtures either are supercritical or exist as liquid mixtures. Figure 2 shows the variation of the critical temperature and pressure for toluene carbon dioxide mixtures. The figure has been generated using literature data (Ng and Robinson, 1978). The present measurements have been mostly conducted at pressures which are higher than the critical pressures for all mixtures investigated.

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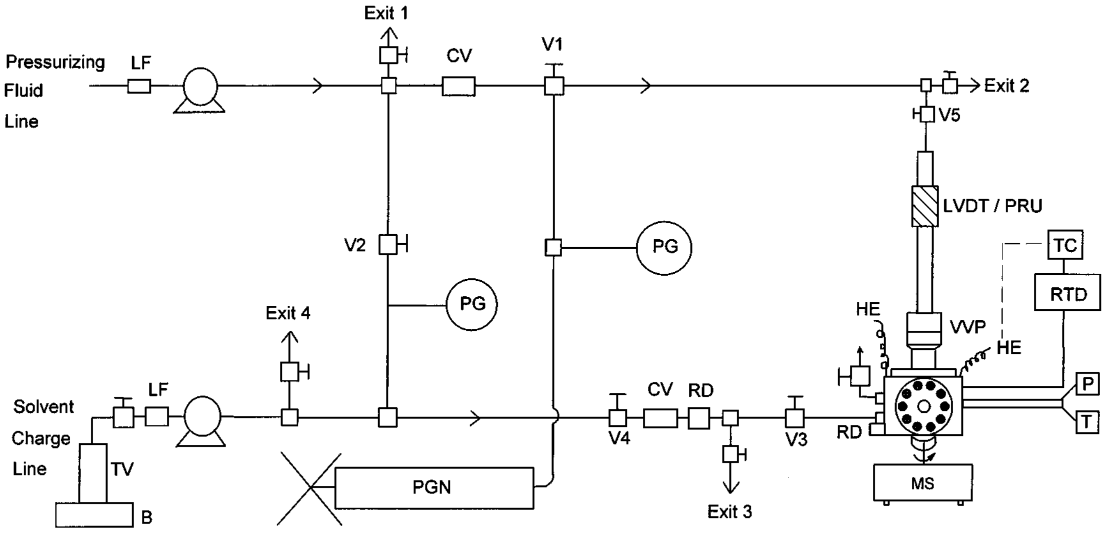

Figure 1. Schematic diagram of the experimental system.

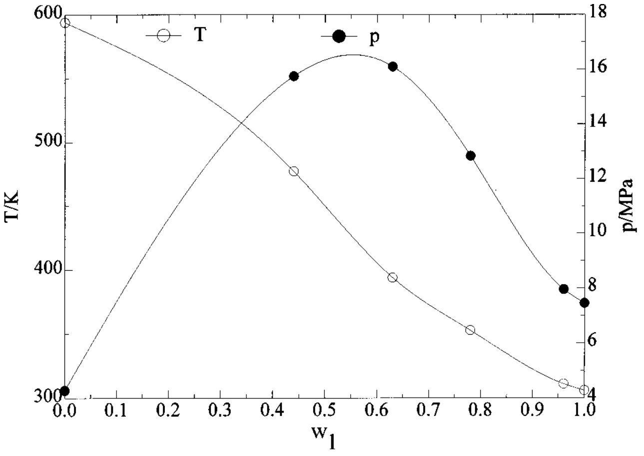

Figure 2. Critical temperature and pressure of the binary mixtures carbon dioxide (1) + toluene (2). Data are from Ng and Robinson (1978).

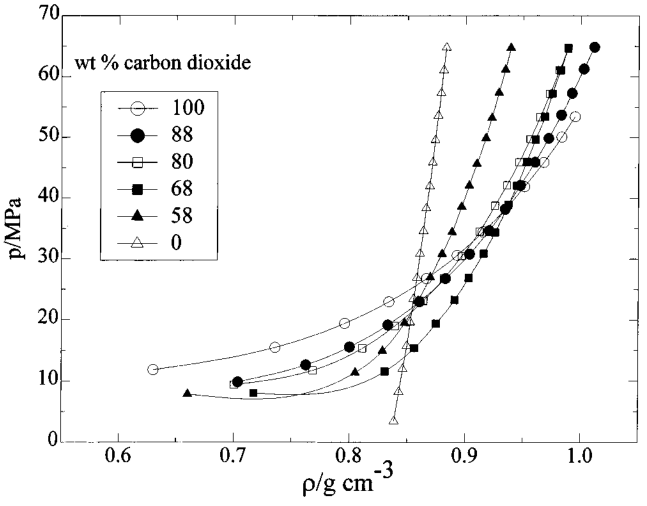

Figure 3. Pressure dependence of density for the binary mixture of carbon dioxide and toluene at 323 K. Compositions are in mass percent.

Figure 3 shows the densities of carbon dioxide/toluene isopleths at 323 K. The figure shows the low compressibility of pure toluene compared to pure carbon dioxide. While the density of carbon dioxide changes from about (0.6292 to 0.9942) g/cm^3, with a pressure change from (11.83 to 53.45) MPa, the density of toluene changes only by a small amount, from (0.8396 to 0.8831) g/cm^3 when the pressure is changed from (3.42 to 64.77) MPa. An interesting feature of the figure is that at about 25 MPa carbon dioxide becomes more dense than toluene. The binary mixtures show intermediate behavior with density cross-

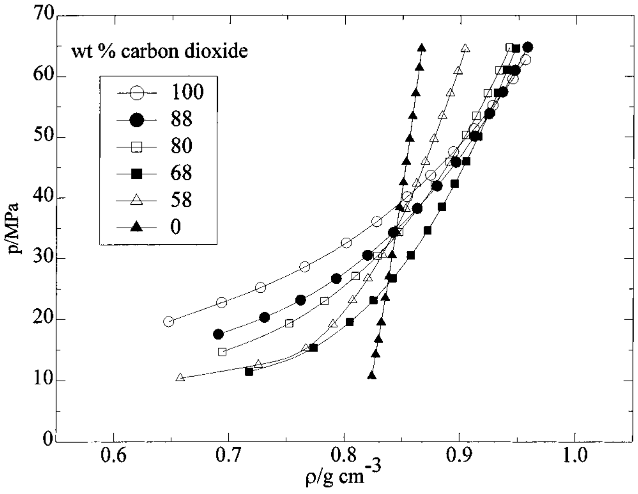

Figure 4. Pressure dependence of density for the binary mixture of carbon dioxide and toluene at 348 K. Compositions are in mass percent.

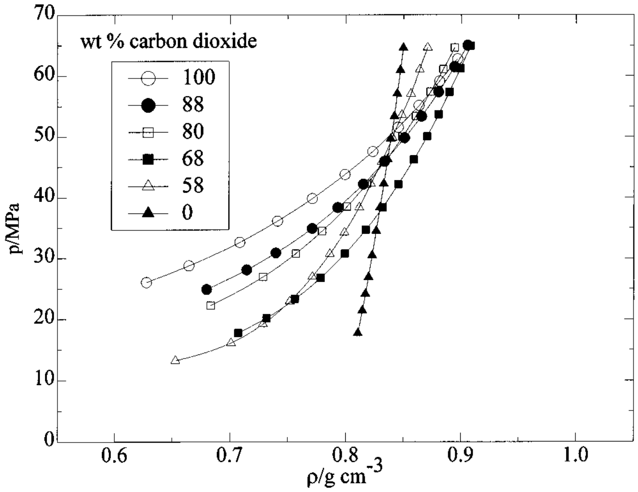

Figure 5. Pressure dependence of density for the binary mixture of carbon dioxide and toluene at 373 K. Compositions are in mass percent.

Table 1. Densities of Carbon Dioxide (1) + Toluene (2) (w = mass fraction)

323 K		348 K		373 K		398 K		423 K	
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
$W_1 = 1$									
0.6292	11.83	0.6475	19.63	0.6282	26.05	0.6298	32.64	0.6281	38.73
0.7348	15.46	0.6932	22.74	0.6644	28.78	0.6711	36.40	0.6410	40.26
0.7954	19.40	0.7271	25.19	0.7087	32.63	0.7053	40.06	0.6726	44.03
0.8343	22.96	0.7648	28.61	0.7408	36.11	0.7346	43.74	0.7014	47.57
0.8659	26.79	0.8010	32.55	0.7710	39.82	0.7644	47.73	0.7293	51.40
0.8925	30.59	0.8270	36.08	0.7986	43.79	0.7881	51.41	0.7537	55.33
0.9145	34.45	0.8534	40.17	0.8232	47.56	0.8088	55.19	0.7757	59.16
0.9347	38.21	0.8743	43.74	0.8454	51.54	0.8289	59.08	0.7962	62.76
0.9595	41.93	0.8927	47.59	0.8634	55.13	0.8472	62.78		
0.9655	45.94	0.9123	51.39	0.8808	59.11				
0.9837	50.09	0.9284	55.22	0.8974	62.75				
0.9942	53.45	0.9502	59.12						
$W_1 = 0.88$									
0.7034	9.84	0.6916	17.53	0.6797	24.89	0.6707	31.91	0.6626	39.05
0.7635	12.61	0.7317	20.31	0.7144	28.10	0.7007	35.43	0.6900	42.97
0.8001	15.55	0.7620	23.15	0.7406	30.87	0.7245	38.80	0.7109	46.05
0.8331	19.14	0.7937	26.69	0.7718	34.89	0.7486	42.32	0.7337	49.93
0.8602	22.97	0.8209	30.54	0.7930	38.34	0.7705	46.11	0.7530	53.79
0.8838	26.76	0.8421	34.29	0.8150	42.19	0.7891	49.81	0.7715	57.48
0.9035	30.81	0.8639	38.25	0.8335	45.93	0.8086	53.59	0.7881	61.46
0.9202	34.66	0.8800	41.97	0.8518	49.81	0.8249	57.43	0.8058	64.45
0.9342	38.24	0.8965	45.86	0.8655	53.36	0.8396	61.10		
0.9474	42.13	0.9122	50.18	0.8802	57.35	0.8530	65.01		
0.9601	45.95	0.9251	53.93	0.8941	61.46				
0.9729	49.90	0.9364	57.46	0.9066	64.97				
0.9839	53.72	0.9479	61.01						
0.9923	57.29	0.9586	64.82						
1.0033	61.28								
1.0124	64.86								
$W_1 = 0.80$									
0.7004	9.38	0.6940	14.66	0.6834	22.25	0.6741	29.77	0.6658	37.02
0.7685	11.73	0.7521	19.32	0.7296	26.94	0.7112	34.54	0.6964	41.74
0.8113	15.34	0.7837	22.98	0.7578	30.78	0.7378	38.45	0.7227	46.17
0.8392	18.99	0.8106	27.09	0.7795	34.46	0.7582	42.23	0.7400	49.78
0.8647	23.13	0.8295	30.46	0.8010	38.49	0.7773	46.02	0.7591	53.96
0.8814	26.83	0.8473	34.37	0.8182	42.24	0.7944	50.00	0.7747	57.36
0.8978	30.51	0.8637	38.07	0.8349	45.96	0.8090	53.62	0.7887	61.04
0.9121	34.52	0.8780	42.09	0.8490	49.96	0.8237	57.37	0.8021	65.07
0.9253	38.76	0.8917	45.94	0.8616	53.38	0.8351	60.98		
0.9367	42.17	0.9055	50.34	0.8732	57.37	0.8479	64.56		
0.9463	45.94	0.9147	53.50	0.8843	61.06				
0.9569	49.75	0.9234	57.24	0.8943	64.62				
0.9644	53.36	0.9333	61.00						
0.9730	57.24	0.9422	64.76						
0.9813	61.00								
0.9898	64.76								
$W_1 = 0.68$									
0.7173	8.02	0.7174	11.42	0.7071	17.76	0.6952	24.70	0.6847	32.18
0.8316	11.55	0.7734	15.32	0.7326	20.19	0.7206	27.94	0.7066	35.42
0.8560	15.38	0.8056	19.55	0.7560	23.28	0.7408	31.05	0.7252	38.73
0.8757	19.36	0.8251	23.12	0.7783	26.78	0.7600	34.63	0.7448	42.36
0.8910	23.25	0.8428	26.76	0.7992	30.77	0.7788	38.28	0.7629	46.26
0.9037	26.89	0.8574	30.53	0.8172	34.66	0.7959	42.20	0.7762	49.75
0.9154	30.87	0.8720	34.61	0.8320	38.39	0.8109	46.10	0.7904	53.56
0.9255	34.36	0.8843	38.55	0.8454	42.19	0.8239	49.72	0.8055	57.62
0.9371	38.94	0.8952	42.32	0.8598	46.21	0.8360	53.78	0.8166	60.98
0.9445	42.06	0.9052	46.02	0.8702	50.04	0.8479	57.43	0.8276	64.65
0.9530	46.01	0.9154	50.08	0.8802	53.67	0.8599	61.81		
0.9605	49.66	0.9249	53.65	0.8906	57.36	0.8677	64.82		
0.9696	53.44	0.9321	57.31	0.8992	61.21				
0.9750	57.23	0.9400	61.08	0.9089	64.90				
0.9822	61.05	0.9485	64.62						
0.9896	64.65								
$W_1 = 0.58$									
0.6601	7.86	0.6575	10.34	0.6539	13.22	0.6489	17.91	0.6396	24.42
0.8051	11.37	0.7254	12.55	0.7018	16.12	0.6749	20.74	0.6654	28.07
0.8298	14.91	0.7677	15.22	0.7295	19.19	0.6939	23.36	0.6838	30.89
0.8487	19.47	0.7900	19.17	0.7527	22.91	0.7166	27.04	0.7049	34.97
0.8591	23.12	0.8079	23.11	0.7711	26.97	0.7346	30.66	0.7202	38.63
0.8706	26.99	0.8203	26.71	0.7862	30.71	0.7506	34.41	0.7355	42.26
0.8807	30.82	0.8337	30.65	0.7997	34.22	0.7650	38.63	0.7489	46.05
0.8884	34.42	0.8434	34.51	0.8114	38.37	0.7777	41.97	0.7592	49.52
0.8965	38.59	0.8530	38.16	0.8226	42.25	0.7889	45.67	0.7717	53.37

Table 1 (continued)

323 K		348 K		373 K		398 K		423 K	
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
				$W_1 = 0.58$					
0.9030	42.10	0.8623	42.35	0.8319	45.83	0.7994	49.65	0.7818	57.08
0.9106	45.67	0.8707	45.94	0.8402	49.83	0.8106	53.75	0.7927	61.21
0.9172	49.92	0.8772	49.70	0.8485	53.56	0.8187	57.15	0.8018	64.83
0.9224	53.24	0.8844	53.51	0.8563	57.03	0.8274	61.31		
0.9296	57.40	0.8912	57.18	0.8647	61.01	0.8346	64.47		
0.9342	61.16	0.8988	60.82	0.8717	64.61				
0.9399	64.75	0.9049	64.51						
				$W_1 = 0$					
0.8396	3.42	0.8249	10.73	0.8104	17.70	0.7982	25.08	0.7875	32.35
0.8438	8.23	0.8272	14.26	0.8143	21.44	0.8026	28.55	0.7902	35.58
0.8460	11.95	0.8294	16.68	0.8170	24.16	0.8056	31.58	0.7941	39.11
0.8506	15.75	0.8320	19.54	0.8207	26.90	0.8089	34.88	0.7978	42.05
0.8524	19.61	0.8353	23.53	0.8237	30.48	0.8111	38.41	0.8016	45.81
0.8552	23.43	0.8384	27.01	0.8263	34.51	0.8159	42.13	0.8040	49.59
0.8580	26.91	0.8412	30.55	0.8306	38.34	0.8183	46.11	0.8081	53.59
0.8617	30.87	0.8445	34.44	0.8339	42.25	0.8213	49.81	0.8110	57.18
0.8646	34.60	0.8475	38.38	0.8361	46.26	0.8250	53.95	0.8145	60.91
0.8660	38.37	0.8518	42.50	0.8398	49.65	0.8286	57.43	0.8174	64.46
0.8699	42.00	0.8532	45.94	0.8420	53.34	0.8305	60.83		
0.8715	45.92	0.8561	49.71	0.8445	57.09	0.8333	64.74		
0.8747	49.59	0.8597	53.46	0.8472	60.93				
0.8763	53.60	0.8612	57.23	0.8507	64.58				
0.8797	57.33	0.8643	61.39						
0.8818	61.07	0.8662	64.55						
0.8831	64.77								

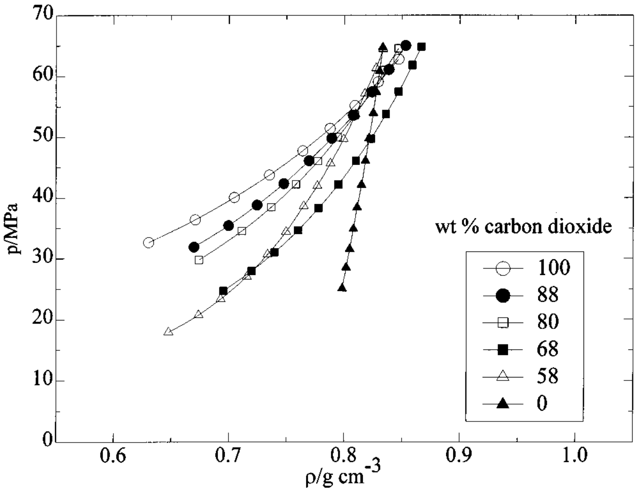

Figure 6. Pressure dependence of density for the binary mixture of carbon dioxide and toluene at 398 K. Compositions are in mass percent.

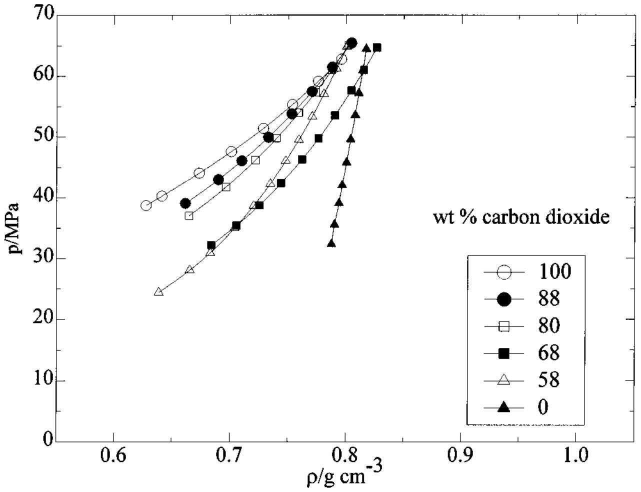

Figure 7. Pressure dependence of density for the binary mixture of carbon dioxide and toluene at 423 K. Compositions are in mass percent.

over occurring at different pressures. Similar general behavior is observed at 348 K (Figure 4). At this temperature, the crossover point for the densities of the pure fluids shifts to 40 MPa. The mixtures display density crossover in the 40−50 MPa range. The crossing of the pure fluid isopleths shifts above 50 MPa at 373 K (Figure 5) to 60 MPa at 398 K (Figure 6). At 423 K (Figure 7) toluene once again becomes more dense than carbon dioxide over the whole experimental range. Similar density crossovers have also been observed for the carbon dioxide + pentane system (Kiran *et al.*, 1996).

Excess Volume. The excess volumes for the mixtures were determined using the following relationship:

$$V^E = V^{mix} - [x_1V_1 + x_2V_2] \tag{1}$$

where V_1 and V_2 are the pure component volumes and x_1 and x_2 are the mass fractions of carbon dioxide and toluene. The V^E values have been plotted as a function of mixture composition. (Even though excess volumes are normally presented as a function of mole fraction, we are interested in our laboratory in direct information on compositions based on weight.) Figures 8−10 show V^E data for these mixtures at three different temperatures as a function of pressure. The error in excess volume data presented in these figures is estimated to be about 11%. In these figures, the compositions for which the mixtures are supercritical at the indicated pressures and the temperatures are also noted (see Figure 2). Pressures are all above the critical pressures of the mixtures.

As shown, the excess volume is observed to be mostly negative for all temperatures and pressures. In the composition range investigated, V^E becomes more negative with increasing temperature, but less negative with increasing pressure. Excess volume appears to assume a minimum value for the mixture with about 50 mass % carbon dioxide.

As discussed in our previous publication (Kiran *et al.*, 1996), literature data on excess volumes of mixtures at high pressures are very limited. Depending upon the system,

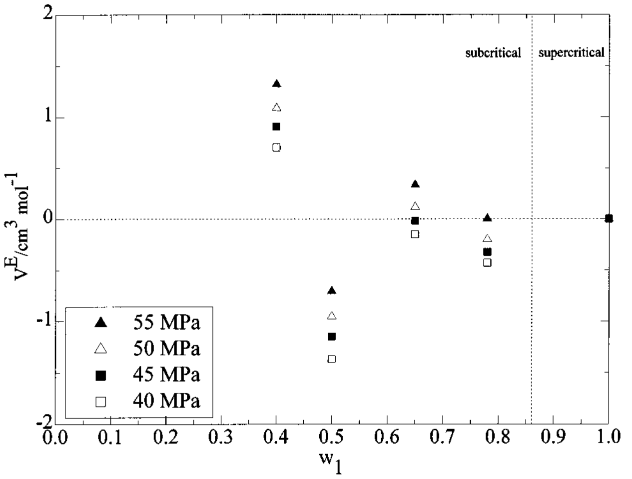

Figure 8. Excess volume for carbon dioxide (1) + toluene (2) at 323 K.

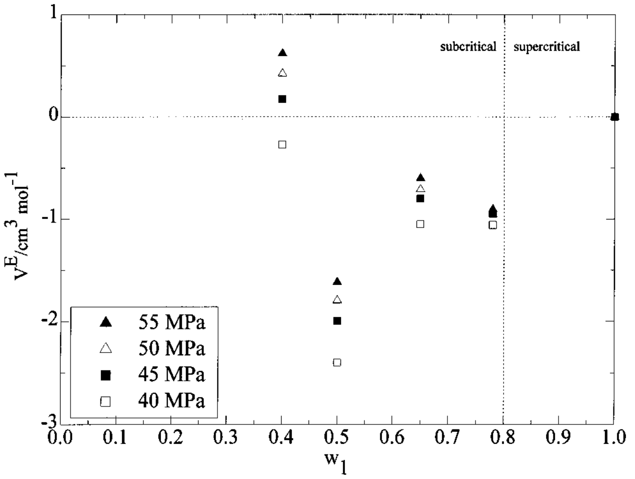

Figure 9. Excess volume for carbon dioxide (1) + toluene (2) at 348 K.

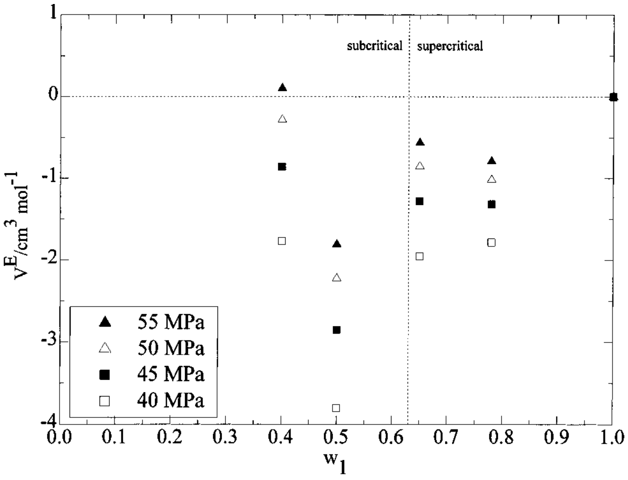

Figure 10. Excess volume for carbon dioxide (1) + toluene (2) at 373 K.

both negative and positive excess volumes have been reported. For example, excess volume for neon nitrogen mixtures is reported to be negative and symmetrical, but becomes less negative with increasing pressure at pressures up to 40 MPa (Battino, 1971). However, excess volume for mixtures of carbon dioxide and methane at pressures around 100 MPa are reported to be positive and symmetrical (Seitz *et al.*, 1994). For mixtures of carbon dioxide and pentane, excess volume shows a sigmoidal shape, being negative at low concentration of carbon dioxide but positive at high carbon dioxide content (Kiran *et al.*, 1996). If evaluated over the full composition range, the excess volume for mixtures of carbon dioxide and toluene may also be sigmoidal. The behavior, at least at the high carbon dioxide end for which the present data have been generated, appears to be opposite to that for the carbon dioxide + pentane system.

Conclusions

It is shown that the density of carbon dioxide becomes greater than that of toluene above a characteristic pressure at a given temperature. The binary mixtures also show density crossover at high pressures. Excess volumes are observed to be mostly negative for mixtures with carbon dioxide contents greater than 60% by mass investigated in this study.

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