Volumetric Properties of Carbon Dioxide + Ethanol at High Pressures

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The volumetric properties of carbon dioxide + ethanol 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, carbon dioxide + toluene, and carbon dioxide + acetone. In the composition range investigated, the excess volume of the mixtures becomes more positive with increasing pressure but more negative with increasing temperature.

Introduction

This paper is a continuation of our ongoing investigation of binary mixtures of carbon dioxide with organic solvents for the development of new supercritical fluid processing technologies. One of the practical objectives is the replacement or reduction of environmentally objectionable organic solvents in physicochemical processing. By employing mixtures, one can also use the fluid composition as an additional parameter to fine-tune the properties of processing fluids for a specific application, such as those involved in polymer processing. 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 in applications ranging from reactions and polymerization to particle formation or foaming (Kiran, 1994).

Data on high-pressure volumetric properties of mixtures is not as extensive as data on vapor−liquid equilibria for such systems. In this respect, mixtures of carbon dioxide + ethanol have probably been investigated to a greater extent. A recent study has reported on the vapor−liquid equilibria and the volumetric expansion of the liquid phases in the binary mixtures of carbon dioxide with ethanol, at pressures up to about 10 MPa and temperatures below 313 K (Kordikowski et al., 1995). They have reported a distinctive maximum in the liquid-phase density. Depending upon the initial density of the pure liquid solvent and the density of pure carbon dioxide at subcritical temperatures, this maximum was observed to be more or less pronounced. Carbon dioxide dissolving in the mixture would increase the density of the liquid phase. A very important observation the authors have made is that the expansion of the liquid phase when plotted as a function of the mole fraction of carbon dioxide is essentially independent of type of the organic solvent, all such curves merging for a wide range of binary mixtures of containing carbon dioxide. A number of other recent publications present data on phase equilibria and densities for liquid and vapor phases for ethanol + carbon dioxide mixtures at pressures below 8 MPa, and temperatures in the range 291−313 K (Day et al., 1996; Tanaka and Kato, 1995) have also been reported. Earlier publications related to vapor−liquid equilibria in carbon dioxide + ethanol mixtures have been reviewed by Jennings et al. (1993) and Dohrn and Brunner (1995). Data are also reported in recent articles on the phase behavior of carbon dioxide + ethanol + water ternary systems (Lim et al., 1994; Yoon et al., 1994). These studies are all limited to pressures below about 12 MPa.

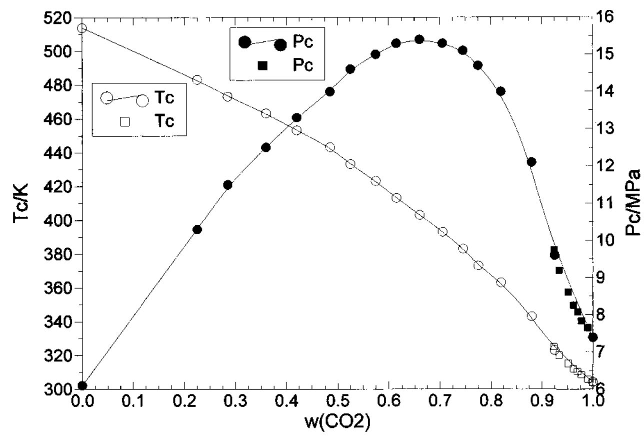

Figure 1. Critical temperature and pressure of the binary mixtures carbon dioxide (1) + ethanol (2). Data are from Gurdial et al. (1993) (squares) and Ziegler et al. (1995) (circles). Compositions corresponding to the critical *P*/*T* data of Ziegler have been calculated from the predictions for critical temperatures for these mixtures.

We have recently reported on the volumetric properties of carbon dioxide + pentane (Kiran et al., 1996), carbon dioxide + sulfur hexafluoride (Gökmenoglu et al., 1996, carbon dioxide + toluene (Pöhler and Kiran, 1996), and carbon dioxide + acetone (Pöhler and Kiran, 1997) over a wide range of compositions and temperatures at pressures up to 70 MPa. We now present similar data for carbon dioxide + ethanol mixtures. 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

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

The description of the experimental system (a variable-volume view cell plus a piston position sensor to determine

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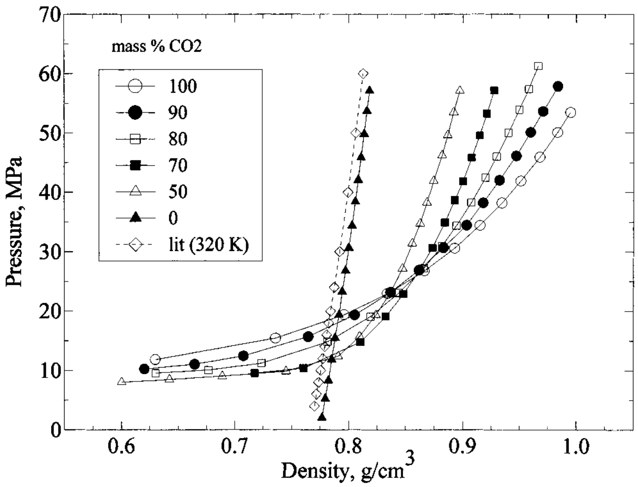

Figure 2. Pressure dependence of density for the binary mixtures of carbon dioxide and ethanol at 323 K (compositions in mass percent). Literature data for pure ethanol at 320 K are from TRC Tables (1995).

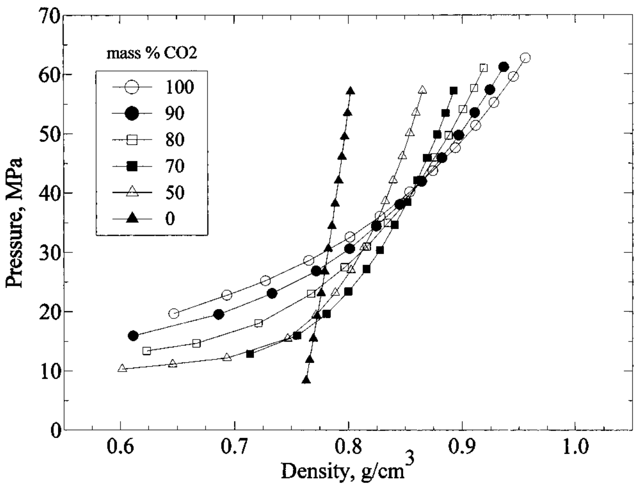

Figure 3. Pressure dependence of density for the binary mixtures of carbon dioxide and ethanol at 348 K (compositions in mass percent).

internal volume) and the procedure for determination of the densities are given in our previous publications (Kiran et al., 1996; Gökmenoglu et al., 1996). Pressures and temperatures are determined with an accuracy of ±0.03 MPa and ±0.5 K, respectively. The mass loading of the cell is determined using a sensitive balance with an accuracy of ±0.01 g. Volume changes are determined with an accuracy of ±0.0025 cm^3. The maximum internal volume of the cell is 22.43 ± 0.05 cm^3. Earlier comparisons with the literature data on densities of pure fluids (such as carbon dioxide, pentane, sulfur hexafluoride) show that the densities with this experimental system are typically determined with an accuracy of ±1.2% (Kiran et al., 1996; Gökmenoglu et al., 1996).

In the present study, the densities for pure fluids and the mixtures were determined at a total mass loading of about 15 g. The density values for pure ethanol were compared (after interpolation to match the temperatures) with the values of the data given in the TRC Thermodynamic Tables (1995) over similar temperature and pressure ranges. Overall, the density values were in agreement within ±1.7% . (The deviations at different temperatures were in the range from ±1.2 to ±2.3%).

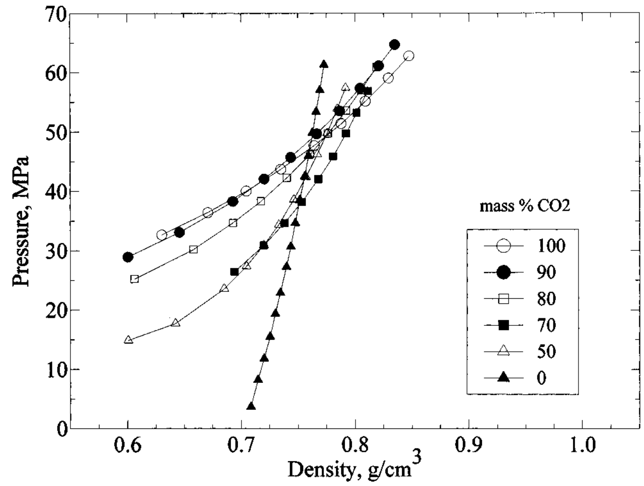

Figure 4. Pressure dependence of density for the binary mixtures of carbon dioxide and ethanol at 398 K (compositions in mass percent).

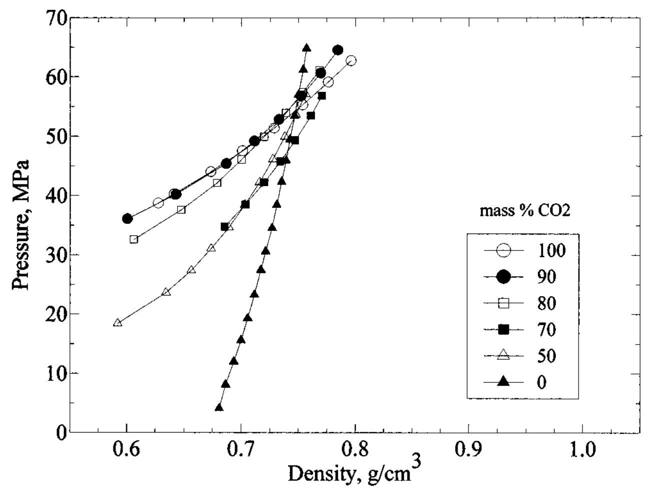

Figure 5. Pressure dependence of density for the binary mixtures of carbon dioxide and ethanol at 423 K (compositions in mass percent).

Results and Discussion

Density. Table 1 summarizes the density data for pure carbon dioxide and ethanol 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 1 shows the variation of the critical pressure and temperature which has been generated using the limited data reported by Gurdial et al. (1993). Recently, experimental data on critical temperatures and pressures obtained by a chromatographic peak shape method (Ziegler et al., 1996) have been reported for these mixtures without, however, providing compositional information. Using the values of the critical temperatures calculated by the method of Li (1971), the data of Ziegler et al. have been related to the compositions and have been included in the figure. As can be assessed from this figure, the present density measurements have been mostly conducted at pressures which are higher than the critical pressures of these mixtures. At pressures above about 15 MPa all these mixtures will be above their critical pressures.

Figure 2 shows the variation of density with pressure for each mixture at 323 K. As shown, ethanol has a relatively low compressibility displayed by the steep increase in pressure with changes in the density of the fluid.

Table 1. Densities of Carbon Dioxide (1) + Ethanol (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						
				$w_1 = 0.9$					
10.23	0.6203	15.87	0.6113	21.79	0.6005	28.93	0.6005	36.06	0.6005
11.05	0.6646	19.49	0.6865	26.58	0.6700	33.08	0.6459	40.22	0.6429
12.46	0.7077	23.03	0.7329	30.84	0.7130	38.29	0.6929	45.42	0.6869
15.69	0.7642	26.84	0.7717	34.57	0.7452	42.08	0.7202	49.22	0.7112
19.35	0.8051	30.59	0.8010	38.33	0.7710	45.72	0.7436	52.86	0.7326
23.17	0.8369	34.41	0.8244	42.16	0.7948	49.69	0.7664	56.82	0.7524
26.89	0.8618	38.06	0.8451	45.65	0.8137	53.54	0.7864	60.67	0.7694
30.66	0.8828	41.95	0.8645	49.53	0.8325	57.40	0.8044	64.54	0.7844
34.48	0.9032	45.93	0.8823	53.56	0.8509	61.16	0.8207		
38.22	0.9176	49.72	0.8970	57.32	0.8661	64.69	0.8347		
42.05	0.9321	53.54	0.9108	61.37	0.8814				
46.14	0.9470	57.38	0.9242	63.62	0.8898				
50.12	0.9597	61.23	0.9356						
53.64	0.977								
57.83	0.9836								
				$w_1 = 0.8$					
9.56	0.6301	13.33	0.6234	18.28	0.6062	25.23	0.6062	32.58	0.6062
10.06	0.6768	14.60	0.6669	22.28	0.6659	30.22	0.6583	37.62	0.6475
11.24	0.7236	18.00	0.7210	26.95	0.7123	34.66	0.6931	42.16	0.6788
14.80	0.7813	23.00	0.7673	30.90	0.7419	38.34	0.7175	46.09	0.7002
19.06	0.8190	27.46	0.7966	34.70	0.7660	42.29	0.7404	49.94	0.7198
23.08	0.8439	30.95	0.8160	38.46	0.7863	46.23	0.7604	53.93	0.7387
27.23	0.8660	34.94	0.8345	42.10	0.8033	49.76	0.7762	57.44	0.7537
30.97	0.8818	38.48	0.8510	46.11	0.8179	53.59	0.7923	61.16	0.7683
34.41	0.8943	42.19	0.8637	49.77	0.8342	57.08	0.8052		
38.31	0.9074	45.98	0.8760	53.67	0.8470	60.92	0.8186		
42.47	0.9198	49.69	0.8882	57.34	0.8584				
46.05	0.9256	54.10	0.9006	61.09	0.8695				
50.03	0.9400	57.68	0.9103						
53.91	0.9497	61.04	0.9188						
57.34	0.9579								
61.26	0.9662								
				$w_1 = 0.7$					
9.56	0.7177	12.84	0.7137	18.69	0.7070	26.44	0.6944	34.76	0.6855
10.39	0.7603	15.95	0.7552	23.47	0.7408	30.86	0.7199	38.50	0.7035
14.79	0.8103	19.59	0.7810	27.28	0.7611	34.67	0.7384	42.22	0.7198
19.08	0.8326	23.37	0.7998	30.89	0.7772	38.21	0.7532	45.77	0.7339
22.86	0.8479	27.15	0.8158	34.32	0.7904	42.04	0.7677	49.32	0.7470
26.92	0.8622	30.34	0.8277	38.04	0.8032	45.87	0.7806	53.48	0.7609
30.62	0.8733	34.59	0.8406	42.00	0.8154	49.75	0.7921	56.81	0.7705
34.92	0.8842	38.48	0.8520	45.85	0.8261	53.21	0.8014		
38.69	0.8928	42.11	0.8605	49.69	0.8360	56.88	0.8110		
41.88	0.8999	45.89	0.8693	53.45	0.8446				
45.80	0.9076	49.84	0.8782	57.26	0.8532				
49.58	0.9146	53.45	0.8854						
53.21	0.9210	57.21	0.8926						
57.15	0.9272								
				$w_1 = 0.5$					
8.02	0.6000	10.26	0.6015	12.73	0.6005	14.88	0.6007	18.40	0.5919
8.49	0.6424	11.07	0.6461	14.17	0.6432	17.69	0.6424	23.62	0.6343
9.04	0.6890	12.15	0.6934	16.37	0.6817	23.58	0.6853	27.37	0.6562
9.85	0.7450	15.44	0.7468	19.21	0.7096	27.37	0.7048	31.05	0.6737
12.40	0.7909	19.45	0.7719	23.12	0.7340	30.93	0.7200	34.62	0.6893
15.73	0.8097	23.16	0.7885	26.78	0.7510	34.38	0.7333	38.47	0.7030
19.35	0.8237	27.00	0.8023	30.79	0.7659	38.62	0.7464	42.27	0.7157
22.79	0.8357	30.85	0.8137	34.41	0.7781	42.42	0.7569	46.16	0.7274
27.18	0.8472	34.56	0.8236	38.30	0.7893	46.24	0.7667	49.96	0.7380
31.40	0.8558	38.62	0.8323	42.37	0.7987	49.82	0.7754	53.67	0.7476
34.76	0.8626	42.13	0.8393	46.24	0.8071	53.88	0.7843	57.14	0.7560
38.31	0.8685	46.20	0.8474	49.97	0.8152	57.43	0.7915		

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}
				$w_1 = 0.5$					
41.93	0.8744	50.09	0.8539	53.91	0.8222				
46.23	0.8816	53.52	0.8595	57.45	0.8291				
49.63	0.8866	57.26	0.8652						
53.48	0.8919								
57.09	0.8971								
				$w_1 = 0$					
2.04	0.7765	8.37	0.7630	27.30	0.7600	3.72	0.7086	4.11	0.6809
5.24	0.7794	11.86	0.7660	30.15	0.7630	8.26	0.7149	8.10	0.6866
8.32	0.7822	15.48	0.7694	34.37	0.7662	11.82	0.7202	12.00	0.6938
11.83	0.7853	19.24	0.7726	38.18	0.7694	15.50	0.7256	15.59	0.6998
15.48	0.7881	23.12	0.7762	41.82	0.7723	19.37	0.7303	19.30	0.7054
19.37	0.7915	26.76	0.7792	45.75	0.7757	22.92	0.7346	23.27	0.7113
23.24	0.7943	30.60	0.7824	49.41	0.7785	27.29	0.7400	27.44	0.7168
26.79	0.7972	34.45	0.7855	53.15	0.7816	30.67	0.7438	30.60	0.7211
30.64	0.8000	38.19	0.7883	57.17	0.7844	34.64	0.7476	34.52	0.7267
34.40	0.8030	42.09	0.7914			38.55	0.7516	38.46	0.7308
38.44	0.8058	46.11	0.7943			42.50	0.7558	42.38	0.7350
42.08	0.8083	49.47	0.7968			46.01	0.7591	45.95	0.7390
45.86	0.8107	53.47	0.7994			49.88	0.7626	49.51	0.7424
49.81	0.8134	57.08	0.8019			53.42	0.7657	53.48	0.7466
53.68	0.8149					57.05	0.7691	57.00	0.7498
57.09	0.8181					61.36	0.7726	61.22	0.7540
								64.81	0.7569

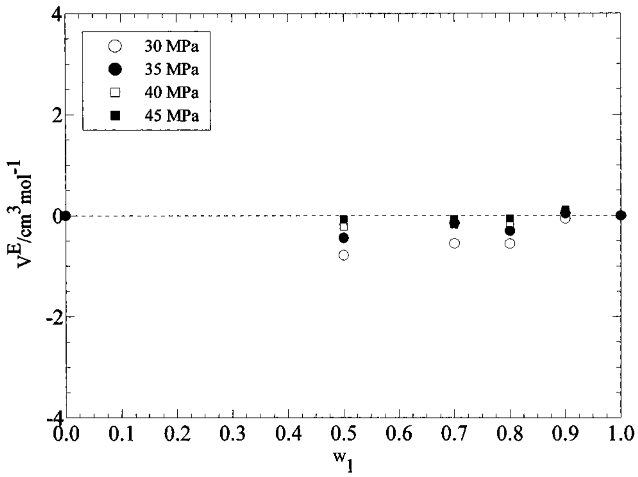

Figure 6. Excess volume for carbon dioxide (1) + ethanol (2) at 323 K.

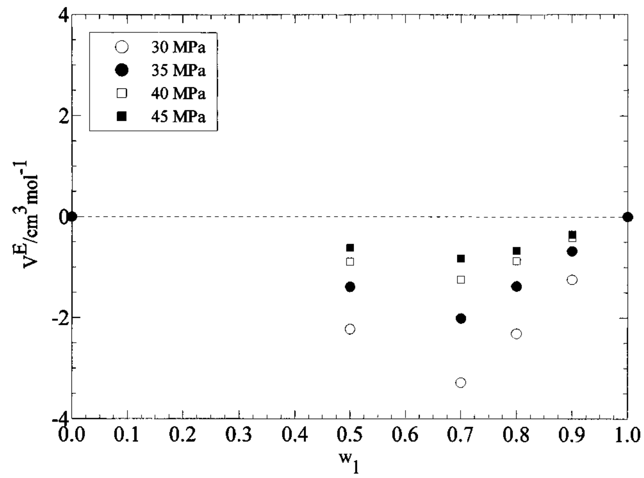

Figure 7. Excess volume for carbon dioxide (1) + ethanol (2) at 348 K.

[Density data from the literature (TRC Tables, 1995) for pure ethanol at 320 K have also been included in the figure for comparisons.] The density changes from about 0.7881 to 0.8134 g/cm^3 when the pressure is changed from about 15 to 50 MPa, while in the same interval the density of carbon dioxide increases from 0.7348 to 0.9837 g/cm^3. With increasing pressure, the density of carbon dioxide becomes greater than that of ethanol at about 15 MPa. As shown in the figure, binary mixtures of carbon dioxide and ethanol are also more compressible than ethanol, and each mixture shows a density crossover (i.e., the density of the mixture becomes greater than that of pure ethanol) at a characteristic pressure. Similar trends are observed in Figures 3−5 which show the variation of density with pressure at 348, 398, and 423 K. With increasing temperature, the density crossover pressures shift to higher pressures.

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

$$V^{E} = V^{mix} - (x_1 V_1 + x_2 V_2)$$

where V_1 and V_2 represent the pure component volumes and x_1 and x_2 are the mole fraction of carbon dioxide and acetone. In Figures 6 and 7 excess volumes are shown at 323 and 348 K for different pressures as a function of carbon dioxide mass fraction w_1. The estimated errors in excess volume for this system, depending upon the composition, were in the range 7.1 to 16.6%, with a mean value of 11.9%. As shown, at these temperatures, in the composition range evaluated, the excess volumes are negative and become more negative with decreasing pressure.

High-pressure excess volume data are available only for a limited number of systems (Seitz et al. 1996; Ott et al., 1996; Kiran et al., 1996; Pöhler and Kiran, 1996a,b). The present trends are similar to the trends reported earlier. That the excess volume becomes more negative with increasing temperature and more positive with increasing pressure was also observed with carbon dioxide + toluene (Pöhler and Kiran, 1996) and carbon dioxide + acetone (Pöhler and Kiran, 1997) mixtures.

Conclusions

The density of carbon dioxide becomes greater than that of ethanol above a characteristic pressure at a given temperature. Binary mixtures also display density crossover. Excess volumes are mostly negative and becoming more negative with increasing temperature, but less negative with increasing pressure.

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