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Volumetric Properties of Carbon Dioxide + Acetone at High Pressures

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The volumetric properties of carbon dioxide + acetone mixtures have been determined at 323, 348, 373, 398, and 423 K at pressures up to 70 MPa using a variable-volume view cell. Densities for pure components and mixtures containing 90, 80, 70, and 50% by mass carbon dioxide are reported as a function of pressure at each temperature. It is shown that this system undergoes a density crossover at high pressures with each composition, a phenomenon previously reported also for mixtures of carbon dioxide + pentane and carbon dioxide + toluene. In the composition range investigated, the excess volume of the mixtures becomes more positive with increasing pressure but more negative with increasing temperature.

Introduction

The investigation of binary mixtures of carbon dioxide with organic solvents is of particular importance for the development of new supercritical fluid processing technologies. This is because supercritical carbon dioxide is recognized as a replacement fluid for environmentally objectionable organic solvents and can be used to reduce their use. From a scientific perspective, binary fluid mixtures introduce a useful parameter, i.e., the fluid composition, which can be used as an additional parameter to fine-tune the properties of processing fluids for a specific application. In our laboratory, we employ near-critical and supercritical fluid mixtures for polymer applications. Mixture composition along with pressure and temperature is used as a key parameter to bring about miscibility or phase separation or changes in viscosity, diffusivity, or reactivity (Kiran, 1994; Kiran and Balkan, 1994; Xiong and Kiran, 1995; Kiran, 1995; Kiran and Gökmenoglu, 1996; Kiran et al., 1996a,b).

Unlike high-pressure vapor−liquid equilibria and critical data, information on the volumetric properties of carbon dioxide + organic solvent mixtures at high pressures is rather limited. We have recently reported on the volumetric properties of carbon dioxide + pentane (Kiran et al., 1996a,b), carbon dioxide + sulfur hexafluoride (Gökmenoglu et al., 1996), and carbon dioxide + toluene (Pöhler and Kiran, 1996) over a wide range of compositions and temperatures at pressures up to 70 MPa. A very interesting study was also recently reported on the vapor−liquid equilibria and the volumetric expansion of the liquid phases in the binary mixtures of carbon dioxide with ethyl acetate, 1,4-dioxane, dimethylformamide, dimethyl sulfoxide, and ethanol, but at pressures up to about 10 MPa and temperatures below 313 K (Kordikowski et al., 1995). For carbon dioxide + acetone mixtures, critical data have been reported for mixtures with acetone content less than 7 mol % (Gurdial et al., 1993). Critical data have also been reported for the ternary mixtures carbon dioxide + acetone + water (Wendland, 1994). A recent publication reports on the vapor−liquid equilibria for carbon dioxide + acetone mixtures and provides data on the liquid- and vapor-phase densities in the temperature range from 291 to 313 K at pressures below 5 MPa (Day et al., 1966) and compares the results with earlier publications by Tanaka and Kato (1995) and Katayama et al. (1975).

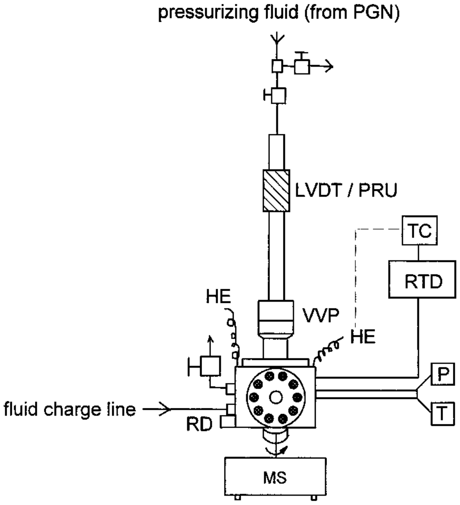

Figure 1. Schematic diagram of the experimental system (LVDT/PRU = piston position readout unit; TC = temperature controller; RDT = resistance temperature detector; HE = heating elements; VVP = variable-volume part; RD = rupture disk; MS = magnetic stirrer).

The present report is on the volumetric behavior of binary mixtures of carbon dioxide and acetone at pressures up to 70 MPa. Pressure−density data are reported for the mixtures containing 0, 50, 70, 80, 90, 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

Apparatus. A detailed description of the experimental system and procedures for determination of the densities is given in our previous publications (Kiran et al., 1995; Gökmenoglu et al., 1996). Figure 1 shows only the essential elements of the system. The main part is a variable-volume view cell. It is heated with four cartridge heaters. The pressure and temperature inside the cell are monitored with flush-mount Dynisco transducers. The pressure is measured with an accuracy of ±0.06 MPa and read with a resolution of ±0.007 MPa. The temperature is measured with an accuracy of ±0.5 K and monitored with

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Table 1. Densities of Carbon Dioxide (1) + Acetone (2) (w = Mass Fraction)

323 K		348 K		373 K		398 K		423 K	
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}
$w_1 = 1$									
11.83	0.6292	19.63	0.6475	26.05	0.6282	32.64	0.6298	38.73	0.6281
15.46	0.7348	22.74	0.6932	28.78	0.6644	36.40	0.6711	40.26	0.6410
19.40	0.7954	25.19	0.7271	32.63	0.7087	40.06	0.7053	44.03	0.6726
22.96	0.8343	28.61	0.7648	36.11	0.7408	43.74	0.7346	47.57	0.7014
26.79	0.8659	32.55	0.8010	39.82	0.7710	47.73	0.7644	51.40	0.7293
30.59	0.8925	36.08	0.8270	43.79	0.7986	51.41	0.7881	55.33	0.7537
34.45	0.9145	40.17	0.8534	47.56	0.8232	55.19	0.8088	59.16	0.7757
38.21	0.9347	43.74	0.8743	51.54	0.8454	59.08	0.8289	62.76	0.7962
41.93	0.9595	47.59	0.8927	55.13	0.8634	62.78	0.8472		
45.94	0.9655	51.39	0.9123	59.11	0.8808				
50.09	0.9837	55.22	0.9284	62.75	0.8974				
53.45	0.9942	59.12	0.9502						
$w_1 = 0.9$									
8.95	0.5890	14.15	0.5830	20.48	0.5722	26.52	0.5640	33.62	0.5640
11.70	0.7055	18.65	0.6784	24.04	0.6295	31.14	0.6198	38.81	0.6138
15.16	0.7596	23.00	0.7313	26.95	0.6655	34.71	0.6536	42.19	0.6407
19.05	0.7996	26.67	0.7648	30.68	0.7024	38.45	0.6850	46.14	0.6686
22.76	0.8282	30.44	0.7921	34.51	0.7334	42.16	0.7107	49.82	0.6916
27.05	0.8546	34.51	0.8174	38.23	0.7588	45.98	0.7348	53.57	0.7133
30.77	0.8742	38.34	0.8384	42.09	0.7816	49.89	0.7564	57.61	0.7342
34.39	0.8906	41.91	0.8550	45.79	0.8010	53.46	0.7745	61.29	0.7520
38.23	0.9063	45.99	0.8723	49.81	0.8202	57.49	0.7925	64.83	0.7673
42.30	0.9291	49.81	0.8867	53.36	0.8355	60.84	0.8067		
46.31	0.9362	54.06	0.9019	57.10	0.8500	64.74	0.8223		
49.95	0.9489	58.15	0.9152	61.08	0.8647				
53.67	0.9599	61.14	0.9246	64.99	0.8781				
57.42	0.9705								
$w_1 = 0.8$									
8.26	0.6208	10.75	0.6147	18.10	0.6147	26.27	0.6147	33.92	0.6148
11.29	0.7499	14.73	0.6908	22.23	0.6653	30.89	0.6559	38.48	0.6480
15.10	0.7874	19.15	0.7354	26.82	0.7058	34.65	0.6836	42.35	0.6720
18.79	0.8116	23.09	0.7632	30.55	0.7307	38.28	0.7064	46.02	0.6921
22.92	0.8337	29.94	0.8008	34.36	0.7527	41.95	0.7263	49.75	0.7113
26.38	0.8500	34.23	0.8192	38.15	0.7714	45.83	0.7449	53.35	0.7275
30.53	0.8662	38.33	0.8349	41.88	0.7879	49.59	0.7609	57.20	0.7430
34.45	0.8793	42.22	0.8486	45.80	0.8036	53.53	0.7761	61.11	0.7575
38.44	0.8910	46.02	0.8604	49.44	0.8162	57.25	0.7894	64.96	0.7705
42.18	0.9012	49.63	0.8715	53.03	0.8278	60.87	0.8016		
46.02	0.9110	53.40	0.8815	57.17	0.8405	64.77	0.8136		
49.72	0.9201	57.27	0.8912	60.87	0.8508				
53.39	0.9285	60.97	0.9011	64.92	0.8622				
57.18	0.9370	64.96	0.9092						
60.93	0.9448								
64.65	0.9522								
$w_1 = 0.7$									
6.31	0.5745	8.72	0.5700	11.27	0.5519	16.80	0.5519	24.94	0.5519
8.68	0.7161	11.71	0.6775	15.38	0.6353	20.11	0.5948	28.09	0.5864
11.95	0.7824	15.24	0.7232	19.13	0.6713	23.28	0.6256	31.00	0.6099
15.79	0.8041	19.21	0.7509	22.87	0.6985	26.92	0.6538	34.56	0.6336
19.46	0.8200	22.77	0.7694	26.97	0.7218	30.81	0.6788	38.37	0.6561
23.50	0.8348	27.16	0.7879	30.60	0.7398	34.35	0.6971	42.27	0.6757
27.32	0.8456	30.90	0.8017	34.60	0.7565	38.51	0.7165	46.01	0.6927
30.68	0.8549	34.91	0.8149	38.52	0.7722	42.11	0.7309	49.78	0.7079
34.60	0.8650	38.34	0.8254	42.11	0.7841	45.82	0.7446	53.45	0.7219
38.49	0.8741	42.42	0.8365	45.98	0.7957	49.69	0.7576	56.97	0.7341
42.39	0.8835	46.06	0.8460	49.58	0.8081	53.76	0.7705	60.61	0.7469
46.11	0.8926	50.15	0.8554	53.32	0.8166	57.16	0.7800	64.30	0.7566
49.84	0.9003	53.63	0.8637	57.41	0.8267	60.98	0.7906		
53.48	0.9072	57.15	0.8730	61.29	0.8359	64.45	0.7997		
57.47	0.9146	61.45	0.8810	64.71	0.8437				
60.79	0.9207								
$w_1 = 0.5$									
5.62	0.7469	7.67	0.7401	15.67	0.7206	25.92	0.7206	37.64	0.7206
7.92	0.7909	11.63	0.7607	18.92	0.7347	30.74	0.7378	41.78	0.7326
11.54	0.8084	15.28	0.7743	23.28	0.7514	64.52	0.7488	45.81	0.7436
15.35	0.8183	19.26	0.7863	26.93	0.7631	38.62	0.7598	49.44	0.7526
19.21	0.8270	13.30	0.7970	30.81	0.7743	41.94	0.7681	53.54	0.7619
23.01	0.8350	27.12	0.8061	34.50	0.7838	45.73	0.7766	57.25	0.7697
26.66	0.8424	30.96	0.8143	38.34	0.7928	49.65	0.7848	61.44	0.7782
30.76	0.8498	34.63	0.8217	42.10	0.8008	53.38	0.7930	65.44	0.7854
34.91	0.8566	38.30	0.8287	45.86	0.8086	57.00	0.7991		
38.43	0.8621	42.23	0.8356	49.12	0.8163	60.99	0.8059		
42.02	0.8675	45.79	0.8416	53.36	0.8224	64.74	0.8122		
45.73	0.8725	49.57	0.8476	57.60	0.8292				
49.72	0.8780	53.74	0.8539	60.98	0.8345				
53.30	0.8826	57.12	0.8585	64.87	0.8401				
57.08	0.8876	60.94	0.8640						
60.88	0.8919	64.24	0.8684						
64.67	0.8961								

Table 1 (Continued)

323 K		348 K		373 K		398 K		423 K	
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}
$w_1 = 0$									
1.65	0.7581	10.20	0.7421	23.86	0.7346	42.55	0.7341	60.12	0.7346
4.30	0.7613	15.01	0.7482	27.17	0.7384	45.51	0.7375	61.84	0.7361
7.59	0.7654	19.58	0.7535	30.70	0.7423	49.85	0.7429	63.93	0.7375
11.79	0.7704	23.21	0.7581	34.43	0.7468	53.64	0.7463	45.49	0.7399
15.27	0.7730	26.41	0.7629	38.14	0.7509	57.24	0.7495		
19.13	0.7771	30.82	0.7650	42.00	0.7547	61.09	0.7537		
22.83	0.7815	34.45	0.7697	45.72	0.7581	64.70	0.7564		
26.55	0.7859	38.15	0.7734	49.62	0.7620				
30.61	0.7884	42.11	0.7762	53.45	0.7660				
34.66	0.7923	45.84	0.7805	57.07	0.7695				
38.23	0.7961	49.72	0.7835	61.04	0.7736				
42.41	0.7990	53.53	0.7874	64.61	0.7761				
45.97	0.8027	57.15	0.7905						
49.52	0.8055	60.88	0.7939						
53.51	0.8079	64.61	0.7936						
57.14	0.8102								
61.01	0.8131								
64.86	0.8169								

a resolution of ±0.1 K. A linear variable differential transformer coil (LVDT) and a position readout unit (PRU) are used to monitor the position of a movable piston inside the variable volume part (VVP) of the cell. This is achieved with the aid of a ferromagnetic metal piece on a steel rod attached to the piston. When the piston is moved to a new position (with a pressurizing fluid from a pressure generator PGN), the LVDT coil is moved to sense the new location of the ferromagnetic element. The position readout unit gives the actual distance traveled from which the internal volume of the cell is determined at any given temperature and pressure. Once the cell is loaded with a known mass of fluid, its density is determined as a function of pressure at each temperature. As we reported earlier (Kiran, 1996b), with this system densities are determined with an accuracy of ±1.22%, and volume changes are determined with an accuracy of ±0.0025 cm^3. The maximum internal volume of the cell is 22.43 cm^3.

Density measurements were conducted for the pure fluids and for mixtures containing a total mass loading of about 15 g.

Materials. Carbon dioxide was bone-dry grade with a purity of 99.8% (Airco; supplied with an eductor tube). Acetone (99.9+% purity) was obtained from Sigma.

Results and Discussion

Density. Table 1 summarizes the density data for pure carbon dioxide and acetone and for their binary mixtures containing 50, 70, 80, and 90 mass % carbon dioxide which were measured at 323, 348, 373, 398, and 423 K at pressures up to 70 MPa. At most of these conditions, the mixtures are either supercritical or exist as liquid mixtures. Figure 2 shows the variation of the critical pressure and temperature which has been generated using the limited data reported by Gurdial et al. (1993). For this mixture more complete experimental data on critical temperatures and pressures have been recently reported (Ziegler et al., 1996) without, however, compositional information. We have estimated the critical temperatures as a function of composition for these mixtures using the method of Li (1971). Using the composition−critical temperature relationship obtained, we then determined for each composition (temperature), the corresponding critical pressure using the critical temperature−pressure data of Ziegler. The results are included in the figure. The present density measurements have been mostly conducted at pressures which are higher than the critical pressures these mixtures display. Above about 12 MPa, the mixtures are all above the critical pressure. The mixtures with high carbon dioxide content were also above their respective critical temperatures and therefore were supercritical at the conditions evaluated.

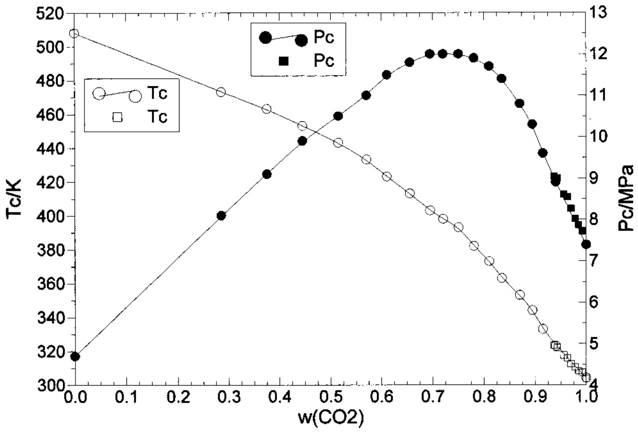

Figure 2. Critical temperature and pressure of the binary mixtures carbon dioxide (1) + acetone (2). Data are from Gurdial et al. (1993) (squares) and Ziegler et al. (1966) (circles). (Compositions corresponding to the critical P/T data of Ziegler et al. have been calculated from predictions of the critical temperatures using the method of Li (1971)).

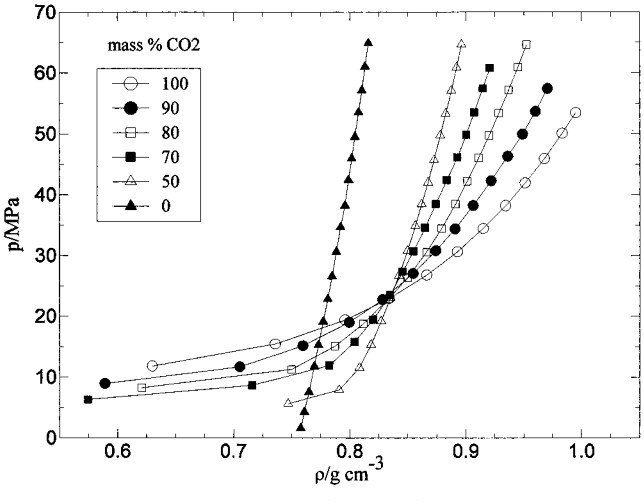

Figure 3. Pressure dependence of density for the binary mixtures of carbon dioxide and acetone at 323 K (compositions in mass percent).

Figure 3 shows the variation of density with pressure for each mixture at 323 K. As shown, acetone has a relatively low compressibility displayed by the steep increase in pressure to bring about even small changes in

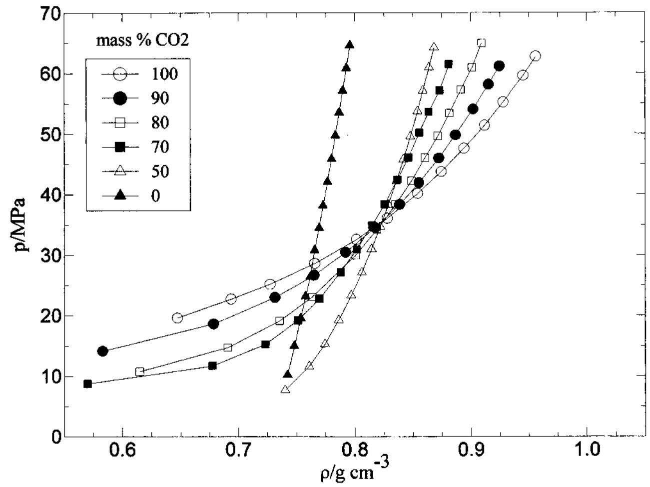

Figure 4. Pressure dependence of density for the binary mixtures of carbon dioxide and acetone at 348 K (compositions in mass percent).

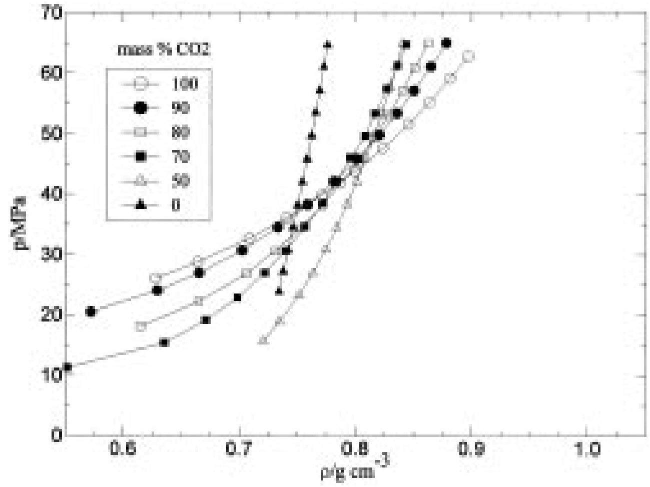

Figure 5. Pressure dependence of density for the binary mixtures of carbon dioxide and acetone at 373 K (compositions in mass percent).

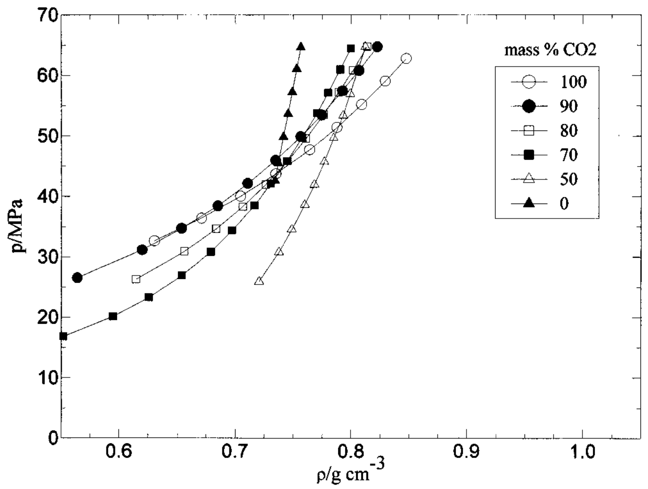

Figure 6. Pressure dependence of density for the binary mixtures of carbon dioxide and acetone at 398 K (compositions in mass percent).

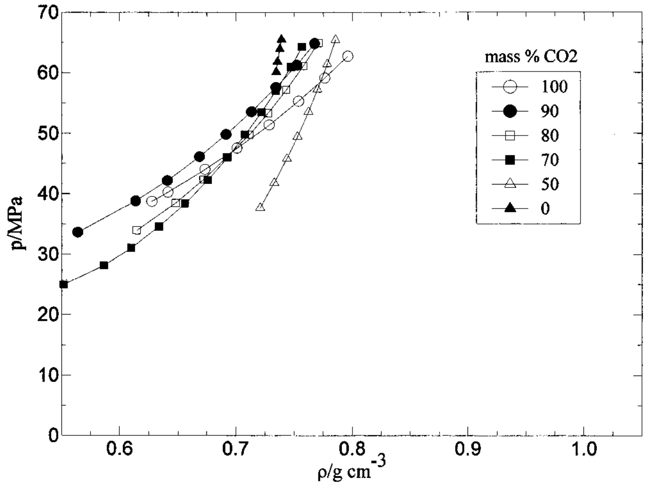

Figure 7. Pressure dependence of density for the binary mixtures of carbon dioxide and acetone at 423 K (compositions in mass percent).

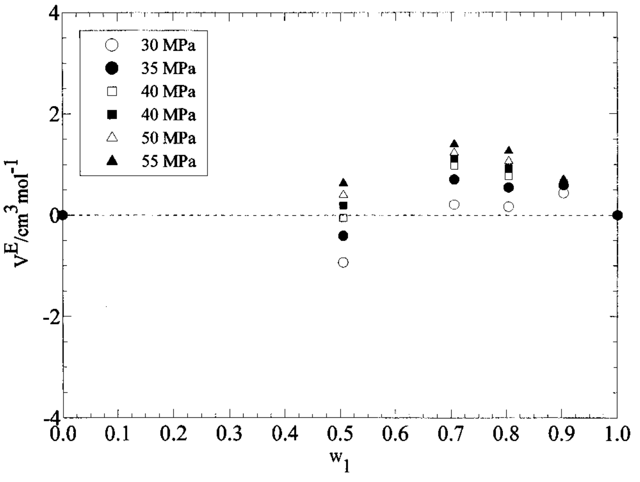

Figure 8. Excess volume for carbon dioxide (1) + acetone (2) at 323 K.

the density of the fluid. The density changes from about 0.7704 to 0.8079 g/cm^3 when the pressure is changed from about 11.8 to 53.5 MPa, while in the same interval the density of carbon dioxide increases from 0.6292 to 0.9942 g/cm^3. It is interesting to note that with increasing pressure, the density of carbon dioxide becomes greater than that of acetone at about 16 MPa. As shown in the figure, binary mixtures of carbon dioxide and acetone are also more compressible than acetone, and each mixture shows a density crossover (i.e., the density of the mixture becomes greater than that of pure acetone) at a characteristic pressure. Similar trends are observed in Figures 4−7 which show the variation of density with pressure at 348, 373, 398, and 423 K. The density crossover pressures shift, however, to higher pressures. As the temperature is increased, the density difference between acetone and carbon dioxide becomes smaller, and consequently for the mixtures, the spacing between isopleths becomes narrower.

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

$$V^{E} = V^{mix} - (x_1V_1 + x_2V_2)$$

where V_1 and V_2 represent the pure component molar volumes and x_1 and x_2 are the mole fractions of carbon dioxide and acetone. In Figures 8 and 9 excess volumes are shown at 323 and 348 K for different pressures as a function of carbon dioxide mass fraction w_1. (In our laboratory, we are interested in compositional information based on mass fractions.) The error in excess volume for this system, depending upon the composition, was estimated to be in the range 6.9 to 15.6% with a mean value

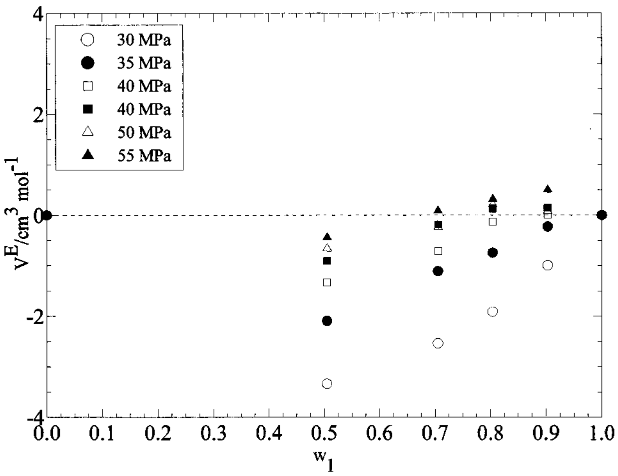

Figure 9. Excess volume for carbon dioxide (1) + acetone (2) at 348 K.

of 9.6%. At 323 K (Figure 8) V^E appears to be mostly positive for these mixtures, though it is likely that the overall shape is sigmoidal with negative excess volumes displayed for mixtures with high acetone content. At 348 K, V^E becomes more negative. At both temperatures, excess volume becomes more positive with increasing pressure.

Excess volumes for carbon dioxide + acetone mixtures have not been previously reported in the literature. In fact, high-pressure excess volume data are available only for a limited number of systems (Battino, 1971; Seitz et al., 1996; Ott et al., 1996; Kiran et al., 1996b; Pöhler and Kiran, 1996). Carbon dioxide + organic solvent systems are the least studied. The present trends are more like the trends that we reported earlier for carbon dioxide + pentane mixtures (Kiran et al., 1996b). That the excess volume becomes more negative with increasing temperature and more positive with increasing pressure were also observed with carbon dioxide + toluene (Pöhler and Kiran, 1996), but for that system excess volumes were found to be negative for mixtures with high carbon dioxide content, which is in contrast with carbon dioxide + pentane or carbon dioxide + acetone systems.

Conclusions

The density of carbon dioxide becomes greater than that of acetone above a characteristic pressure at a given temperature. Binary mixtures also display density crossover. Excess volumes are shown to decrease with temperature but increase with pressure.

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