Compressed Liquid Densities and Excess Volumes for the Binary Systems Carbon Dioxide + 1-Propanol and Carbon Dioxide + 2-Propanol Using a Vibrating Tube Densimeter up to 25 MPa

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The *PvT* behavior was determined for the binary systems carbon dioxide + 1-propanol and carbon dioxide + 2-propanol in the homogeneous state. The measurements were performed for different compositions at temperatures ranging from 313 to 363 K and pressures up to 25 MPa using a vibrating tube densimeter. The accuracy of the density determinations was better than ±0.05%, and the densities presented in this work agree well with data reported in the literature. The excess volumes were calculated from the experimental *PvT* data.

Introduction

Reliable and accurate phase equilibrium and *PvT* data of pure compounds and mixtures at high pressures are required for the development of supercritical fluid extraction processes. The present work is a continuation of systematic experimental studies focused on carbon dioxide + alcohol mixtures. Alcohols from ethanol to decanol are considered in these investigations[1−10] as model compounds in order to define suitable operating conditions for industrial supercritical extraction processes, for example, the extraction of carotenes from the chili Poblano of Mexico (*Capsicum annum*) with carbon dioxide.

Galicia-Luna et al.[1,2] have reported vapor−liquid equilibrium data for the binary systems CO_2 + ethanol, CO_2 + 1-propanol, and CO_2 + 2-propanol at temperatures ranging from 313 to 373 K. The liquid densities for pure 1-propanol and 2-propanol as well as for binary CO_2 + ethanol mixtures have already been published too.[9,10] In this work, liquid densities for binary mixtures of CO_2 + 1-propanol and CO_2 + 2-propanol were experimentally determined at different compositions, temperatures from 313 to 363 K, and pressures up to 25 MPa. The excess volumes for these mixtures and their variation with composition, temperature, and pressure are also reported.

The reliability of the experimental procedure was demonstrated by Zúñiga-Moreno and Galicia-Luna[9] by comparing their *PvT* data for pure 1-propanol and 2-propanol with the data reported by other authors.[14,15]

Experimental Section

Apparatus and Procedure. The apparatus and experimental procedure used in this work were described previously.[7−10] The vibrating U-tube made of Hastelloy C-276 contains an ~1 cm^3 sample. The calibration of the vibrating tube was performed with the classic method with the reference compounds water and nitrogen, and with vacuum. Reference density values of the H_2O and N_2 were obtained with the equations of state of Haar et al.[12] and Span et al.,[13] respectively. Details about the calibrating procedures of the platinum temperature probes and the pressure transducer are also given in previous articles.[9,10] The estimated uncertainties of the experimental quantities presented in this work are ±0.03 K for temperature, ±0.008 MPa for pressure, and ±0.05% for liquid density in the range of the reported data, as previously reported.[10]

Table 1. Purity and Origin of Pure Compounds

compound	certified purity (%)	supplier
1-propanol	99.5	Merck
2-propanol	99.5	Merck
CO_2	99.995	Air Products-Infra
water	99.95 (HPLC)	Fisher
nitrogen	99.995	Air Products-Infra

Loading of the Measurement Cell. The complete procedure is presented in a preceding paper.[10] The samples with the desired compositions are prepared by successive loadings of the pure compounds in a sapphire feeding cell with a maximum volume of 12 cm^3. The amounts of the compounds are determined by weightings carried out within $\pm 10^{-7}$ kg accuracy with a Sartorius comparator balance (MCA1200), which is periodically calibrated with a standard mass of 1 kg class E1. The resulting uncertainty for the mole fraction composition of the mixtures is lower than $\pm 10^{-4}$.

Results

The purity and source of chemicals used in this work are given in Table 1. They were used without any purification except careful degassing of water, 1-propanol, and 2-propanol, as explained previously.[10]

The liquid densities of CO_2 + 1-propanol and CO_2 + 2-propanol mixtures and their excess volumes were determined for three or four different compositions at six temperatures from 313 to 363 K and are reported in Tables 2−8.

The reliability of the measurements was proved by comparison of our own results for the pure compounds

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Table 2. Experimental Densities and Excess Volumes for the CO_2 (1) + 1-Propanol (2) Mixture at Six Temperatures and $x_1 = 0.1226$'

P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}
	T/K = 313.14			T/K = 323.09			T/K = 332.98	
3.465	797.00	−72.263	3.156	787.54	−85.477			
4.058	797.74	−58.365	4.056	788.56	−61.831	4.485	779.70	−56.907
5.077	798.86	−41.630	5.053	789.67	−45.122	5.091	780.40	−47.581
6.082	799.91	−29.926	6.047	790.72	−33.557	6.005	781.42	−36.877
7.006	800.83	−21.271	7.012	791.73	−24.994	7.004	782.52	−28.101
8.065	801.83	−12.517	8.026	792.78	−17.714	8.047	783.64	−20.986
9.029	802.73	−3.870	9.045	793.77	−11.823	9.125	784.76	−15.205
10.054	803.69	−2.401	10.018	794.72	−7.370	10.023	785.70	−11.474
11.067	804.60	−1.867	11.050	795.72	−4.068	11.027	786.73	−8.249
12.092	805.53	−1.531	12.053	796.68	−2.834	12.024	787.75	−5.808
13.043	806.37	−1.303	13.045	797.63	−2.219	13.043	788.77	−4.136
14.052	807.26	−1.114	14.034	798.53	−1.821	13.957	789.65	−3.226
15.027	808.11	−0.965	15.058	799.48	−1.523	15.054	790.73	−2.534
16.077	809.00	−0.830	16.050	800.37	−1.299	16.071	791.70	−2.094
17.056	809.84	−0.723	17.042	801.27	−1.119	17.065	792.65	−1.773
18.138	810.74	−0.618	18.013	802.12	−0.969	18.060	793.58	−1.518
19.099	811.54	−0.537	19.040	803.03	−0.835	19.071	794.52	−1.307
20.018	812.30	−0.467	20.061	803.91	−0.719	20.035	795.40	−1.137
21.033	813.14	−0.398	20.935	804.63	−0.627	21.055	796.33	−0.983
22.097	813.99	−0.331	22.103	805.67	−0.527	22.021	797.20	−0.857
23.000	814.74	−0.280	23.001	806.43	−0.455	23.022	798.10	−0.741
24.056	815.59	−0.226	24.052	807.32	−0.379	24.109	799.09	−0.633
25.337	816.65	−0.168	25.255	808.36	−0.304	25.260	800.13	−0.531
	T/K = 342.92			T/K = 352.91			T/K = 362.80	
			4.530	759.86	−61.998	4.798	749.71	−60.147
5.199	770.73	−48.920	5.052	760.52	−53.653	5.161	750.23	−54.668
6.051	771.76	−39.087	6.054	761.81	−41.574	6.084	751.50	−43.604
7.091	772.94	−30.111	6.999	763.00	−33.245	7.064	752.83	−34.966
8.085	774.09	−23.540	8.063	764.29	−26.112	8.085	754.17	−28.136
9.086	775.22	−18.308	9.055	765.50	−20.927	9.097	755.48	−22.864
10.047	776.28	−14.331	10.011	766.65	−16.934	10.032	756.67	−18.961
11.087	777.42	−11.006	11.022	767.82	−13.588	10.982	757.87	−15.753
12.105	778.52	−8.514	12.072	769.03	−10.881	12.103	759.25	−12.749
13.053	779.52	−6.694	13.058	770.15	−8.886	13.042	760.40	−10.757
14.057	780.59	−5.208	14.085	771.30	−7.227	14.055	761.61	−9.013
15.020	781.56	−4.158	15.009	772.31	−6.021	15.123	762.88	−7.524
16.093	782.69	−3.327	16.111	773.52	−4.882	16.050	763.93	−6.456
17.034	783.61	−2.793	17.026	774.50	−4.140	17.057	765.10	−5.497
18.038	784.60	−2.357	18.024	775.56	−3.499	18.123	766.29	−4.662
19.104	785.66	−1.998	19.040	776.61	−2.983	19.037	767.31	−4.073
20.091	786.63	−1.729	20.075	777.68	−2.561	20.103	768.50	−3.505
21.116	787.60	−1.495	21.070	778.69	−2.228	21.071	769.55	−3.075
22.050	788.48	−1.314	22.082	779.72	−1.947	22.057	770.60	−2.706
23.007	789.40	−1.155	23.038	780.67	−1.719	23.023	771.62	−2.397
24.103	790.43	−0.994	24.071	781.71	−1.509	24.081	772.73	−2.108
25.268	791.56	−0.851	25.212	782.85	−1.309	25.402	774.12	−1.804

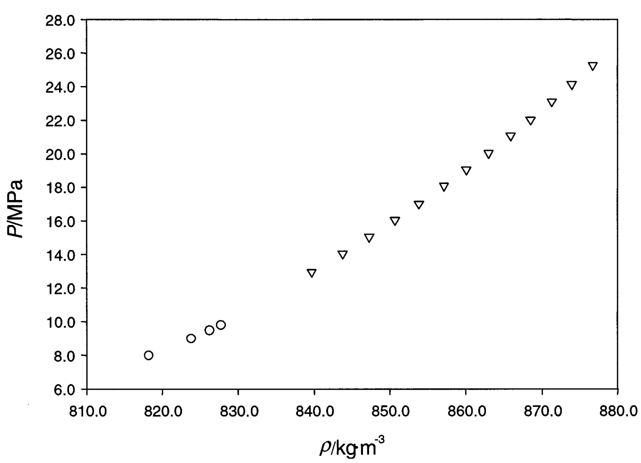

Figure 1. Liquid densities of carbon dioxide (1) + 1-propanol (2) binary mixtures: ▽, this work at 313.15 K and $x_1 = 0.7031$; ○, Yaginuma et al.[14] at 313.15 K and $x_1 = 0.7$.

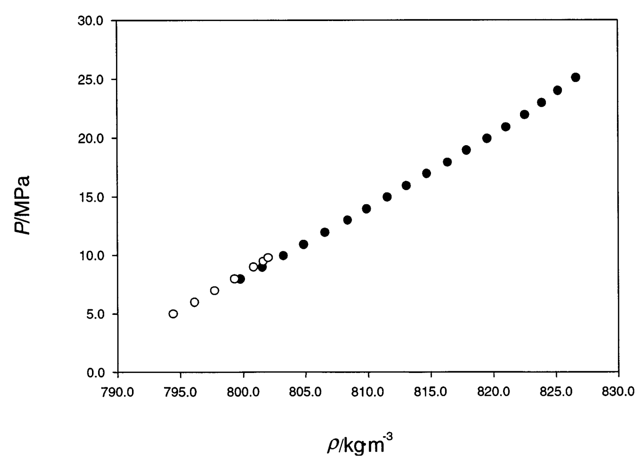

Figure 2. Liquid densities of CO_2 (1) + 2-propanol (2) binary mixtures: ●, this work at 313.16 K and $x_1 = 0.3042$; ○, Yaginuma et al.[15] at 313.15 K and $x_1 = 0.3$.

1-propanol and 2-propanol with experimental data reported by Yaginuma et al.[14,15] For CO_2 + 1-propanol and CO_2 + 2-propanol mixtures experimental liquid densities at different compositions at 313.15 K and pressures up to 9.8 MPa were published by the same authors.[14,15] However, for the CO_2 + 1-propanol system, temperature (313.15 K)

Table 3. Experimental Densities and Excess Volumes for the CO_2 (1) + 1-Propanol (2) Mixture at Six Temperatures and x_1 = 0.3121

P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}
	T/K = 313.15			T/K = 323.08			T/K = 332.98	
8.080	822.68	−32.263	7.957	808.97	−46.701	8.509	792.51	−46.598
8.946	824.29	−11.529	8.945	811.19	−31.960	8.948	794.24	−40.913
9.948	826.10	−7.091	9.953	813.30	−20.080	9.958	797.78	−30.042
10.961	827.86	−5.684	10.991	815.36	−11.335	10.976	800.39	−21.709
11.955	829.52	−4.855	11.990	817.25	−8.089	12.008	802.75	−15.300
12.947	831.11	−4.268	12.984	819.05	−6.518	12.981	804.95	−11.246
13.926	832.68	−3.829	13.983	820.80	−5.524	13.962	807.11	−8.803
15.040	834.37	−3.428	14.962	822.45	−4.830	14.871	809.02	−7.362
15.946	835.75	−3.162	15.960	824.07	−4.286	15.995	811.28	−6.152
16.967	837.24	−2.905	16.925	825.61	−3.867	16.946	813.12	−5.409
17.912	838.77	−2.713	17.963	827.22	−3.495	17.895	814.86	−4.826
18.931	840.20	−2.520	18.979	828.77	−3.191	18.945	816.75	−4.310
19.929	841.57	−2.352	19.944	830.22	−2.943	19.921	818.41	−3.911
20.954	843.00	−2.203	20.929	831.66	−2.722	20.891	820.02	−3.577
21.937	844.38	−2.076	21.943	833.11	−2.521	21.864	821.58	−3.287
22.912	845.63	−1.957	22.836	834.43	−2.369	22.946	823.33	−3.012
23.958	846.97	−1.840	24.018	836.07	−2.184	23.949	824.91	−2.788
25.044	848.34	−1.731	25.109	837.58	−2.033	25.142	826.77	−2.558
	T/K = 342.94			T/K = 352.89			T/K = 362.80	
10.056	782.09	−36.258	9.947	762.08	−42.753			
10.934	784.60	−29.096	10.922	765.29	−34.543	10.941	748.44	−39.126
11.981	787.15	−22.436	11.930	768.47	−27.896	11.929	753.05	−32.538
12.955	789.31	−17.623	12.944	771.51	−22.663	12.936	755.94	−27.052
13.904	791.47	−13.995	13.909	774.24	−18.697	13.962	758.14	−22.528
14.925	793.77	−11.132	14.958	777.13	−15.265	14.963	760.93	−19.014
16.024	796.16	−8.987	15.967	779.79	−12.668	15.910	763.57	−16.288
16.949	798.13	−7.696	16.937	782.25	−10.717	16.978	766.43	−13.767
17.935	800.16	−6.654	17.956	784.73	−9.127	17.933	768.93	−11.927
18.919	802.14	−5.850	18.923	787.02	−7.947	18.934	771.49	−10.350
19.955	804.16	−5.175	19.991	789.46	−6.916	19.940	773.96	−9.053
20.959	806.05	−4.642	20.914	791.53	−6.197	20.934	776.34	−8.001
21.961	807.92	−4.201	21.976	793.82	−5.515	21.997	778.80	−7.072
22.826	809.50	−3.874	22.943	795.85	−4.998	22.904	780.84	−6.406
24.004	811.59	−3.492	23.974	797.98	−4.531	24.079	783.43	−5.682
25.114	813.55	−3.188	25.178	800.39	−4.071	25.180	785.73	−5.108

Table 4. Experimental Densities and Excess Volumes for the CO_2 (1) + 1-Propanol (2) Mixture at Six Temperatures and x_1 = 0.4086

P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}
	T/K = 313.15			T/K = 323.10			T/K = 332.99	
7.953	821.27	−44.681						
8.960	825.61	−14.126	9.228	807.43	−36.100			
9.916	829.52	−8.787	9.989	810.27	−24.839	10.460	792.60	−32.504
10.885	833.12	−7.090	10.954	813.71	−14.233	10.937	794.48	−27.734
11.977	836.87	−6.003	11.991	817.16	−9.805	11.945	798.09	−19.484
12.848	839.78	−5.417	12.996	820.33	−7.810	12.952	801.44	−13.915
13.950	843.16	−4.857	13.956	823.20	−6.626	13.963	804.64	−10.636
14.941	846.01	−4.467	14.933	826.04	−5.780	15.041	808.04	−8.529
15.888	848.40	−4.148	15.954	828.86	−5.116	15.946	810.49	−7.305
16.994	851.13	−3.843	16.957	831.53	−4.607	16.937	813.24	−6.322
17.910	853.28	−3.626	17.973	834.13	−4.191	17.967	815.98	−5.540
18.937	855.57	−3.413	18.938	836.51	−3.861	18.930	818.48	−4.961
19.962	857.74	−3.225	19.902	838.80	−3.580	20.048	821.23	−4.411
20.938	859.77	−3.069	20.949	841.14	−3.314	20.971	823.47	−4.037
21.922	861.76	−2.928	22.016	843.45	−3.078	21.943	825.75	−3.697
22.953	863.79	−2.795	22.849	845.17	−2.912	22.832	827.79	−3.429
23.986	865.76	−2.676	23.995	847.50	−2.712	24.026	830.46	−3.116
25.077	867.82	−2.564	25.088	849.67	−2.544	25.155	833.01	−2.870
	T/K = 342.94			T/K = 352.89			T/K = 362.79	
			10.449	752.35	−49.061			
10.458	772.98	−41.664	10.934	754.66	−44.081			
10.948	775.04	−36.759	11.991	759.27	−35.096			
12.010	779.26	−28.065	13.002	763.46	−28.411			
13.042	783.02	−21.572	13.954	767.11	−23.388			
13.923	786.03	−17.283	14.975	770.89	−19.078	13.955	746.67	−28.459
14.922	789.31	−13.681	15.895	774.00	−15.974	14.894	750.60	−24.192
15.956	792.53	−11.055	16.966	777.54	−13.166	15.953	754.77	−20.247
16.956	795.50	−9.246	17.948	780.60	−11.182	16.959	758.51	−17.195
17.948	798.33	−7.913	18.930	783.57	−9.628	17.963	762.11	−14.713
18.965	801.12	−6.862	19.931	786.47	−8.371	18.916	765.35	−12.779
19.962	803.77	−6.046	19.917	786.42	−8.386	19.928	768.64	−11.097
20.954	806.31	−5.385	20.907	789.19	−7.380	20.977	771.92	−9.675
21.928	808.73	−4.844	21.922	791.92	−6.532	21.966	774.88	−8.568
22.911	811.12	−4.383	22.889	794.46	−5.858	22.960	777.78	−7.637
23.968	813.59	−3.958	23.963	797.18	−5.226	23.963	780.59	−6.841
25.097	816.18	−3.571	25.160	800.12	−4.635	25.181	783.91	−6.029

Table 5. Experimental Densities and Excess Volumes for the CO_2 (1) + 1-Propanol (2) Mixture at Six Temperatures and x_1 = 0.7031

P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}
	T/K = 313.15			T/K = 323.11			T/K = 333.02	
			12.286	809.67	−13.158			
12.941	839.70	−6.504	13.064	813.39	−10.763			
14.039	843.81	−5.474	14.044	817.86	−8.730	14.680	793.82	−13.189
15.040	847.32	−4.732	15.041	822.13	−7.263	15.094	795.89	−12.014
16.042	850.71	−4.124	16.057	826.30	−6.137	16.093	800.77	−9.816
17.003	853.86	−3.632	17.053	830.14	−5.262	17.081	805.29	−8.214
18.071	857.18	−3.163	18.030	833.72	−4.557	18.084	809.66	−6.960
19.040	860.08	−2.793	19.019	837.23	−3.960	19.063	813.69	−5.978
20.035	863.00	−2.461	20.112	840.96	−3.402	20.088	817.70	−5.132
21.063	865.86	−2.152	21.091	844.15	−2.971	21.093	821.49	−4.439
22.016	868.50	−1.900	22.042	847.12	−2.600	22.081	825.04	−3.857
23.092	871.32	−1.639	23.063	850.19	−2.247	23.110	828.59	−3.331
24.121	873.96	−1.415	24.077	853.18	−1.936	24.062	831.77	−2.906
25.241	876.78	−1.195	25.206	856.41	−1.628	25.267	835.65	−2.436
	T/K = 342.95			T/K = 352.83			T/K = 362.80	
15.032	766.75	−20.211	15.345	737.86	−27.270			
16.082	773.01	−15.912	16.062	743.18	−23.537	15.970	709.90	−31.102
17.068	778.57	−13.043	17.153	750.65	−19.016	17.153	719.98	−25.400
18.069	783.72	−10.861	18.124	756.68	−15.927	18.135	727.46	−21.587
19.129	788.82	−9.092	19.007	761.91	−13.706	19.139	734.45	−18.397
20.031	793.01	−7.895	20.111	767.84	−11.485	20.116	740.89	−15.870
21.038	797.44	−6.795	21.106	772.92	−9.889	21.117	746.79	−13.716
22.108	801.82	−5.820	22.078	777.57	−8.600	22.070	752.20	−12.019
23.063	805.59	−5.088	23.108	782.28	−7.458	23.090	757.57	−10.486
24.060	809.41	−4.431	24.185	786.94	−6.452	24.178	762.94	−9.111
25.262	813.77	−3.748	25.264	791.35	−5.593	25.351	768.40	−7.861

Table 6. Experimental Densities and Excess Volumes for the CO_2 (1) + 2-Propanol (2) Mixture at Six Temperatures and x_1 = 0.1939'

P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}	P/MPa	ρ/ kg·m^{-3}	v^E/cm^3·mol^{-1}
	T/K = 313.13			T/K = 323.11			T/K = 333.00	
6.007	787.09	−48.479	11.669	783.70	−28.346			
7.055	788.39	−32.917	7.799	778.22	−30.372	8.067	767.13	−32.693
8.039	789.59	−20.077	8.767	779.47	−21.067	9.051	768.51	−24.317
9.029	790.77	−6.077	9.761	780.75	−13.374	10.022	769.86	−17.879
10.059	792.00	−3.759	10.777	782.02	−7.656	11.041	771.24	−12.729
11.041	793.15	−2.946	11.755	783.23	−4.906	12.093	772.65	−8.720
12.035	794.28	−2.431	12.790	784.48	−3.641	13.058	773.90	−6.281
13.051	795.41	−2.052	13.799	785.71	−2.919	14.021	775.13	−4.805
14.032	796.52	−1.771	14.778	786.84	−2.434	15.025	776.39	−3.823
15.021	797.60	−1.540	15.779	787.99	−2.060	16.082	777.72	−3.113
16.023	798.67	−1.344	16.813	789.18	−1.755	17.034	778.87	−2.635
17.048	799.76	−1.174	17.835	790.31	−1.505	18.062	780.11	−2.230
18.007	800.76	−1.035	18.848	791.42	−1.298	19.091	781.32	−1.903
19.040	801.82	−0.904	19.782	792.44	−1.133	20.028	782.41	−1.653
20.007	802.81	−0.794	20.819	793.57	−0.974	21.057	783.60	−1.419
21.010	803.82	−0.692	21.838	794.67	−0.837	22.037	784.71	−1.227
22.026	804.84	−0.599	22.811	795.69	−0.719	23.084	785.91	−1.050
23.004	805.83	−0.520	23.859	796.78	−0.606	24.063	787.01	−0.904
24.043	806.85	−0.441	24.948	797.94	−0.503	25.307	788.40	−0.740
	T/K = 342.96			T/K = 352.90			T/K = 362.80	
6.086	751.91	−60.813						
7.138	753.59	−46.644	6.931	740.65	−52.842			
8.053	755.03	−37.121	8.108	742.70	−40.336	8.151	729.68	−43.246
9.087	756.61	−28.551	9.057	744.29	−32.552	9.086	731.43	−35.614
10.022	758.02	−22.433	10.051	745.92	−26.045	10.115	733.29	−28.906
11.040	759.52	−17.258	11.006	747.45	−21.078	11.079	734.99	−23.883
12.059	760.99	−13.278	12.068	749.14	−16.763	12.143	736.79	−19.474
13.082	762.44	−10.183	13.036	750.63	−13.676	13.071	738.38	−16.406
14.047	763.76	−7.943	14.032	752.13	−11.131	14.045	739.99	−13.783
15.053	765.13	−6.231	15.034	753.61	−9.075	15.060	741.63	−11.550
16.095	766.52	−4.974	16.133	755.20	−7.309	16.113	743.30	−9.662
17.060	767.79	−4.126	17.072	756.54	−6.132	17.023	744.70	−8.310
18.072	769.10	−3.452	18.050	757.89	−5.162	18.087	746.31	−7.005
19.085	770.39	−2.926	19.092	759.33	−4.351	19.047	747.74	−6.042
20.082	771.65	−2.509	20.104	760.70	−3.721	20.079	749.23	−5.187
21.105	772.90	−2.154	21.032	761.93	−3.246	21.108	750.73	−4.487
22.021	774.02	−1.885	22.016	763.22	−2.823	22.071	752.08	−3.935
23.047	775.26	−1.626	23.061	764.58	−2.445	23.031	753.42	−3.468
24.151	776.57	−1.386	24.113	765.92	−2.120	24.099	754.93	−3.029
25.224	777.84	−1.183	25.263	767.37	−1.817	25.279	756.49	−2.610

Table 7. Experimental Densities and Excess Volumes for the CO_2 (1) + 2-Propanol (2) Mixture at Six Temperatures and $x_1 = 0.3042$'

P /MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}	P/MPa	ρ/kg·m^{-3}	v^E/cm^3·mol^{-1}
	T/K = 313.16			T/K = 323.09			T/K = 332.99	
7.972	799.75	−32.971	7.953	787.00	−45.027	8.398	770.71	−46.358
8.989	801.52	−10.143	8.942	789.23	−30.629	8.956	772.40	−39.193
9.979	803.22	−6.251	9.927	791.34	−19.296	9.916	775.24	−29.040
10.942	804.85	−4.954	11.017	793.54	−10.377	10.943	778.14	−20.788
11.972	806.56	−4.116	11.945	795.35	−7.434	11.968	780.87	−14.557
13.006	808.37	−3.540	12.987	797.31	−5.811	13.017	783.54	−10.317
13.975	809.89	−3.120	13.917	799.02	−4.908	13.942	785.78	−8.101
14.964	811.56	−2.787	14.963	800.86	−4.183	14.931	788.02	−6.600
15.936	813.07	−2.510	15.952	802.56	−3.667	15.980	790.28	−5.523
16.975	814.69	−2.264	16.920	804.21	−3.265	16.964	792.29	−4.785
17.928	816.35	−2.088	17.979	805.97	−2.905	17.913	794.13	−4.229
18.943	817.85	−1.907	18.946	807.53	−2.631	18.992	796.18	−3.726
19.921	819.48	−1.771	19.938	809.12	−2.391	19.902	797.82	−3.373
20.919	821.01	−1.640	20.948	810.69	−2.178	20.967	799.73	−3.029
21.973	822.50	−1.510	21.890	812.20	−2.009	21.938	801.42	−2.761
22.975	823.87	−1.398	22.934	813.96	−1.854	22.912	803.08	−2.528
23.990	825.17	−1.289	23.966	815.65	−1.718	23.977	804.85	−2.305
25.115	826.61	−1.181	25.125	817.39	−1.574	25.126	806.75	−2.099
	T/K = 342.95			T/K = 352.91			T/K = 362.79	
8.831	752.34	−47.137	8.931	735.67	−51.523			
9.958	756.53	−35.303	9.897	738.71	−41.398	9.785	715.78	−46.637
10.947	759.76	−27.397	10.943	741.86	−32.762	10.907	720.62	−37.196
12.001	763.06	−20.960	11.955	745.09	−26.306	11.981	724.95	−30.184
12.973	765.94	−16.372	12.938	748.13	−21.393	12.952	728.64	−25.171
13.928	768.64	−12.887	13.931	751.22	−17.453	13.921	732.11	−21.141
14.899	771.30	−10.281	14.973	754.26	−14.163	14.958	735.66	−17.651
15.952	774.06	−8.290	15.911	756.91	−11.821	15.926	738.80	−14.989
16.963	776.60	−6.938	16.973	759.79	−9.756	16.983	742.08	−12.613
17.912	778.91	−5.994	17.956	762.37	−8.289	17.924	744.88	−10.885
18.955	781.35	−5.195	18.959	764.91	−7.119	18.953	747.85	−9.343
19.954	783.61	−4.592	19.958	767.37	−6.198	19.997	750.74	−8.077
20.939	785.74	−4.108	20.976	769.80	−5.445	20.944	753.27	−7.136
21.929	787.87	−3.706	21.947	772.05	−4.856	21.985	755.96	−6.280
22.937	789.88	−3.353	22.928	774.25	−4.356	22.927	758.32	−5.633
23.984	791.95	−3.043	23.955	776.52	−3.918	24.029	761.02	−4.997
25.159	794.21	−2.747	25.141	779.06	−3.490	25.161	763.69	−4.450

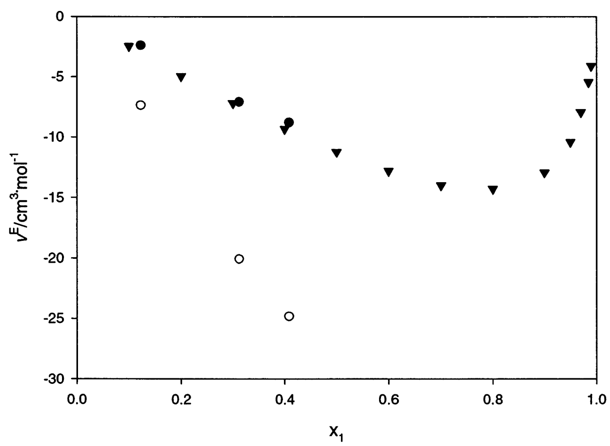

Figure 3. Excess molar volumes v^E for the CO_2 (1) + 1-propanol (2) system: ●, this work at ~313 K and ~10 MPa; ○, this work at ~323 K and ~10.0 MPa; ▼, Yaginuma et al.[14] at 313.15 K and 9.8 MPa.

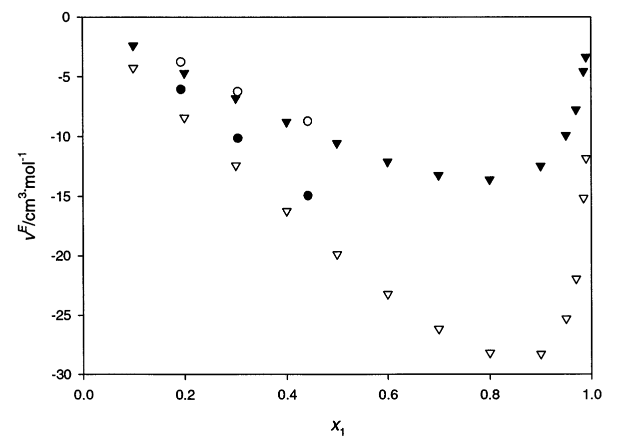

Figure 4. Excess molar volumes v^E for the CO_2 (1) + 2-propanol (2) system at ~313 K: ○, this work at ~10 MPa; ●, this work at ~9 MPa; ▼, Yaginuma et al.[15] at 9.8 MPa; ∇, Yaginuma et al.[15] at 9.0 MPa.

and composition ($x_1 = 0.7$) are similar or slightly different, respectively, to the data reported in this work (313.15 K and $x_1 = 0.7031$) whereas the pressure is lower, as can be seen in Figure 1. In Figure 2, the liquid densities for the CO_2 (1) + 2-propanol (2) binary mixture at 313.16 K and $x_1 = 0.3042$ reported in this work are compared with the data of Yaginuma et al.[15] at 313.15 K and $x_1 = 0.3$. Neglecting the excess contribution to the liquid density (ideal mixture, $v^E = 0$), the composition difference leads to 0.6 kg/m^3 lower densities of our data compared to the data of Yaginuma, which corresponds well with the difference of the data shown in Figure 2. The contribution of the excess volume (ca. −6.251 cm^3/mol at $x_1 = 0.3042$ and $P = 9.979$ MPa) is very small compared to the ideal change of density with composition. This means also that the calculation of excess volumes is a very sensitive criterion for the quality of the experimental density data.

The excess volumes for the mixtures were calculated by the following equation:

$$v^E = v^{mix} - (x_1 v_1 + x_2 v_2) \qquad (1)$$

where v_1 and v_2 are the pure component molar volumes and x_1 and x_2 are the mole fractions of carbon dioxide (1)

Table 8. Experimental Densities and Excess Volumes for the CO_2 (1) + 2-Propanol (2) Mixture at Six Temperatures and $x_1 = 0.4425$'

P/MPa	ρ/kg·m^{-3}	v^E/ cm^3·mol^{-1}	P/MPa	ρ/ kg·m^{-3}	v^E/ cm^3·mol^{-1}	P/MPa	ρ/ kg·m^{-3}	v^E/ cm^3·mol^{-1}
	T/K = 313.16			T/K = 323.10			T/K = 333.01	
7.326	799.35	−65.992						
7.934	802.55	−48.238						
8.943	807.47	−14.973	9.130	782.95	−39.654	8.958	756.38	−54.991
9.969	811.99	−8.721	9.954	787.06	−26.342	9.956	762.18	−39.920
11.005	816.26	−6.881	10.880	791.35	−14.981	10.969	767.56	−28.344
11.999	820.04	−5.861	11.995	796.16	−9.674	11.949	772.43	−19.805
12.934	823.38	−5.195	12.976	800.19	−7.627	12.951	776.94	−13.900
14.122	827.14	−4.560	13.916	803.78	−6.411	13.945	781.17	−10.467
14.976	829.60	−4.196	14.997	807.65	−5.447	14.916	785.11	−8.412
15.998	832.39	−3.834	15.986	811.11	−4.809	15.948	789.03	−6.951
17.117	834.97	−3.483	16.957	814.32	−4.318	16.969	792.73	−5.921
17.922	836.92	−3.277	17.995	817.60	−3.896	17.945	796.09	−5.172
19.034	839.57	−3.032	18.965	820.57	−3.575	18.986	799.55	−4.548
19.960	841.69	−2.854	19.973	823.48	−3.291	19.910	802.53	−4.102
20.948	843.90	−2.686	20.957	826.25	−3.056	21.021	805.91	−3.654
21.977	846.13	−2.531	21.927	828.86	−2.854	21.952	808.67	−3.342
22.879	848.10	−2.413	22.910	831.40	−2.673	22.919	811.46	−3.064
24.052	850.49	−2.269	23.997	834.18	−2.502	23.900	814.21	−2.822
25.230	852.84	−2.140	25.120	836.85	−2.339	25.101	817.45	−2.564
	T/K = 342.96			T/K = 352.91			T/K = 362.80	
9.354	732.99	−57.815						
9.942	736.91	−49.527						
10.952	743.06	−37.937	10.906	715.67	−45.535	10.878	682.87	−51.049
11.983	748.81	−28.922	11.996	723.06	−35.735	11.953	695.04	−41.524
12.945	753.71	−22.393	12.993	729.17	−28.795	12.961	702.70	−34.248
13.981	758.66	−17.023	13.939	734.44	−23.526	13.925	709.16	−28.650
14.955	762.98	−13.369	14.960	739.79	−18.993	14.917	715.39	−23.974
15.958	767.22	−10.718	16.006	744.86	−15.356	15.949	721.21	−20.001
16.947	771.15	−8.857	16.924	749.02	−12.872	16.989	726.67	−16.749
17.919	774.87	−7.508	17.932	753.37	−10.755	17.962	731.50	−14.278
18.985	778.72	−6.385	18.923	757.46	−9.144	18.901	736.04	−12.336
19.968	782.12	−5.576	19.977	761.53	−7.801	20.063	740.99	−10.372
21.030	785.68	−4.877	20.950	765.15	−6.814	20.996	744.82	−9.105
22.041	788.90	−4.330	21.933	768.65	−5.998	21.971	748.67	−8.005
22.954	791.73	−3.916	22.909	772.04	−5.328	22.984	752.54	−7.057
23.985	794.81	−3.516	23.959	775.49	−4.720	24.028	756.34	−6.238
25.105	798.07	−3.148	25.133	779.22	−4.154	25.226	760.54	−5.457

and 1-propanol (or 2-propanol) (2), respectively. The pure component molar volumes of CO_2, 1-propanol, and 2-propanol were calculated with the EoS reported by Starling and Han[17] (BWRS) using the parameters given by Zúñiga-Moreno and Galicia-Luna.[9,10] The calculated values are given in Tables 2−8.

For the CO_2 + 1-propanol and CO_2 + 2-propanol mixtures large negative values are obtained for the excess volumes. A similar behavior was found for the system CO_2 + ethanol (Pöhler and Kiran[16] and Zuñiga-Moreno and Galicia-Luna[10]).

No experimental excess volumes for the binary mixtures presented in this work are available in the literature. But liquid densities for CO_2, 1-propanol, and 2-propanol and their mixtures are reported by Yaginuma et al.[14,15] at 313.15 K, so that excess volumes can be calculated from these PvT data in order to compare both sets of data. Both the temperature and the pressure have a strong influence on the excess volumes. The graphical comparison is shown in Figures 3 and 4. It can be seen that for both systems similar values of excess volumes are obtained. For CO_2 + 1-propanol (Figure 3), the strong temperature dependence is demonstrated. Increasing the temperature from 313 to 323 K leads to duplication of the excess volume values. In Figure 4, the pressure dependence for the system CO_2 + 2-propanol is represented. A decrease in pressure from 10 to 9 MPa also leads to significantly larger (almost duplicated in magnitude) excess volumes. The difference of the excess volume data of Yaginuma and of this work at 9 MPa in Figure 1 may be explained by the fact that the pressure is very close to the critical pressure for the mixture at the given temperature, and thus the pressure dependence of both the density and the excess volume is very large. The comparison of our results with values from the literature proves the reliability of the used experimental procedure for studying the PvT behavior of mixtures.

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