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Compressed Liquid Densities of Carbon Dioxide + Ethanol Mixtures at Four Compositions via a Vibrating Tube Densimeter up to 363 K and 25 MPa

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PvT properties in a single phase were determined for carbon dioxide + ethanol mixtures at four compositions from 313 to 363 K and up to 25 MPa with an uncertainty less than (± 0.04 kg·m^{-3}) using a vibrating tube densimeter. The classical calibration method of the vibrating tube densimeter was used with N_2 and H_2O as the reference fluids.

Introduction

PvT properties and vapor−liquid, vapor−liquid−liquid, and liquid−liquid equilibria of pure compounds and mixtures at high pressures are required in the development of supercritical fluid extraction processes.

For over 20 years the vibrating tube principle has been widely and successfully applied for the experimental study of *PvT* properties of various fluids. High precision and applicability of this method for liquid density measurements in a wide temperature/pressure range make it attractive for experimenters and even competitive compared with the classical *PvT* methods.

This research focused on a systematic study to get experimental vapor−liquid equilibria[1−4] and *PvT* data[5−7] of CO_2 + alcohol mixtures for knowledge, development, and application of techniques directed toward supercritical extraction processes. The main objective is to perform systematic studies of *PvT* and phase equilibria of CO_2 + alcohol binary mixtures containing from ethanol to decanol in order to select the best supercritical operating conditions focused on industrial applications such as extraction of carotenes from the *cempasuchil* flower of Mexico (*tagetes erecta*) and from the *Chile Poblano* of Mexico (*Capsicum annum*).

Galicia-Luna et al.[1,2] reported vapor−liquid equilibrium data of the CO_2 + ethanol system at temperatures from 313 to 373 K. Zúñiga-Moreno and Galicia-Luna[5,6] reported *PvT* data for ethanol and CO_2 from 313 to 363 K and for pressures up to 25 MPa. In this work are presented liquid densities of binary mixtures at four compositions from 313 to 363 K and at pressures up to 25 MPa. The excess volumes for these mixtures and their dependence on composition, temperature, and pressure are reported.

The reliability of the measurements for pure compounds has been checked by comparing the data calculated through the BRWS EoS fitted on data reported by Zúñiga-Moreno and Galicia-Luna[5,6] (ethanol,[5] 1-propanol,[6] 2-propanol,[6] and 1-pentanol[5]) with the data reported by several authors. The experimental results are in good agreement.

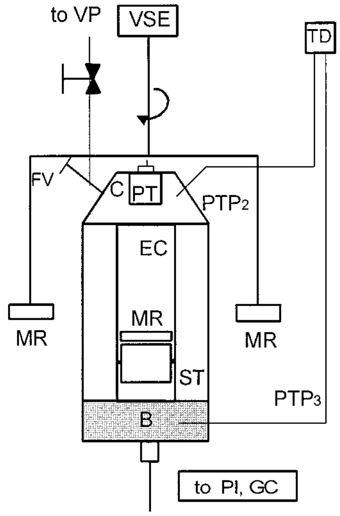

Figure 1. Feed cell: B and C, caps in titanium; EC, equilibrium cell; FV, feeding valve; GC, gas compressor; MR, magnetic rod; PI, Isco pump; PT, pressure transducer; PTP*i*, platinum probe *i*; ST, sapphire tube; TD, temperature digital indicator F250; VSE, variable speed engine; VP, vacuum pump.

Experimental Section

Apparatus and Procedure. The apparatus used in this work is that reported by Zúñiga-Moreno and Galicia-Luna.[6] This apparatus is designed to determine simultaneous VLE and *PvT* properties of pure and binary mixtures containing CO_2 and alcohols.

The measuring cell consists of a vibrating tube (Hastelloy C-276 U-tube) containing 1 cm^3 of sample. We use the same experimental procedure described by Galicia-Luna et al.[8] and Zúñiga-Moreno and Galicia-Luna.[6]

The pressure measurements are made directly in the equilibrium cell (see Figure 1) by means of a 25 MPa Sedeme pressure transducer. The pressure transducer is thermoregulated at a specific value and calibrated periodically to ensure the best precision (the gauge output is slightly temperature dependent and could be affected by some shift with time).

The experimental procedure consists of four steps: 1, sensor calibration; 2, cell loading; 3, setting up of the

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Table 1. Purity and Origin of Pure Compounds

compound	certified purity (%)	max. water content (%)	supplier
ethanol	99.8	0.02	Merck
CO_2	99.995		Air Products-Infra
water	99.95 (HPLC)		Fisher
nitrogen	99.995		Air Products-Infra

Table 2. Selected Data of Excess Molar Volumes V^E versus $x(CO_2)$, Mole Fraction of Carbon Dioxide, at Different Pressures of the CO_2 + Ethanol Mixtures (see Figure 5)

$x(CO_2)$	P/MPa	$V^{E\,a}$/cm^3·mol^{-1}	$x(CO_2)$	P/MPa	$V^{E\,b}$/cm^3 mol^{-1}
		This Work			
10.945	0.2317	−8.7079	10.945	0.2317	−9.3421
11.939	0.4076	−13.1307	11.099	0.4076	−14.1492
10.959	0.5569	−15.4711	10.959	0.5569	−16.9666
11.000	0.7703	−18.5684	11.000	0.7703	−20.5978
		Pholer and Kiran[13]			
			11.050	0.9000	−17.01
			11.000	0.8000	−20.00
			11.000	0.7000	−22.50
			11.000	0.5000	−18.17

[a] Calculated excess molar volumes using the BWRS EoS[12] for CO_2 and ethanol. [b] Calculated excess molar volumes using the BWRS EoS[12] for ethanol and the MBWRS EoS[11] for CO_2.

experimental conditions; and 4, measurements at equilibrium. A detailed procedure regarding the calibrations of the platinum temperature probes and the pressure transducer is given in previous papers by Galicia-Luna et al.[1,6]

Both platinum probes (Specitec, France) connected to a digital indicator (Automatic Systems, USA, model F250) were calibrated as described in detail by Zúñiga-Moreno and Galicia-Luna.[7] The resulting uncertainty is estimated to be less than ±0.03 K. The 25 MPa Sedeme pressure transducer connected to a 6 1/2 digital multimeter (HP-34401A, USA) gives pressures with uncertainties within ±0.008 MPa.

Loading of the Feed Cell. A pure liquid, such as water, is first degassed and then distilled under vacuum into the evacuated feed cell.

Loading is more complex for a binary mixture. First the degassed, less volatile component is transferred by low-pressure distillation into the weighed (empty) feed cell. Then a new weighing of the feed cell is performed to determine the exact amount introduced. Afterward, if it is a liquid, the second component is transferred in the same manner into the feed cell. If it is a gas, at feed conditions, it is introduced into the feed cell under pressure. A third weighing yields the mass of the second component and therefore the mixture composition.

Weighing is carried out within 10^{-7} kg (maximum contents of the feed cell, 12 cm^3; mass of the empty cell, ≅1 kg). A Sartorius (Sartorius, Germany) comparator balance was used (model MCA1200; accuracy, ±10^{-7} kg); it is calibrated with a mass of 1 kg class E1 (Sartorius, Germany).

Measurements performed with water and nitrogen are used to calibrate the vibrating tube following the classical method procedure. Reference density values of H_2O and

Table 3. Densities and Excess Molar Volumes for the Carbon Dioxide (1) + Ethanol (2) Mixture at Six Temperatures and x_1 = 0.2317

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 = 312.95 K			T = 322.91 K			T = 332.79 K	
9.968	815.33	−5.4970	7.963	799.42	−35.6948	7.927	784.85	−42.1712
10.938	816.71	−4.2472	8.956	801.31	−24.9601	8.917	786.95	−32.3290
11.953	818.21	−3.5723	9.984	803.19	−15.2871	9.984	789.13	−23.6042
13.028	819.70	−3.1094	10.946	804.90	−9.3421	10.960	791.11	−17.0393
13.935	820.96	−2.8264	11.992	806.73	−6.4075	12.019	793.20	−11.7409
14.950	822.41	−2.5807	12.926	808.33	−5.1434	13.061	795.19	−8.5033
15.995	823.82	−2.3754	13.970	810.06	−4.3107	13.959	796.88	−6.8147
16.948	825.10	−2.2203	14.937	811.57	−3.7956	14.978	798.72	−5.5952
17.998	826.59	−2.0842	15.953	813.16	−3.4013	15.918	800.38	−4.8380
18.905	827.74	−1.9760	16.931	814.64	−3.1076	16.958	802.18	−4.2390
19.949	829.09	−1.8673	17.953	816.18	−2.8622	17.887	803.74	−3.8358
20.949	830.36	−1.7770	18.932	817.62	−2.6691	18.991	805.58	−3.4625
21.999	831.71	−1.6948	19.994	819.12	−2.4917	19.911	807.02	−3.2116
22.953	832.93	−1.6297	20.957	820.50	−2.3565	20.990	808.75	−2.9694
23.939	834.40	−1.5823	21.963	821.89	−2.2321	21.952	810.22	−2.7867
25.112	835.82	−1.5138	22.889	823.15	−2.1309	22.913	811.64	−2.6291
			24.016	824.65	−2.0223	24.044	813.33	−2.4706
			25.082	826.07	−1.9325	25.119	814.91	−2.3408
	T = 342.73 K			T = 352.67 K			T = 362.56 K	
7.936	767.75	−46.7830	8.929	754.25	−41.2488	9.868	739.13	−37.2463
8.947	770.58	−37.0257	9.916	757.13	−33.6036	10.920	742.63	−29.0469
9.955	773.25	−29.1914	10.923	759.91	−27.2394	12.020	745.83	−24.9037
10.963	775.72	−22.7541	12.014	762.68	−21.6044	13.042	748.65	−20.5794
11.920	778.00	−17.7371	12.948	765.01	−17.6539	13.933	751.04	−17.4360
12.997	780.47	−13.3204	13.944	767.38	−14.2345	14.964	753.71	−14.4181
13.922	782.51	−10.5457	14.985	769.79	−11.4550	15.924	756.10	−12.1438
14.942	784.69	−8.3856	15.945	771.94	−9.5104	16.981	758.65	−10.1556
15.914	786.71	−6.9662	16.962	774.14	−7.9614	17.869	760.73	−8.8261
16.978	788.83	−5.8726	17.930	776.17	−6.8517	18.973	763.20	−7.5196
17.890	790.61	−5.1889	19.013	778.39	−5.9105	19.968	765.40	−6.5993
19.020	792.73	−4.5500	19.903	780.17	−5.3101	20.930	767.43	−5.8842
19.909	794.36	−4.1585	20.985	782.26	−4.7286	22.024	769.72	−5.2295
20.958	796.23	−3.7868	21.903	784.02	−4.3305	22.930	771.57	−4.7847
21.922	797.91	−3.5066	22.965	785.98	−3.9510	24.015	773.72	−4.3417
23.004	799.76	−3.2450	23.904	787.70	−3.6702	25.169	775.95	−3.9532
23.906	801.24	−3.0584	25.135	789.90	−3.3647			
25.062	803.14	−2.8564						

Table 4. Densities and Excess Molar Volumes for the Carbon Dioxide (1) + Ethanol (2) Mixture at Six Temperatures and $x_1 = 0.4076$

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 = 313.16 K			T = 323.11 K			T = 333.01 K	
7.995	818.40	−44.3915	10.012	803.10	−25.2875	9.945	776.16	−40.0295
8.977	822.64	−17.5797	11.099	807.58	−14.1492	10.976	781.43	−28.0018
9.984	826.71	−8.8111	11.939	810.93	−10.2222	11.967	786.10	−19.3406
10.996	830.56	−6.6161	12.980	814.78	−7.7748	12.974	790.58	−13.7152
12.002	834.17	−5.5443	13.930	818.16	−6.5068	13.936	794.60	−10.4991
12.942	837.32	−4.9072	14.966	821.63	−5.6028	14.969	798.66	−8.3859
13.973	840.61	−4.4157	15.958	824.81	−4.9916	15.930	802.32	−7.1019
14.925	843.44	−4.0708	16.917	827.80	−4.5478	16.939	805.92	−6.1535
16.000	846.38	−3.7590	17.939	830.86	−4.1774	17.987	809.57	−5.4395
16.933	848.75	−3.5347	18.955	833.77	−3.8822	18.911	812.66	−4.9578
17.974	851.31	−3.3260	20.022	836.71	−3.6284	19.999	816.14	−4.5090
18.883	853.46	−3.1724	20.923	839.10	−3.4487	20.915	818.96	−4.2041
19.966	855.89	−3.0106	21.942	841.78	−3.2771	21.960	822.06	−3.9171
20.937	858.04	−2.8870	22.974	844.36	−3.1256	22.994	825.05	−3.6820
21.920	860.10	−2.7739	23.937	846.77	−3.0056	23.991	827.83	−3.4885
23.031	862.42	−2.6637	25.115	849.55	−2.8767	25.125	830.95	−3.3053
23.936	864.28	−2.5848						
25.084	866.57	−2.4947						
	T = 342.95 K			T = 352.90 K			T = 362.79 K	
11.928	754.02	−28.3867	12.390	732.52	−31.9373	12.924	708.50	−33.3956
12.940	759.95	−21.2617	12.954	736.16	−28.0624	13.938	716.40	−27.4081
13.881	765.04	−16.3537	13.960	742.22	−22.2370	14.911	722.77	−22.6424
14.911	770.22	−12.6261	14.969	747.89	−17.6889	15.937	729.04	−18.5912
15.894	774.82	−10.1776	16.005	753.36	−14.1906	16.919	734.51	−15.4996
17.005	779.83	−8.3035	16.970	758.03	−11.7648	17.972	739.85	−12.9041
17.875	783.53	−7.2523	17.999	762.69	−9.8358	18.923	744.55	−11.0835
18.973	787.96	−6.2623	19.007	767.12	−8.4285	20.082	749.77	−9.3475
19.920	791.59	−5.6144	20.055	771.50	−7.3165	20.970	753.67	−8.3114
20.978	795.52	−5.0495	20.900	774.79	−6.6010	22.060	758.18	−7.2841
21.916	798.82	−4.6484	21.942	778.67	−5.8891	22.864	761.38	−6.6650
22.976	802.42	−4.2770	22.874	782.08	−5.3786	24.021	765.78	−5.9278
23.999	805.86	−3.9897	24.009	786.04	−4.8672	25.098	769.73	−5.3750
25.204	809.69	−3.7059	25.098	789.71	−4.4698			

N_2 are obtained from the equations of state (EoS's) of Harr et al.[9] and Span et al.,[10] respectively.

The square of the vibration period, $\tau^2(P,T)$, of the U-tube is represented in the classical method, as a first approximation, by eq 1, where $\rho_i(P,T)$ is the density of the fluid i:

$$\rho_F(P,T) = \rho_{H_2O}(P,T) + \frac{1}{A}(P,\ T)[{\tau_F}^2(P,T) - {\tau_{H_2O}}^2(P,T)] \tag{1}$$

with

$$\frac{1}{A} = \frac{\rho_{H_2O} - \rho_{N_2}}{{\tau_{H_2O}}^2 - {\tau_{N_2}}^2} \tag{2}$$

Taking into account all uncertainties and the dispersions on vibrating periods, a cumulative uncertainty has been estimated to be ±0.05% for the densities in the liquid region.

Results

The purity and origin of chemicals used in this work are given in Table 1. Chemicals were used without any purification except for a careful degassing of water and ethanol. The main objectives of the determinations of the densities of pure compounds were to test the capabilities and limitations of this apparatus and confirm its capability to determine densities with an accuracy better than 0.04 kg·m^{-3}. For mixtures the liquid densities have the same accuracy, with the same equations (eqs 1 and 2) being used.

The densities of the CO_2 + ethanol liquid system at each composition have been determined at six temperatures from 313 to 363 K (see Tables 2−7). The excess volumes for these mixtures and their variation with composition, temperature, and pressure are reported in these tables. The data for CO_2 reported by Zúñiga-Moreno and Galicia-Luna[6] are correlated in the whole reported range of pressures and temperatures using the BWRS equation of state.[11] The detailed description of the method used here is presented by Zúñiga-Moreno and Galicia-Luna.[7] For ethanol data are taken the BWRS parameters reported by Zúñiga-Moreno and Galicia-Luna[7] (see Table 7).

Density data in the liquid region were correlated using a least-squares optimization procedure with the following objective function:

$$S = \sum_i \left[\frac{(\rho_{i,\mathrm{exp}} - \rho_{i,\mathrm{cal}})}{\rho_{i,\mathrm{exp}}}\right]^2 \tag{3}$$

The adjusted parameters for the BWRS EoS are reported in Table 7. The units for pressure, temperature, and density are bar, kelvin, and cubic centimeter per mole.

Previous papers[5,7] had as a main focus the elimination of experimental determinations of the vibrating period of N_2 without lost precision in measurements. In this paper the vibrating period of the tube under vacuum is used as a reference point and H_2O is used as a reference fluid. The density ρ_F is given by

$$\rho_F(P,T) = \rho_{H_2O}(P,T)\left(\frac{{\tau_F}^2(P,T) - {\tau_{\mathrm{vac}}}^2(T)}{{\tau_{H_2O}}^2(P,T) - {\tau_{\mathrm{vac}}}^2(T)}\right) \tag{4}$$

The vibrating period of the tube under vacuum was measured at all reported measurement temperatures. The corresponding results were correlated as a function of

Table 5. Densities and Excess Molar Volumes for the Carbon Dioxide (1) + Ethanol (2) Mixture at Six Temperatures and x_1= 0.5569

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 = 313.16 K			T = 323.10 K			T = 333.00 K	
8.326	787.05	−44.9931	9.189	743.74	−47.5606	10.425	673.55	−37.2347
8.898	793.08	−23.2671	9.979	756.00	−30.8967	10.919	711.42	−33.0105
9.940	802.75	−9.4960	10.959	768.21	−16.9666	11.927	728.88	−21.8319
10.930	811.03	−6.6710	11.958	778.51	−10.6260	12.983	742.84	−14.4143
11.997	819.02	−5.3056	12.928	787.29	−7.8191	13.912	753.25	−10.6417
12.916	825.42	−4.6233	13.999	795.85	−6.1587	14.947	763.35	−8.1337
13.925	831.74	−4.1115	14.916	802.61	−5.2913	15.904	771.74	−6.6878
14.962	837.81	−3.7431	15.933	809.44	−4.6219	16.913	779.80	−5.6651
15.896	842.99	−3.5009	16.899	815.50	−4.1734	17.930	787.09	−4.9338
17.053	848.86	−3.2648	17.934	821.50	−3.8102	18.902	793.63	−4.4266
17.921	853.13	−3.1302	18.894	826.83	−3.5563	20.003	800.53	−3.9946
18.910	857.68	−3.0017	19.981	832.38	−3.3213	20.934	806.05	−3.7146
19.857	861.87	−2.9028	20.897	836.93	−3.1709	21.956	811.69	−3.4640
20.929	866.42	−2.8121	21.933	841.71	−3.0225	22.914	816.78	−3.2797
21.900	870.35	−2.7438	22.903	846.12	−2.9162	23.982	822.05	−3.1046
22.928	874.43	−2.6864	23.972	850.62	−2.8109	25.170	827.79	−2.9586
23.939	878.22	−2.6369	25.046	855.08	−2.7293			
25.061	882.26	−2.5905						
	T = 342.94 K			T = 352.89 K			T = 362.78 K	
11.513	615.56	−30.5690	12.917	619.94	−27.7217	14.013	602.84	−25.8713
11.906	659.59	−30.6649	13.913	642.24	−21.6117	14.951	622.61	−21.3388
12.919	680.85	−22.3535	14.939	662.62	−16.7797	15.878	640.32	−17.6887
13.934	698.56	−16.2948	15.953	681.04	−13.3153	16.953	657.48	−14.2334
14.972	712.97	−12.0346	16.907	694.70	−10.8119	17.969	671.47	−11.6968
15.909	724.57	−9.4969	17.926	706.76	−8.7870	18.933	683.15	−9.8156
16.964	735.95	−7.5577	18.889	717.11	−7.3989	19.998	694.89	−8.2352
17.969	746.02	−6.3297	19.890	727.28	−6.3603	20.943	704.14	−7.1293
18.915	754.44	−5.4904	20.933	736.68	−5.5302	21.964	713.45	−6.2034
19.909	762.55	−4.8343	21.889	744.05	−4.9029	22.952	721.81	−5.5021
20.948	770.13	−4.3048	22.983	752.43	−4.3860	23.969	729.64	−4.9120
21.921	776.93	−3.9367	23.966	759.39	−4.0181	25.132	738.13	−4.3880
22.938	783.47	−3.6239	25.089	766.69	−3.6736			
23.974	789.90	−3.3852						
25.064	796.30	−3.1861						

Table 6. Densities and Excess Molar Volumes for the Carbon Dioxide (1) + Ethanol (2) Mixture at Two Temperatures and x_1 = 0.7703

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 = 313.16 K			T = 323.12 K	
11.033	797.49	−7.2089	11.000	735.72	−20.5978
12.000	806.31	−5.5240	12.000	751.30	−12.3188
13.000	815.04	−4.4956	14.001	775.83	−6.5808
14.001	822.80	−3.7907	16.000	794.88	−4.4794
16.000	836.92	−2.9126	18.000	810.88	−3.4085
18.000	849.25	−2.3771	20.000	824.49	−2.7476
20.000	860.16	−2.0122	22.000	836.35	−2.2940
22.004	870.16	−1.7562			
24.000	879.50	−1.5788			

Table 7. BWRS EoS Adjusted Parameters for Carbon Dioxide and Ethanol Pure Compounds

parameter	CO$_2$	ethanol
B_0	$1.585\,379\,4 \times 10^{2}$	$3.749\,651\,8 \times 10^{2}$
A_0	$9.568\,502\,3 \times 10^{6}$	$2.143\,685\,1 \times 10^{7}$
C_0	$-9.865\,927\,4 \times 10^{11}$	$-7.549\,718\,2 \times 10^{11}$
D_0	$-3.328\,431\,3 \times 10^{14}$	$-1.810\,587\,0 \times 10^{14}$
E_0	$-3.580\,283\,6 \times 10^{16}$	$-1.126\,914\,2 \times 10^{16}$
b	$2.933\,672\,2 \times 10^{3}$	$-8.817\,157\,5 \times 10^{1}$
a	$-1.997\,299\,2 \times 10^{5}$	$-5.841\,306\,3 \times 10^{6}$
d	$7.908\,083\,2 \times 10^{7}$	$5.717\,613\,1 \times 107$
c	$-5.296\,886\,7 \times 10^{12}$	$-3.207\,622\,8 \times 10^{12}$
α	$3.169\,048\,7 \times 10^{7}$	$-1.698\,839\,8 \times 10^{7}$
u	$5.738\,158\,6 \times 10^{4}$	$3.326\,626\,3 \times 10^{2}$

temperature using a simple polynomial function:

$$\tau_{\text{vac}}^{2}(T) = a + bT + cT^{2} \tag{5}$$

To check the stability of the vibrating period of the tube under vacuum over a period of time (eight months), it was measured at 313 K as reference before and after measurement campaigns of liquid densities of several alcohols, CO$_2$, and their mixtures from 313 to 363 K and at pressures up to 25 MPa. After this, it was found that the periods could fluctuate within $\pm 5 \times 10^{-6}$ ms for the tube under vacuum and pure fluids and within $\pm 1 \times 10^{-5}$ ms for mixtures. It was found that the values issued from the nonclassical method overestimate the liquid densities, increasing two times the uncertainty in the full scale of the preceding results,[5] and the final uncertainty in this case is ±0.12% in densities. This is valid only in the range of densities reported in this work.

Pöhler and Kiran[13] have reported volumetric properties and excess volumes for CO$_2$ + ethanol mixtures at four compositions, temperatures from 323 to 423 K, and pressures up to 70 MPa with the following estimated uncertainties: ±0.5 K; ±0.03 MPa; ±1.2% for densities.

In Figure 2 are plotted the densities of ethanol at 320 K up to 200 MPa from ref 14, those at 322.70 K up to 25 MPa from ref 5, and the data reported at 323.0 K by Pöhler and Kiran.[13] Zúñiga-Moreno and Galicia-Luna[5] found good agreement for all isotherms between their data and those published by Takiguchi and Uematsu;[14] the maximum relative deviation in densities is ±0.2%. In Figure 3 are presented the liquid densities of binary mixtures of carbon dioxide (1) and ethanol (2), reported in this work, at 323.12 K and x_1 = 0.7703, and those published by Pöhler and Kiran,[17] at 323.0 and x_1 = 0.8. The two sets of data agree well.

As shown in Figure 4, binary mixtures of CO$_2$ + ethanol are more compressible than pure ethanol. Similar trends were found with those reported by Pöhler and Kiran;[13] that is, the density of the mixture becomes more than that of

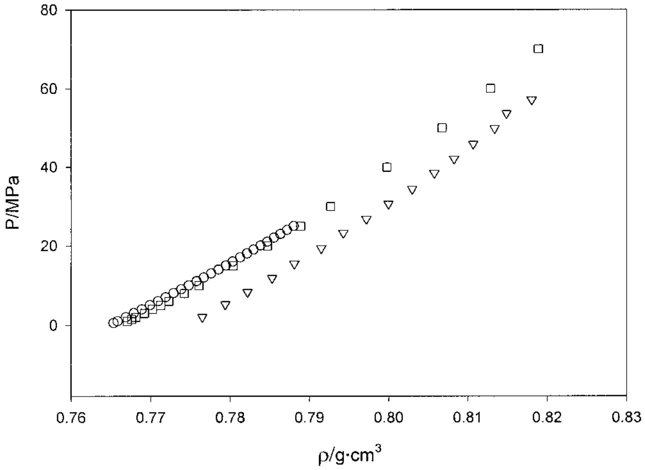

Figure 2. Liquid densities for ethanol: ○, Zuñiga-Moreno and Galicia-Luna,[5] at 322.70 K; ▽, Pöhler and Kiran,[13] at 323.0 K; □, Takiguchi and Uematsu,[14] at 320.00 K.

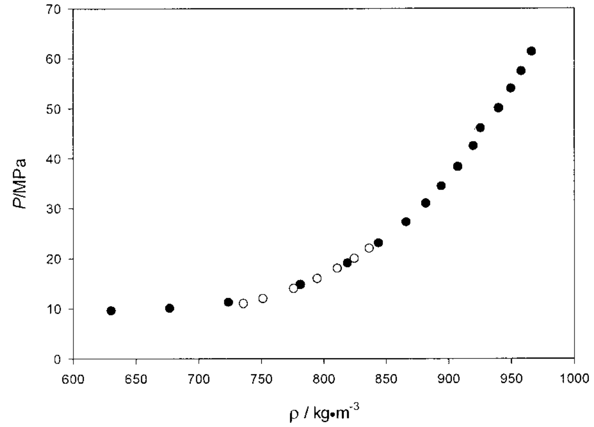

Figure 3. Liquid densities of the binary mixtures of carbon dioxide (1) and ethanol (2) at 323 K: ○, this work, at 323.12 K and $x_1 = 0.7703$; ●, Pöhler and Kiran,[13] at 323.0 and $x_1 = 0.8$.

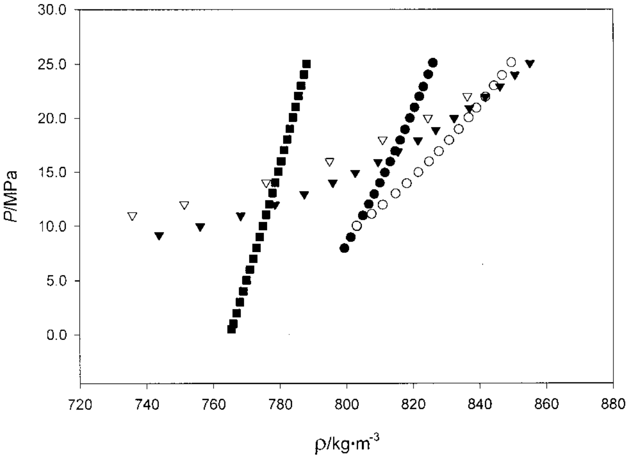

Figure 4. Pressure dependence of density for the binary mixtures of carbon dioxide (1) and ethanol (2) at 323 K (see Tables 4–7): literature data for pure ethanol at 323 K are from Zuñiga-Moreno and Galicia-Luna;[5] ●, $x_1 = 0.2317$; ○, $x_1 = 0.4076$; ▼, $x_1 = 0.5569$; ▽, $x_1 = 0.7703$; ■, $x_1 = 0.0$.

pure ethanol, and each mixture shows a density crossover at a typical pressure.

The temperatures were selected taking into account the industrial applications of CO_2, and of binary mixtures containing CO_2 and alcohols, as a supercritical fluid for extracting components of natural products of Mexico.

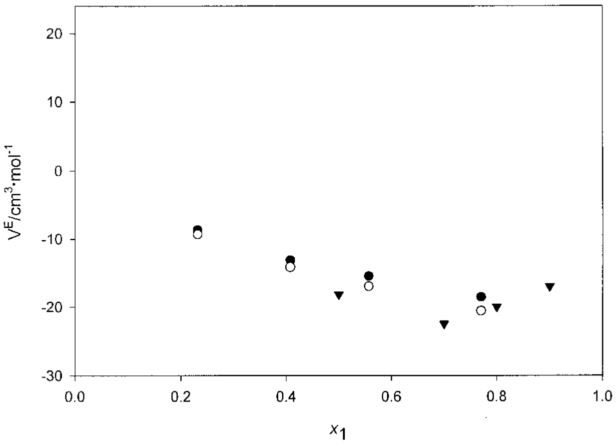

Figure 5. Excess molar volumes V^E versus x and x_1 for carbon dioxide at 11 MPa and 323 K: ●, calculated molar volumes with the BWRS EoS[12] for CO_2 and ethanol (method A, this work); ○, calculated molar volumes with the BWRS EoS[12] for ethanol and the MBWRS EoS[11] for CO_2 (method B, this work); ▼, calculated molar volumes with the BWRS EoS[12] for ethanol and the MBWRS EoS[11] for CO_2 (method B, Pholer and Kiran data).

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

$$V^E = V^{mix} - (x_1 V_1 + x_2 V_2) \qquad (6)$$

where V_1 and V_2 represent the pure component volumes and x_1 and x_2 are the mole fractions of carbon dioxide and ethanol, respectively. The pure component molar volumes were calculated with the BWRS equation of state reported by Starling[12] using the parameters presented inside Table 7. In addition, molar volumes for CO_2 were calculated with the 32-term modified Benedict–Webb–Rubin (MBWRS-32) EoS proposed by Ely et al.[11]

To have a real comparison of the excess molar volumes data reported in this work with those published by Pholer and Kiran,[13] and since they do not publish their calculated method, in this work the excess molar volumes were calculated using the two EoS mentioned above. The excess volume of mixtures presented in Table 2 in the third column (method A) for CO_2 (1) + ethanol (2) at the selected temperature of 323 K were calculated using the BWRS equation of state reported by Starling[12] using the parameters of Table 7. Furthermore, in the same table in column 6 are presented the calculated values of the excess molar volumes using the BWRS EoS[12] for ethanol and the MBWRS-32 EoS[11] for CO_2 (method B).

The estimated uncertainty of the excess volumes for this system is not higher than ±2.5%. As shown in Figure 5 and in Table 2, the excess volumes of the CO_2 + ethanol mixtures reported in this work at 323 K and those published by Pholer and Kiran[13] agree well.

Conclusions

Experimental determinations of densities were carried out at temperatures from 313 to 363 K and pressures up to 25 MPa for the carbon dioxide + ethanol mixtures at four compositions with an uncertainty lower than ±0.05%, using a vibrating tube densimeter DTV.

Excess volumes are reported for the carbon dioxide + ethanol mixtures at four compositions; the corresponding uncertainties do not exceed ±2.5%.

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