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Measurements of Compressed Liquid Densities for CO_2 (1) + Butan-1-ol (2) via a Vibrating Tube Densimeter at Temperatures from (313 to 363) K and Pressures up to 25 MPa

Abel Zúñiga-Moreno,[†] Luis A. Galicia-Luna,*,[†] and Stanley I. Sandler[‡]

Instituto Politécnico Nacional, ESIQIE, Laboratorio de Termodinámica, Edif. Z, Secc. 6, 1er piso, UPALM Zacatenco, 07738, Lindavista, México, D.F., México, and Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716-3119, USA

Studies of compressed liquid densities of butan-1-ol and of CO_2 (1) + butan-1-ol (2) binary mixtures were carried out at temperatures from (313 to 363) K and pressures up to 25 MPa. Densities were measured for binary mixtures at eight different compositions (x_1 = 0.0251, 0.0857, 0.1842, 0.3749, 0.4972, 0.5965, 0.8663, and 0.9698). A vibrating tube densimeter using two reference calibration fluids was used to measure the volumetric properties. The uncertainty in the experimental densities is estimated to be better than ± 0.2 $kg \cdot m^{-3}$. Densities of butan-1-ol are correlated using a short explicit volume equation and the Benedict−Webb−Rubin−Starling equation of state (BWRS EoS). Experimental densities of butan-1-ol were compared with two available correlations. The compressed liquid densities determined here for CO_2 (1) + butan-1-ol (2) mixtures are the first set of data for this mixture reported in the literature. Volumes of mixing were determined using butan-1-ol densities calculated with the BWRS EoS and CO_2 densities calculated with a reference EoS.

Introduction

New phase equilibrium and $P\upsilon T$ data of pure compounds and mixtures involving CO_2 + alcohol at high pressure are needed for the development of supercritical fluid extraction processes.[1−4] CO_2 + alcohol mixtures are used as solvents in supercritical fluid technology.[4−6] There is a wide variety of applications of these kinds of mixtures, including extraction of natural products from natural resources,[5,6] nanotechnology,[7] and reactions.[8] Thus it is very important to perform measurements on the phase equilibria and volumetric properties of potential solvents composed of CO_2 + alcohol. Extractions with supercritical fluids are mainly based on the fact that the solvent power depends on the density of the solvent, and this is significantly dependent on pressure. Small pressure fluctuations can generate great changes in density; this type of behavior is of great importance for the design of storage and extraction vessels and circuit pumps where the pressure drops could affect the density of the solvent causing a change in its solvent power. Such data is of significance from both the industrial and fundamental points of view; for example, the testing and development of new models depends on the availability of reliable and accurate experimental data. Multiparameter equations of state[9−13] and volume explicit equations[14−19] have been used to represent compressed liquid densities of pure compounds and mixtures. These expressions can be easily implemented in computer calculations, and their use is of importance in the chemical industry.

This work focuses on the study of the volumetric properties of the CO_2 + butan-1-ol system, having as the main objective the development of data for supercritical fluid processes.[1−3] The phase equilibria of the CO_2 + butan-1-ol system have been extensively studied.[2,4,20−31] Critical points of CO_2 + 1-butanol have been measured by Gurdial et al.,[24] Ziegler et al.,[26] Yeo et al.,[29] Silva-Oliver et al.,[2] and Elizalde-Solis et al.[31] However, compressed liquid densities for CO_2 + alcohol mixtures have been published only for light alcohols,[32−42] and there is still a gap in the experimental data for the volumetric behavior of such mixtures. The $p\upsilon Tx$ properties of the system CO_2 + methanol have been the most studied in the literature.[32−36] However, the systems CO_2 + ethanol,[37−39] CO_2 + propan-1-ol,[40,41] CO_2 + propan-2-ol,[41,42] and CO_2 + hexan-1-ol[43] have received very little attention in the literature, and mixtures of CO_2 + butan-1-ol have not been studied at all.

Compressed liquid densities of butan-1-ol and CO_2 + butan-1-ol mixtures at eight different compositions were measured in this work using a vibrating tube densimeter. These densities of butan-1-ol and of each mixture at fixed composition are correlated with a short explicit volume equation[19] and with the Benedict−Webb−Rubin−Starling equation of state (BWRS EoS).[9] Densities of pure butan-1-ol are compared with two available correlations.[14,15] The volumes for these mixtures and their variation with composition, temperature, and pressure are also reported.

Experimental Section

Materials. CO_2 (M = 44.010 $g \cdot mol^{-1}$, Chemical Abstracts Service Registry No. (CASRN) 124-38-9) was research grade, and nitrogen (M = 28.014 $g \cdot mol^{-1}$, CASRN 7727-37-9) was chromatographic grade. Both gases were supplied by Infra Air Products (Mexico) with a certified purity of x_1 = 0.99995. Water (M = 18.015 $g \cdot mol^{-1}$, CASRN 7732-18-5) was HPLC grade with a specified purity of x_1 = 0.9995, and butan-1-ol (M = 74.123 $g \cdot mol^{-1}$, CASRN 71-36-3) had a specified purity of x_1

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* To whom correspondence should be addressed. E-mail: lgalicial@ipn.mx. Phone: (52) 55-5729-6000, ext. 55133. Fax: (52) 55-5586-2728.

[†] Instituto Politécnico Nacional.

[‡] University of Delaware.

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Table 1. Compressed Liquid Densities, ρ, of Butan-1-ol at Six Temperatures

T/K = 313.08		T/K = 323.05		T/K = 332.93		T/K = 342.86		T/K = 352.79		T/K = 362.67	
p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
1.006	795.22	0.999	787.38	1.013	779.33	1.026	770.92	1.020	762.66	1.043	753.50
2.017	796.08	2.026	788.22	2.026	780.27	2.007	771.87	2.014	763.68	2.116	754.77
3.007	796.85	3.007	789.03	3.014	781.21	3.003	772.85	3.007	764.68	3.026	755.74
4.010	797.64	4.024	789.91	4.006	782.04	4.051	773.84	3.998	765.67	4.013	756.82
5.016	798.44	5.012	790.75	5.000	782.91	5.008	774.72	4.998	766.69	5.024	757.87
6.017	799.22	6.016	791.57	6.013	783.78	6.023	775.59	5.997	767.68	6.047	758.93
7.011	800.00	7.023	792.40	6.997	784.60	7.010	776.55	7.006	768.64	7.014	759.93
8.006	800.77	8.004	793.16	8.003	785.50	8.000	777.42	8.005	769.61	8.012	760.98
9.019	801.53	9.009	793.98	9.005	786.32	9.001	778.28	9.007	770.53	9.025	762.03
10.008	802.27	10.007	794.78	10.001	787.17	10.005	779.20	9.997	771.44	10.015	762.94
11.014	803.01	11.004	795.57	10.996	787.97	11.006	780.06	11.008	772.38	11.002	763.92
12.016	803.73	11.995	796.32	12.003	788.80	12.010	780.90	12.000	773.26	12.002	764.89
13.016	804.46	13.007	797.09	12.993	789.62	13.033	781.77	13.043	774.22	13.011	765.86
14.013	805.18	14.022	797.85	14.001	790.38	14.017	782.62	14.002	775.11	14.011	766.84
15.010	805.91	14.989	798.63	15.016	791.22	15.001	783.45	15.000	775.98	15.014	767.70
16.003	806.58	16.006	799.33	15.998	791.96	16.009	784.29	16.000	776.85	16.006	768.67
16.999	807.29	16.998	800.10	16.999	792.72	17.016	785.14	16.992	777.72	17.009	769.58
17.999	807.98	18.001	800.84	18.009	793.53	17.991	785.93	17.988	778.56	18.008	770.48
19.024	808.67	19.025	801.56	18.986	794.29	19.023	786.79	18.994	779.41	18.993	771.37
20.005	809.33	19.993	802.28	20.043	795.08	19.999	787.57	20.012	780.22	19.990	772.21
21.013	810.09	21.032	803.06	21.056	795.87	21.000	788.37	21.003	781.04	21.007	773.10
22.003	810.75	22.006	803.74	22.040	796.59	22.003	789.15	22.010	781.87	21.997	773.96
23.024	811.41	22.993	804.41	23.009	797.30	22.989	789.91	22.971	782.68	23.014	774.89
24.027	812.09	24.012	805.16	24.001	798.04	24.004	790.69	24.021	783.49	24.000	775.58
24.234	812.21	24.418	805.43	24.515	798.46	24.621	791.20	24.573	783.95	24.563	776.12

= 0.998. Both liquids were supplied by Aldrich (USA). Butan-1-ol was stored over a 3 Å molecular sieve to avoid contamination by moisture and was used without any further purification. The purities of the liquid samples were tested using a gas chromatograph (HP 5890 Series II) fitted with a flame ionization detector (FID) and a packed column. The verified guaranteed purity was $x_1 = 0.998$. Liquids were degassed under a vacuum with vigorous stirring before they were used to perform density measurements.

Apparatus and Procedure. The apparatus and experimental procedure used in this work has been described previously.[39,44] The measuring cell consists of a vibrating tube (Hastelloy C-276 U-tube) containing a sample of approximately 1 cm^3. It was connected to a sapphire tube cell, which was used to feed the fluids to the vibrating tube densimeter (VTD). The pressure measurements were made directly in the sapphire tube cell by means of a 25 MPa Sedeme pressure transducer. The pressure transducer was thermoregulated and calibrated periodically at each temperature measured in this work. The temperature was measured by three platinum probes located at the top and bottom of the sapphire cell and in the vibrating tube densimeter. Temperature calibrations were made using a calibration system (Automatic Systems F300S, USA) with a 25 Ω reference probe (Rosemount, England, model 162CE; ± 0.005 K certified uncertainty traceable to the ITS-90 scale). Calibration of the vibrating tube was performed using water and nitrogen as the reference fluids. Density reference values of nitrogen and water were calculated with the equations of state of Span et al.[11] and Wagner and Pruss,[12] respectively. Details of the calibrating procedures of the platinum temperature probes, the pressure transducer, and the vibrating tube densimeter were given previously.[1,39,41,44]

The uncertainties in the experimental quantities presented in this work were estimated to be ± 0.03 K for temperature, ± 0.008 MPa for pressure, and ± 0.2 kg·m^{-3} for density.

Density measurements were carried out at constant temperature, and the beginning pressure for each isotherm was greater than the corresponding equilibrium pressure of the vapor−liquid equilibrium curve. Some experimental data and models reported in the literature[2,4,29,30] were used to ensure that the measurements were made in the single liquid phase, and this was also done by observing the mixture under study through the sapphire tube cell.

Loading of the Measurement Cell. A detailed explanation of this procedure was reported by Galicia-Luna et al.[33] The samples with the desired compositions were prepared by successive loadings[33,41] of the pure compounds in the sapphire cell with a maximum volume of 12 cm^3. The amounts of the compounds were determined by weighting carried out with an uncertainty of ± 10^{-7} kg using a Sartorius comparator balance (MCA1200), which was periodically calibrated with a standard mass of 1 kg class E1. The resulting uncertainty for the mole fraction composition of the mixtures was lower than ± 10^{-4}.

Correlation Data

Density. A short equation of six parameters[19] was used to correlate the densities reported herein. This equation is expressed as follows

$$v = \frac{d_1 + d_2 P}{d_3 - d_4 T + d_5 T^{1/2} + d_6 P} \tag{1}$$

where v is the specific volume and d_i are adjustable parameters.

The BWRS EoS[9] is also used to correlate the experimental densities; this EoS is expressed as follows

$$p = \frac{RT}{V_m} + \frac{(B_0 RT - A_0 - C_0/T^2 + D_0/T^3 - E_0/T^4)}{V_m^2} + \frac{(bRT - a - d/T)}{V_m^3} + \frac{\alpha(a + d/T)}{V_m^6} + \frac{c(1 + u/V_m^2)\exp(-u/V_m^2)}{V_m^3 T^2} \tag{2}$$

Table 2. Compressed Liquid Densities, ρ, and Volumes of Mixing, ΔV_m, for the CO_2 (1) + Butan-1-ol (2) System; $x_1 = 0.0251$

p / MPa	ρ / $kg \cdot m^{-3}$	ΔV_m / $cm^3 \cdot mol^{-1}$	p / MPa	ρ / $kg \cdot m^{-3}$	ΔV_m / $cm^3 \cdot mol^{-1}$	p / MPa	ρ / $kg \cdot m^{-3}$	ΔV_m / $cm^3 \cdot mol^{-1}$
	T/K = 313.10			T/K = 323.05			T/K =332.94	
1.008	798.08	−60.83	1.017	789.88	−62.47	1.010	781.57	−65.12
2.011	798.90	−28.46	2.015	790.73	−29.60	2.077	782.55	−29.77
3.006	799.70	−17.62	3.003	791.59	−18.55	3.046	783.47	−19.09
4.012	800.54	−12.06	4.007	792.48	−12.85	3.990	784.30	−13.65
5.008	801.32	−8.68	5.026	793.33	−9.35	5.002	785.22	−10.07
6.013	802.14	−6.32	5.975	794.14	−7.11	6.026	786.15	−7.64
7.004	802.94	−4.52	7.085	795.08	−5.19	6.975	786.98	−6.00
8.023	803.75	−2.89	7.991	795.85	−3.96	8.009	787.91	−4.62
9.037	804.53	−1.19	9.003	796.68	−2.79	9.084	788.83	−3.48
10.005	805.29	−0.73	10.032	797.56	−1.77	9.985	789.62	−2.70
11.011	806.08	−0.59	10.996	798.32	−1.13	11.024	790.52	−1.95
12.018	806.83	−0.52	12.028	799.15	−0.82	12.040	791.34	−1.41
13.003	807.56	−0.47	13.030	799.93	−0.67	12.968	792.12	−1.09
14.007	808.31	−0.43	14.030	800.72	−0.59	13.994	792.95	−0.87
15.009	809.03	−0.40	15.018	801.45	−0.52	15.041	793.85	−0.73
16.004	809.77	−0.38	16.017	802.24	−0.48	16.061	794.54	−0.62
17.005	810.49	−0.36	17.014	802.97	−0.44	17.001	795.37	−0.57
18.019	811.19	−0.34	18.025	803.71	−0.41	18.031	796.18	−0.52
19.019	811.89	−0.32	19.034	804.49	−0.39	19.042	796.95	−0.47
20.020	812.59	−0.31	20.052	805.21	−0.36	20.027	797.73	−0.44
21.027	813.29	−0.30	21.014	805.95	−0.35	20.987	798.46	−0.41
22.005	813.97	−0.29	22.027	806.68	−0.33	22.013	799.22	−0.38
23.011	814.69	−0.28	23.002	807.38	−0.31	23.023	800.00	−0.36
24.004	815.36	−0.27	24.035	808.13	−0.30	24.078	800.80	−0.34
25.028	816.10	−0.26	25.023	808.84	−0.29	25.033	801.51	−0.32
	T/K = 342.85			T/K = 352.77			T/K = 362.67	
1.014	772.92	−66.95	1.022	763.98	−68.55	1.053	755.01	−68.47
2.013	773.93	−32.00	2.029	765.11	−32.85	2.066	756.19	−33.31
2.982	774.90	−20.43	3.006	766.15	−21.05	3.045	757.27	−21.54
4.039	775.94	−14.12	4.015	767.17	−14.88	4.013	758.36	−15.54
5.057	776.91	−10.52	5.041	768.25	−11.13	5.068	759.49	−11.60
5.993	777.79	−8.27	5.988	769.24	−8.80	6.009	760.49	−9.25
7.067	778.78	−6.40	7.026	770.25	−6.96	6.988	761.58	−7.48
8.025	779.69	−5.15	8.000	771.20	−5.66	7.985	762.59	−6.11
9.013	780.60	−4.12	9.059	772.24	−4.55	9.006	763.64	−5.03
10.012	781.51	−3.28	10.017	773.14	−3.75	10.031	764.70	−4.16
11.010	782.43	−2.59	11.016	774.17	−3.08	11.027	765.69	−3.48
11.969	783.27	−2.05	12.004	775.04	−2.51	12.000	766.65	−2.92
13.080	784.23	−1.56	13.003	775.95	−2.05	13.054	767.68	−2.43
13.925	784.95	−1.29	14.039	776.91	−1.67	14.008	768.61	−2.06
15.055	785.93	−1.03	14.988	777.75	−1.39	14.993	769.57	−1.74
16.002	786.72	−0.88	16.084	778.74	−1.15	16.000	770.52	−1.48
17.016	787.57	−0.76	17.004	779.54	−1.00	17.046	771.48	−1.26
18.007	788.39	−0.67	18.003	780.41	−0.87	17.989	772.34	−1.10
19.019	789.22	−0.60	19.004	781.28	−0.76	19.009	773.27	−0.97
20.027	790.06	−0.55	20.007	782.15	−0.68	20.045	774.19	−0.85
20.996	790.82	−0.50	21.029	783.01	−0.61	21.017	775.08	−0.77
22.019	791.65	−0.46	22.044	783.86	−0.56	22.075	775.99	−0.68
23.034	792.46	−0.43	22.995	784.65	−0.51	23.006	776.82	−0.63
24.052	793.28	−0.40	24.056	785.52	−0.47	24.007	777.69	−0.57
25.090	794.07	−0.38	25.098	786.41	−0.44	25.062	778.61	−0.53

where V_m is the molar volume. A Marquardt−Levenberg least-squares optimization procedure[17−19,39] was used to fit the parameters in eqs 1 and 2 using the next objective function, S

$$S = \sum_{i=1}^{n} \left[\frac{\rho_i(\text{exptl}) - \rho_i(\text{calcd})}{\rho_i(\text{exptl})} \right]^2 \tag{3}$$

where n is the number of experimental data points, and exptl and calcd represent the experimental density and the value obtained from the model, respectively. The average absolute deviation (AAD), the mean deviation (bias), the standard deviation (SDV), and the root-mean-square (rms) are used to evaluate the different correlations. These statistical values were used according to the definitions given previously.[17−19]

Results and Discussion

Compressed liquid densities of butan-1-ol were measured along six isotherms between (313.08 and 362.67) K at approximately 10 K intervals and at pressures from (1 to 25) MPa. A total of 150 experimental points were obtained, and these results are presented in Table 1. Measurements of density for the CO_2 (1) + butan-1-ol (2) system were undertaken at eight compositions covering the whole composition interval with x_1 = 0.0251, 0.0857, 0.1842, 0.3749, 0.4972, 0.5965, 0.8663, and 0.9698. Measurements were made at temperatures from (313 to 363) K and at pressures from (1 to 25) MPa in the compressed liquid state. A total of 680 experimental points were obtained, and they are presented in Tables 2 to 9. For each mixture and for butan-1-ol, the measured densities were correlated with eqs 1 and 2. The parameters in the equations along with statistical values are reported in Table 10. For butan-1-ol, both models

Table 3. Compressed Liquid Densities, ρ, and Volumes of Mixing, ΔV_m, for the CO_2 (1) + Butan-1-ol (2) System; $x_1 = 0.0857$

p / MPa	ρ / $kg \cdot m^{-3}$	ΔV_m / $cm^3 \cdot mol^{-1}$	p / MPa	ρ / $kg \cdot m^{-3}$	ΔV_m / $cm^3 \cdot mol^{-1}$	p / MPa	ρ / $kg \cdot m^{-3}$	ΔV_m / $cm^3 \cdot mol^{-1}$
	T/K = 313.11			T/K = 323.07			T/K =332.96	
1.990	802.76	−98.16	1.981	794.04	−102.93	2.025	785.34	−104.47
3.001	803.63	−60.06	3.013	795.05	−62.88	3.025	786.35	−65.55
4.009	804.54	−40.95	4.009	795.99	−43.60	3.995	787.30	−46.30
5.013	805.41	−29.30	5.021	796.91	−31.69	5.006	788.30	−34.09
6.014	806.27	−21.24	6.010	797.83	−23.76	6.029	789.27	−25.79
7.009	807.15	−15.07	6.995	798.74	−17.90	6.996	790.20	−20.07
8.011	807.98	−9.59	7.985	799.59	−13.23	8.001	791.20	−15.50
9.009	808.79	−3.81	9.047	800.55	−9.02	9.060	792.17	−11.66
10.011	809.65	−2.11	10.028	801.40	−5.70	10.005	793.04	−8.84
10.994	810.46	−1.65	11.003	802.22	−3.49	11.020	793.96	−6.35
12.007	811.26	−1.39	12.005	803.07	−2.46	12.043	794.89	−4.49
13.022	812.06	−1.22	12.995	803.91	−1.96	13.021	795.74	−3.34
13.999	812.83	−1.10	14.273	805.01	−1.60	14.023	796.64	−2.62
15.014	813.63	−1.00	15.019	805.58	−1.44	15.013	797.55	−2.18
16.013	814.38	−0.92	15.998	806.41	−1.29	15.989	798.30	−1.86
16.994	815.12	−0.85	16.977	807.17	−1.17	17.015	799.17	−1.63
18.005	815.89	−0.79	18.030	808.01	−1.06	18.001	799.98	−1.45
19.008	816.61	−0.74	18.995	808.74	−0.98	18.996	800.80	−1.31
20.010	817.40	−0.70	19.987	809.54	−0.91	20.012	801.65	−1.20
20.990	818.09	−0.66	21.040	810.38	−0.85	21.010	802.47	−1.10
22.028	818.85	−0.62	21.992	811.09	−0.79	22.025	803.27	−1.02
22.900	819.47	−0.59	23.011	811.87	−0.74	22.983	804.05	−0.95
23.996	820.30	−0.56	24.000	812.60	−0.70	24.061	804.91	−0.88
25.047	821.11	−0.54	25.007	813.42	−0.66	25.000	805.68	−0.83
	T/K = 342.88			T/K = 352.83			T/K = 362.69	
1.975	776.20	−111.50	2.007	766.96	−113.53	2.045	757.33	−114.98
2.955	777.28	−70.36	3.023	768.13	−71.31	3.006	758.53	−74.50
4.033	778.42	−48.12	3.953	769.18	−51.67	3.982	759.72	−53.38
5.015	779.45	−36.10	5.008	770.34	−38.17	5.010	760.91	−40.01
5.957	780.40	−28.24	5.991	771.43	−29.83	5.976	762.09	−31.62
7.027	781.49	−21.82	7.011	772.54	−23.62	6.994	763.25	−25.27
7.999	782.50	−17.42	7.992	773.57	−19.12	7.999	764.42	−20.58
9.007	783.51	−13.82	9.016	774.63	−15.45	8.998	765.51	−16.94
10.003	784.47	−10.94	10.033	775.71	−12.54	10.048	766.67	−13.91
11.007	785.43	−8.56	10.983	776.62	−10.30	11.028	767.74	−11.61
11.951	786.34	−6.74	12.020	777.74	−8.31	11.999	768.75	−9.72
13.010	787.34	−5.14	13.038	778.75	−6.71	12.994	769.85	−8.12
14.012	788.24	−4.03	13.990	779.64	−5.51	14.018	770.91	−6.76
15.065	789.20	−3.22	14.986	780.63	−4.52	15.014	771.91	−5.67
15.994	790.07	−2.71	16.028	781.61	−3.73	15.995	772.93	−4.81
17.007	790.98	−2.31	16.995	782.54	−3.17	17.061	773.98	−4.05
17.999	791.83	−2.01	17.994	783.45	−2.73	18.008	774.96	−3.52
18.990	792.72	−1.79	18.991	784.40	−2.39	19.008	775.88	−3.06
20.029	793.58	−1.59	20.014	785.33	−2.11	20.060	776.81	−2.67
20.993	794.43	−1.45	21.017	786.18	−1.88	21.044	777.83	−2.39
22.004	795.26	−1.32	21.993	787.09	−1.71	22.045	778.82	−2.15
23.039	796.17	−1.21	23.041	788.01	−1.55	23.036	779.68	−1.93
24.019	796.97	−1.12	24.037	788.92	−1.42	24.037	780.65	−1.77
25.064	797.88	−1.04	25.058	789.81	−1.31	25.015	781.57	−1.62

represent the experimental densities with similar accuracy, according to the statistical values reported in Table 10. Relative deviations of experimental densities of butan-1-ol (ρ(exptl)) with calculated values (ρ(calcd)) with the different correlations are plotted in Figure 1. The maximum relative deviations were ± 0.035 % for the six-parameter equation and ± 0.037 % with the BWRS EoS, as can be seen in Figure 1. The two models (six-parameter and BWRS EoS) were able to represent the experimental density data of butan-1-ol within the experimental uncertainty.

The consistency of our experimental densities for butan-1-ol was tested by comparing our experimental data with correlations reported in the literature. A Tait-type correlation model published by Cibulka and Zikova[14] and the TRIDEN correlation model published by Ihmels and Gmehling[15] were compared with our experimental data. The correlation of Cibulka and Zikova was developed using density data sets published before 1993,[14] and the TRIDEN correlation was based only on the data measured by Ihmels and Gmehling.[15] The relative deviations of experimental densities of this work (ρ(exptl)) from the values calculated (ρ(calcd)) with those two models are shown in Figure 2. Excellent agreement was found with the TRIDEN model,[15] with the maximum deviations of +0.08 % and −0.06 %, as can be seen in Figure 2. The maximum deviations with the TRIDEN model from the data reported in ref 15, for the same range of temperatures and pressures as that employed here, are +0.07 % and −0.02 %. To perform a better evaluation, the absolute (rmsd) and relative (rmsdr) root-mean-square deviations and the mean deviation (bias) as defined in ref 15 are calculated for our set of data, and the results are 0.198 $kg \cdot m^{-3}$, 0.026 %, and 0.038 $kg \cdot m^{-3}$, respectively. These values are lower than those reported for the TRIDEN model,[15] which points out the self-consistency between both data sets where the uncertainty in density for both cases is ± 0.2 $kg \cdot m^{-3}$. Using the correlation of ref 14, the relative deviations are all positive (maximum value, +0.1 %); the rmsd, rmsdr, and bias, calculated using our set of data, results are 0.043 $kg \cdot m^{-3}$, 0.006 %, and 0.003 $kg \cdot m^{-3}$, respectively. These values are lower than those reported

Table 4. Compressed Liquid Densities, ρ, and Volumes of Mixing, ΔV_m, for the CO_2 (1) + Butan-1-ol (2) System; $x_1 = 0.1842$

p / MPa	ρ / $kg \cdot m^{-3}$	ΔV_m / $cm^3 \cdot mol^{-1}$	p / MPa	ρ / $kg \cdot m^{-3}$	ΔV_m / $cm^3 \cdot mol^{-1}$	p / MPa	ρ / $kg \cdot m^{-3}$	ΔV_m / $cm^3 \cdot mol^{-1}$	p / MPa	ρ / $kg \cdot m^{-3}$	ΔV_m / $cm^3 \cdot mol^{-1}$
	T/K = 333.08			T/K = 343.00			T/K = 352.82			T/K = 362.78	
6.035	792.00	−54.92	6.024	782.23	−59.27	6.041	772.14	−62.81	6.018	761.83	−66.80
7.047	793.11	−42.18	7.050	783.43	−46.20	7.041	773.40	−49.90	6.995	763.16	−53.81
8.021	794.16	−32.73	8.037	784.59	−36.68	8.024	774.60	−40.30	8.099	764.64	−42.88
9.035	795.25	−24.84	9.052	785.73	−28.96	9.042	775.87	−32.51	9.002	765.81	−35.92
10.030	796.30	−18.46	10.057	786.87	−22.79	10.044	777.07	−26.37	10.022	767.06	−29.57
11.057	797.37	−13.10	11.053	787.96	−17.78	11.026	778.23	−21.45	10.995	768.34	−24.64
12.025	798.41	−9.33	12.027	789.03	−13.80	12.073	779.44	−17.16	12.059	769.68	−20.22
13.041	799.39	−6.74	13.076	790.12	−10.46	13.001	780.49	−14.05	13.056	770.87	−16.81
14.034	800.34	−5.21	14.026	791.16	−8.24	14.050	781.67	−11.22	14.029	772.05	−14.05
15.074	801.36	−4.21	15.081	792.24	−6.49	15.000	782.72	−9.22	15.026	773.24	−11.74
16.022	802.27	−3.58	16.028	793.21	−5.38	15.999	783.84	−7.60	16.010	774.38	−9.88
16.957	803.20	−3.12	17.031	794.24	−4.54	17.008	784.88	−6.35	17.020	775.53	−8.35
18.103	804.27	−2.69	18.020	795.22	−3.91	18.066	786.01	−5.36	18.041	776.68	−7.11
19.053	805.14	−2.41	19.009	796.20	−3.43	19.002	787.01	−4.68	19.031	777.79	−6.16
20.044	806.03	−2.17	20.030	797.20	−3.03	20.015	788.03	−4.09	20.045	778.90	−5.37
21.090	807.01	−1.96	21.066	798.20	−2.70	21.043	789.11	−3.62			
21.974	807.82	−1.81	21.978	799.07	−2.46	22.025	790.10	−3.24			
22.960	808.70	−1.66	23.062	800.09	−2.22	23.024	791.11	−2.92			
24.014	809.64	−1.52	24.031	801.02	−2.03	24.015	792.10	−2.65			
25.045	810.58	−1.40	25.044	801.97	−1.87	25.100	793.18	−2.40			

Table 5. Compressed Liquid Densities, ρ, and Volumes of Mixing, ΔV_m, for the CO_2 (1) + Butan-1-ol (2) System; $x_1 = 0.3749$

p / MPa	ρ / $kg \cdot m^{-3}$	ΔV_m / $cm^3 \cdot mol^{-1}$
	T/K = 313.14	
9.008	824.89	−15.45
9.996	826.10	−7.95
11.012	827.34	−5.88
12.008	828.53	−4.80
13.037	829.73	−4.05
14.009	830.85	−3.54
15.034	832.02	−3.11
16.014	833.13	−2.78
17.013	834.21	−2.50
18.012	835.29	−2.25
19.027	836.37	−2.04
20.015	837.44	−1.86

for the correlation and for individual sets of data used in the correlation.[14] This reflects the good quality of our results.

The densities of the CO_2 + butan-1-ol system have not been reported in the literature, and therefore comparisons were not possible. The experimental densities of CO_2 + butan-1-ol at 313.13 K at different compositions are plotted in Figure 3. The binary mixtures become more compressible as the CO_2 composition increases.

For the case of mixtures, the accuracy of the correlations with the six-parameter equation decreases as the composition of CO_2 increases in the mixture. The error of the calculation is largest for mixtures with CO_2 mole fractions of 0.8663 and 0.9698. The BWRS EoS is more able to represent the densities of the mixtures including mixtures with high CO_2 compositions.

Volumes of Mixing. The volumes of mixing, ΔV_m, can be calculated from our experimental density values using the following relation

$$\Delta V_m = \left(\frac{x_1 M_1 + x_2 M_2}{\rho^{mix}} - (x_1 V_{m1} + x_2 V_{m2})\right) \tag{4}$$

where ρ^{mix} is the density of the mixture; V_{m1} and V_{m2} are the pure component molar volumes at the measured temperature and pressure of the mixture; M_1 and M_2 are the molecular

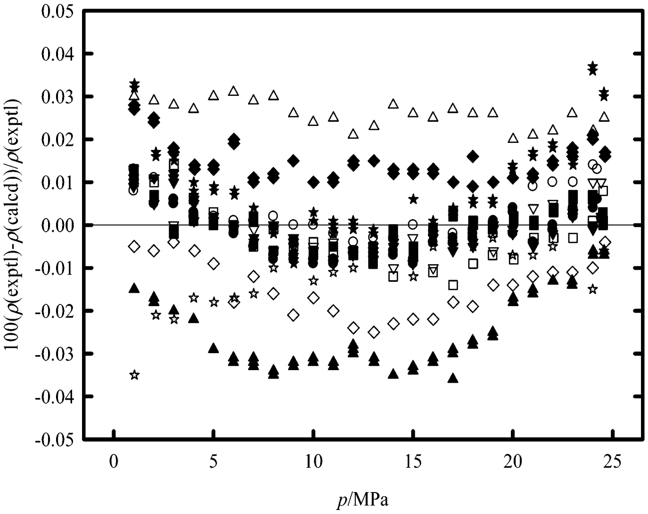

Figure 1. Relative deviations of experimental densities of butan-1-ol reported here (ρ(exptl)) and values calculated (ρ(calcd)) with the two correlations used in this work, using the adjusted parameters reported in Table 10 at the following temperatures: ○, 313.08 K; ▽, 323.05 K; □, 332.93 K; ◇, 342.86 K; △, 352.79 K; ☆, 362.67 K. Open and closed symbols are for the six-parameter equation and the BWRS EoS, respectively.

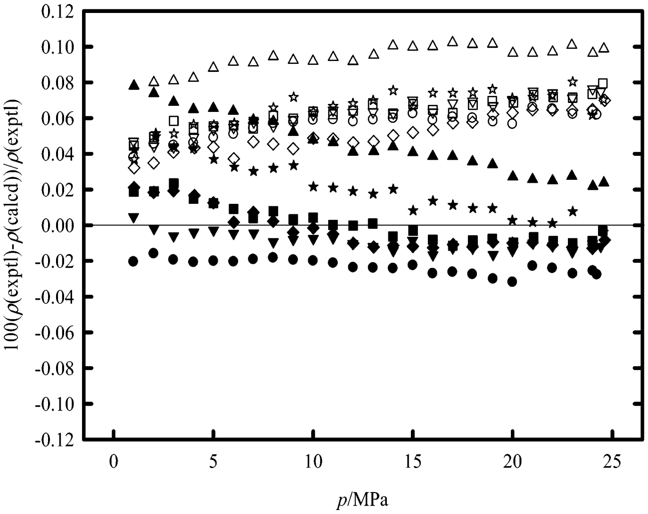

Figure 2. Relative deviations of experimental densities of butan-1-ol from this work (ρ(exptl)) and values calculated (ρ(calcd)) with the Cibulka and Zikova[14] model and TRIDEN model[15] at the following temperatures: ○, 313.08 K; ▽, 323.05 K; □, 332.93 K; ◇, 342.86 K; △, 352.79 K; ☆, 362.67 K. Open and closed symbols are for the Cibulka and Zikova[14] model and the TRIDEN model,[15] respectively.

Table 6. Compressed Liquid Densities, ρ, and Volumes of Mixing, ΔV_m, for the CO_2 (1) + Butan-1-ol (2) System; $x_1 = 0.4972$

p / MPa	ρ / kg·m^{-3}	ΔV_m / cm^3·mol^{-1}	p / MPa	ρ / kg·m^{-3}	ΔV_m / cm^3·mol^{-1}	p / MPa	ρ / kg·m^{-3}	ΔV_m / cm^3·mol^{-1}
	T/K = 313.15			T/K = 323.10			T/K =332.99	
9.101	830.36	−18.12						
10.085	831.83	−9.82	10.109	818.96	−29.61			
11.056	833.28	−7.34	11.078	820.55	−17.53	11.100	807.58	−33.71
12.062	834.75	−5.93	12.051	822.08	−12.02	12.062	809.21	−23.75
13.043	836.14	−5.00	13.049	823.64	−9.20	13.082	810.88	−16.95
14.050	837.54	−4.30	14.053	825.18	−7.48	14.115	812.58	−12.83
15.053	838.90	−3.76	15.041	826.62	−6.32	15.061	814.12	−10.44
16.037	840.22	−3.32	16.058	828.14	−5.44	16.035	815.66	−8.73
17.055	841.56	−2.94	17.051	829.54	−4.76	17.108	817.32	−7.37
18.037	842.85	−2.64	18.061	830.96	−4.21	18.040	818.75	−6.47
19.023	844.11	−2.37	19.022	832.33	−3.77	19.036	820.22	−5.69
20.041	845.39	−2.12	20.021	833.69	−3.39	20.051	821.73	−5.05
21.003	846.61	−1.92	21.047	835.06	−3.04	21.048	823.17	−4.53
22.068	847.91	−1.72	22.036	836.36	−2.75	22.048	824.60	−4.08
23.079	849.14	−1.55	23.045	837.69	−2.50	23.047	826.00	−3.69
24.016	850.27	−1.40	23.996	838.91	−2.28	24.018	827.36	−3.37
25.033	851.48	−1.26	25.012	840.21	−2.07	25.056	828.77	−3.06
	T/K = 342.92			T/K = 352.85			T/K = 362.74	
12.062	795.68	−35.77						
13.090	797.59	−27.05	13.091	783.81	−36.18			
14.017	799.27	−21.22	13.958	785.52	−29.90	14.112	771.83	−36.17
15.047	801.10	−16.62	15.066	787.67	−23.61	15.096	773.91	−30.13
16.026	802.79	−13.56	16.029	789.49	−19.46	15.985	775.76	−25.67
17.041	804.51	−11.28	17.077	791.44	−16.04	17.043	777.90	−21.38
18.053	806.18	−9.60	18.031	793.15	−13.67	18.079	779.94	−18.07
19.028	807.77	−8.35	19.033	794.93	−11.74	19.117	781.94	−15.45
20.046	809.40	−7.32	20.018	796.63	−10.23	20.051	783.68	−13.54
21.062	810.98	−6.48	21.055	798.40	−8.96	21.025	785.45	−11.91
22.043	812.48	−5.81	22.035	800.00	−7.97	22.018	787.27	−10.55
22.996	813.92	−5.25	23.067	801.70	−7.11	23.076	789.13	−9.34
24.003	815.43	−4.75	24.007	803.18	−6.45	24.063	790.85	−8.40
25.073	816.99	−4.29	25.035	804.81	−5.82	25.140	792.64	−7.53

Table 7. Compressed Liquid Densities, ρ, and Volumes of Mixing, ΔV_m, for the CO_2 (1) + Butan-1-ol (2) System; $x_1 = 0.5965$

p / MPa	ρ / kg·m^{-3}	ΔV_m / cm^3·mol^{-1}	p / MPa	ρ / kg·m^{-3}	ΔV_m / cm^3·mol^{-1}	p / MPa	ρ / kg·m^{-3}	ΔV_m / cm^3·mol^{-1}
	T/K = 313.16			T/K = 323.10			T/K = 333.00	
10.073	836.70	−11.59						
11.059	838.66	−8.57	11.078	822.90	−20.67			
12.075	840.60	−6.88	12.072	825.03	−13.99	12.077	809.05	−27.87
13.069	842.49	−5.79	13.059	827.10	−10.70	13.047	811.32	−20.11
14.098	844.39	−4.96	14.067	829.16	−8.67	14.101	813.70	−15.05
15.059	846.11	−4.35	15.063	831.15	−7.30	15.079	815.86	−12.11
16.037	847.81	−3.85	16.046	833.04	−6.29	16.069	817.96	−10.07
17.032	849.52	−3.43	17.030	834.90	−5.51	17.045	820.00	−8.60
18.048	851.21	−3.06	18.049	836.78	−4.86	18.064	822.10	−7.44
19.055	852.88	−2.75	19.044	838.57	−4.33	19.045	824.02	−6.55
20.044	854.46	−2.48	20.039	840.32	−3.89	20.044	825.94	−5.82
21.042	856.04	−2.24	21.064	842.09	−3.50	21.039	827.80	−5.20
22.053	857.62	−2.02	22.041	843.75	−3.17	22.043	829.66	−4.68
23.031	859.12	−1.83	23.023	845.38	−2.88	23.048	831.48	−4.24
24.038	860.62	−1.66	24.008	847.00	−2.63	24.011	833.21	−3.86
25.036	862.12	−1.50	25.040	848.65	−2.39	25.086	835.10	−3.50
	T/K = 342.94			T/K = 352.88			T/K = 362.76	
13.074	795.03	−32.02						
14.051	797.49	−24.72	14.075	780.49	−34.25			
15.068	799.99	−19.36	15.042	783.18	−27.80	15.085	765.37	−35.28
16.064	802.35	−15.69	16.039	785.88	−22.69	16.042	768.34	−29.61
17.076	804.68	−13.03	17.076	788.55	−18.68	17.060	771.36	−24.77
18.056	806.85	−11.11	18.030	790.96	−15.87	18.019	774.09	−21.13
19.037	808.99	−9.63	19.037	793.41	−13.57	19.023	776.91	−18.09
20.067	811.18	−8.41	20.049	795.80	−11.76	20.064	779.68	−15.58
21.031	813.15	−7.48	21.030	798.05	−10.35	21.026	782.15	−13.70
22.050	815.20	−6.66	22.036	800.27	−9.17	22.023	784.67	−12.10
23.030	817.14	−6.00	23.019	802.43	−8.21	23.058	787.18	−10.72
24.031	819.08	−5.43	24.039	804.60	−7.37	24.078	789.61	−9.59
25.028	820.94	−4.93	25.092	806.79	−6.64	25.110	791.98	−8.62

weights; and x_1 and x_2 are the mole fractions of CO_2 and butan-1-ol, respectively. The corresponding molar volumes of butan-1-ol (V_{m1}) were calculated with the BWRS EoS using the adjusted parameters reported in Table 10, and the molar volumes of CO_2 (V_{m2}) were obtained using the reference EoS for CO_2 proposed by Span and Wagner.[13] The uncertainty in the volumes

Table 8. Compressed Liquid Densities, ρ, and Volumes of Mixing, ΔV_m, for the CO_2 (1) + Butan-1-ol (2) System; $x_1 = 0.8663$

p/MPa	ρ/kg·m^{-3}	ΔV_m/cm^3·mol^{-1}	p/MPa	ρ/kg·m^{-3}	ΔV_m/cm^3·mol^{-1}	p/MPa	ρ/kg·m^{-3}	ΔV_m/cm^3·mol^{-1}
	T/K = 313.16			T/K = 323.10			T/K = 332.99	
10.087	805.12	−12.76						
11.082	813.86	−8.84						
12.061	821.60	−6.86	12.077	777.48	−15.25			
13.043	828.71	−5.61	13.046	787.33	−11.12			
14.076	835.52	−4.68	14.029	796.15	−8.69	14.087	752.33	−15.89
15.061	841.57	−4.03	15.050	804.37	−7.05	15.053	762.95	−12.31
16.043	847.15	−3.52	16.077	811.86	−5.89	16.081	772.94	−9.82
17.052	852.59	−3.10	17.044	818.37	−5.07	17.073	781.43	−8.14
18.056	857.69	−2.75	18.024	824.54	−4.43	18.052	789.26	−6.92
19.039	862.42	−2.47	19.033	830.52	−3.90	19.049	796.49	−5.97
20.027	866.99	−2.23	20.028	835.95	−3.46	20.021	803.04	−5.23
21.068	871.52	−2.01	21.026	841.13	−3.10	21.046	809.49	−4.61
22.034	875.60	−1.83	22.054	846.30	−2.79	22.064	815.51	−4.10
23.061	879.74	−1.66	23.023	850.85	−2.53	23.005	820.74	−3.70
24.054	883.63	−1.52	24.006	855.33	−2.31	24.028	826.19	−3.33
25.015	887.21	−1.40	25.041	859.75	−2.10	25.067	831.43	−3.02
	T/K = 342.94			T/K = 352.88			T/K = 362.75	
15.189	716.88	−19.49						
16.052	728.37	−15.81						
17.059	740.13	−12.74						
18.027	749.98	−10.60	18.449	712.26	−14.04			
19.050	759.30	−8.91	19.044	719.05	−12.65			
20.036	767.54	−7.66	20.064	729.73	−10.72			
21.038	775.36	−6.68	21.052	739.04	−9.25			
22.085	782.79	−5.84	22.047	747.62	−8.07	21.992	710.63	−10.67
23.032	789.07	−5.22	23.067	755.76	−7.09	23.010	720.36	−9.33
24.045	795.41	−4.66	24.035	762.91	−6.32	24.074	729.68	−8.18
25.042	801.31	−4.20	25.048	769.99	−5.64	25.130	738.23	−7.24

Table 9. Compressed Liquid Densities, ρ, and Volumes of Mixing, ΔV_m, for the CO_2 (1) + Butan-1-ol (2) System; $x_1 = 0.9698$

p/MPa	ρ/kg·m^{-3}	ΔV_m/cm^3·mol^{-1}	p/MPa	ρ/kg·m^{-3}	ΔV_m/cm^3·mol^{-1}	p/MPa	ρ/kg·m^{-3}	ΔV_m/cm^3·mol^{-1}
	T/K = 313.10			T/K = 323.05			T/K = 332.94	
9.990	711.97	−7.56						
11.014	740.16	−4.43	11.029	630.03	−15.60			
12.040	761.46	−3.12	12.005	671.01	−8.64			
12.987	777.57	−2.44	12.996	700.08	−5.63	12.999	600.03	−11.99
14.020	792.52	−1.96	14.024	723.36	−4.04	14.036	638.84	−7.98
15.028	805.22	−1.64	15.024	741.89	−3.12	15.021	667.05	−5.80
16.029	816.46	−1.40	16.009	757.40	−2.52	16.014	689.92	−4.43
17.000	826.34	−1.22	17.001	771.14	−2.10	17.022	709.37	−3.51
18.024	835.89	−1.08	18.016	783.62	−1.78	18.009	725.81	−2.88
19.027	844.46	−0.96	19.020	794.82	−1.54	19.010	740.47	−2.41
20.021	852.41	−0.86	20.048	805.21	−1.35	20.028	753.70	−2.05
21.013	859.87	−0.79	21.055	814.54	−1.19	21.042	765.72	−1.78
22.032	867.02	−0.71	22.017	822.92	−1.07	21.997	776.05	−1.57
23.006	873.50	−0.66	23.087	831.58	−0.96	22.983	785.85	−1.39
24.011	879.83	−0.60	24.055	838.92	−0.87	23.838	793.78	−1.26
	T/K = 342.87			T/K = 352.79			T/K = 362.66	
15.510	598.32	−8.20						
16.022	613.97	−7.14						
17.033	640.58	−5.54						
17.988	661.78	−4.48	18.068	596.97	−6.14			
19.001	681.25	−3.67	18.999	619.03	−5.11			
20.036	698.56	−3.05	20.007	639.88	−4.24	20.602	595.03	−4.84
21.044	713.53	−2.59	21.053	659.01	−3.56	21.041	604.05	−4.52
22.014	726.53	−2.25	22.011	674.59	−3.07	22.017	622.53	−3.89
23.003	738.60	−1.96	23.058	690.00	−2.64	23.022	639.79	−3.38
24.019	749.89	−1.72	24.106	703.93	−2.30	24.038	655.56	−2.94
24.944	759.52	−1.55	25.050	715.49	−2.04	25.046	669.85	−2.59

of mixing was estimated to be ± 0.15 %, as previously reported.[18] The concept of excess property cannot be applied to this mixture because the light component carbon dioxide is in the supercritical phase due to the temperature and pressure ranges studied here and not in the liquid phase.[45,46] The calculated volumes of mixing are given in Tables 2 to 9. The measurements covered the volumes of mixing between (−0.26 and −115) cm^3·mol^{-1}. Some volumes of mixing for the temperature range between (313 and 363) K at (21 and 25) MPa are presented in Figure 4. At the temperatures and pressures measured in this work, the volumes of mixing are all negative and asymmetrical at high CO_2 composition. At fixed composition and temperature, ΔV_m is more negative when the pressure decreases, and at fixed composition and pressure, ΔV_m becomes more negative when the temperature increases. This can be seen in Figure 5 for a mixture with $x_1 = 0.5965$. The same behavior can be found for the different mixture compositions studied here.

Table 10. Temperature *T*, Pressure *p*, and Density *ρ* Range, Data Points *n*, and Parameters for the Two Correlation Models for Butan-1-ol and CO_2 (1) + Butan-1-ol (2) Mixtures, along with Statistical Values: Average Absolute Deviation (AAD), Mean Deviation (Bias), Standard Deviation (SDV), and Root-Mean-Square (rms)

	butan-1-ol	$x_1 = 0.0251$	$x_1 = 0.0857$	$x_1 = 0.1842$	$x_1 = 0.3749$	$x_1 = 0.4972$	$x_1 = 0.5965$	$x_1 = 0.8663$	$x_1 = 0.9698$
T_{min}/K	313.08	313.10	313.11	333.08	313.14	313.15	313.16	313.16	313.10
T_{max}/K	362.67	362.67	362.69	362.78	313.14	362.74	362.76	362.75	362.66
p_{min}/MPa	0.999	1.008	1.975	6.018	9.008	9.101	10.073	10.087	9.990
p_{max}/MPa	24.563	25.098	25.064	25.100	20.015	25.14	25.110	25.13	25.050
ρ_{min}/kg·m^{-3}	753.30	755.01	757.33	761.83	824.89	771.83	765.37	710.63	595.03
ρ_{max}/kg·m^{-3}	812.21	816.10	821.11	810.58	837.44	851.48	862.12	887.21	879.83
n	150	150	144	75	12	87	81	65	66
Six-Parameter Equation (eq 1)									
d_1/MPa·m^3·kg^{-1}	−11.2250	−15.2660	−2.1760	−416.3520	−2.3947	−23.9940	−92.9320	−17.0980	0.1030
d_2/m^3·kg^{-1}	−0.07000	−0.09490	−0.01447	−3.27660	−0.02120	−0.29690	−1.74000	−2.95770	−0.03780
d_3/MPa	−6042.2	−9095.2	−1259.9	−264486.3	−122.7	−6325.4	23812.2	250148.8	2260.3
d_4/MPa·K^{-1}	−26.732	−34.790	−5.318	−1044.953	5.112	−111.207	−666.133	−1295.323	−13.173
d_5/MPa·K$^{-1/2}$	−635.4	−789.3	−121.4	−22487.1	−12.6	−2715.0	−17397.1	−37545.4	−351.1
d_6	−65.1	−88.9	−13.6	−3079.6	−20.7	−287.9	−1684.0	−2878.5	−36.5
AAD/%	0.011	0.004	0.007	0.006	0.001	0.001	0.018	0.090	0.398
bias/%	−0.003	−0.002	−0.002	0.001	0.001	0.005	0.001	−0.001	−0.260
SDV/%	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.12	0.39
rms/%	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.12	0.47
BWRS EoS (eq 2)									
B_0/cm^3·mol^{-1}	588.78	1195.27	1248.55	1298.41	782.41	583.89	583.46	161.82	49.25
A_0/bar·cm^6·mol^{-2}	$3.6382 \cdot 10^7$	$6.0367 \cdot 10^7$	$5.8394 \cdot 10^7$	$4.8784 \cdot 10^7$	$1.0420 \cdot 10^7$	$9.0880 \cdot 10^6$	$8.2451 \cdot 10^6$	$1.0837 \cdot 10^7$	$3.2916 \cdot 10^6$
C_0/bar·K^2·cm^6·mol^{-2}	$-1.8205 \cdot 10^{11}$	$-5.8636 \cdot 10^{11}$	$-9.9423 \cdot 10^{11}$	$-1.6021 \cdot 10^{12}$	$1.6581 \cdot 10^{11}$	$-1.1770 \cdot 10^{11}$	$-2.8911 \cdot 10^{11}$	$-1.1732 \cdot 10^{12}$	$-4.2846 \cdot 10^{11}$
D_0/bar·K^3·cm^6·mol^{-2}	$-1.1605 \cdot 10^{12}$	$4.3059 \cdot 10^{14}$	$2.9153 \cdot 10^{14}$	$-9.7077 \cdot 10^{13}$	$-3.6568 \cdot 10^{14}$	$-4.3049 \cdot 10^{14}$	$-4.0039 \cdot 10^{14}$	$-3.6721 \cdot 10^{14}$	$-3.4306 \cdot 10^{14}$
E_0/bar·K^4·cm^6·mol^{-2}	$-1.6497 \cdot 10^{16}$	$1.1154 \cdot 10^{17}$	$9.6377 \cdot 10^{16}$	$3.6313 \cdot 10^{16}$	$-8.8456 \cdot 10^{16}$	$-9.5340 \cdot 10^{16}$	$-8.6685 \cdot 10^{16}$	$-4.4563 \cdot 10^{16}$	$-5.8501 \cdot 10^{16}$
b/cm^6·mol^{-2}	$1.3682 \cdot 10^4$	$1.9848 \cdot 10^3$	$-9.3629 \cdot 10^3$	$-4.1759 \cdot 10^4$	$-5.9189 \cdot 10^4$	$-3.7706 \cdot 10^4$	$-3.7324 \cdot 10^4$	$1.7649 \cdot 10^4$	$1.2802 \cdot 10^4$
a/bar·cm^9·mol^{-3}	$8.6409 \cdot 10^7$	$3.8570 \cdot 10^8$	$3.6242 \cdot 10^8$	$3.7495 \cdot 10^8$	$3.5965 \cdot 10^8$	$3.0511 \cdot 10^8$	$2.8364 \cdot 10^8$	$1.2787 \cdot 10^9$	$1.0568 \cdot 10^9$
d/bar·K·cm^9·mol^{-3}	$1.4321 \cdot 10^{10}$	$-2.0406 \cdot 10^9$	$-1.0182 \cdot 10^{10}$	$-3.9993 \cdot 10^{10}$	$-5.2140 \cdot 10^{10}$	$-5.0105 \cdot 10^{10}$	$-5.3968 \cdot 10^{10}$	$-4.3668 \cdot 10^{11}$	$-3.9833 \cdot 10^{11}$
c/bar·K^2·cm^9·mol^{-3}	$-1.1012 \cdot 10^{14}$	$-6.4947 \cdot 10^{16}$	$-6.4947 \cdot 10^{16}$	$-6.4947 \cdot 10^{16}$	$1.1808 \cdot 10^{15}$	$1.1808 \cdot 10^{15}$	$1.1808 \cdot 10^{15}$	$-5.4909 \cdot 10^{13}$	$-4.4277 \cdot 10^{13}$
α/cm^9·mol^{-3}	$1.4074 \cdot 10^7$	$4.1622 \cdot 10^6$	$3.9282 \cdot 10^6$	$4.0377 \cdot 10^6$	$2.7461 \cdot 10^6$	$1.9905 \cdot 10^6$	$1.6366 \cdot 10^6$	$4.7435 \cdot 10^4$	$2.6134 \cdot 10^4$
u/cm^6·mol^{-2}	$1.5987 \cdot 10^3$	$1.8961 \cdot 10^9$	$1.8961 \cdot 10^9$	$1.8961 \cdot 10^9$	$3.8643 \cdot 10^7$	$3.8643 \cdot 10^7$	$3.8643 \cdot 10^7$	$-1.4122 \cdot 10^3$	$-1.0562 \cdot 10^3$
AAD/%	0.010	0.008	0.009	0.009	0.003	0.007	0.010	0.008	0.018
bias/%	−0.0006	−0.0002	−0.0003	−0.001	−0.0006	−0.0001	−0.0001	−0.0005	−0.0003
SDV/%	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02
rms/%	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02

Conclusions

Densities of butan-1-ol were measured and correlated with two different models. Both correlations were able to represent the density data within the experimental uncertainty. Our data were in excellent agreement with the correlations reported by Ihmels and Gmehling[15] and Cibulka and Zikova.[14] The volumetric behavior of CO_2 + butan-1-ol mixtures was measured at eight different compositions. There are no experimental volumetric data reported in the literature for this system. The experimental densities of the mixtures at fixed temperature were better represented with the BWRS EoS, and the accuracy of representation of the six-parameter equation decreased as the composition of CO_2 increased in the mixture. The volumes of mixing were calculated for the range of temperatures, pressures, and compositions measured here. The volumes of mixing were all negative in the range of measurements. The range of

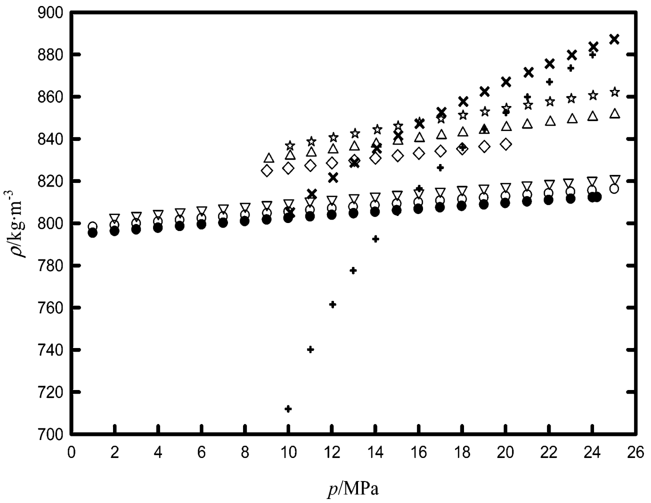

Figure 3. Experimental densities for CO_2 (1) + butan-1-ol (2) mixtures at 313.13 K as a function of pressure at the following compositions, x_1: ○, 0.0251; ▽, 0.0857; ◇, 0.3749; △, 0.4972; ☆, 0.5965; **x**, 0.8663; +, 0.9698; ●, butan-1-ol.

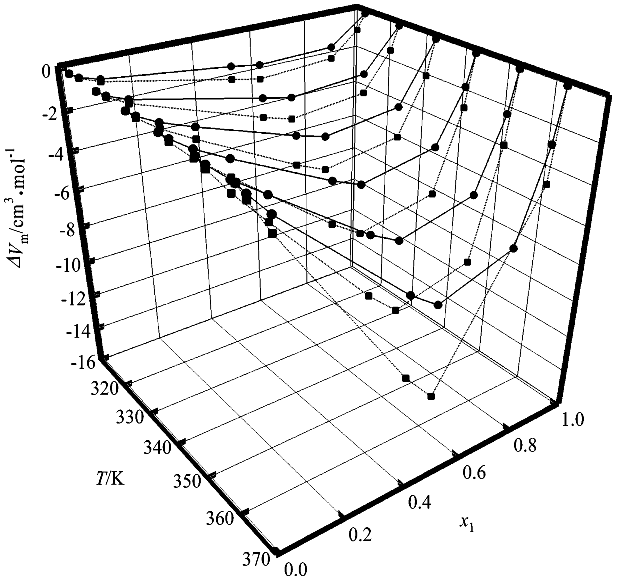

Figure 4. Volumes of mixing for the binary mixture CO_2 (1) + butan-1-ol (2) at temperatures between 313 and 363 K: ●, 21 MPa; ■, 25 MPa; —, and ···, lines to guide the eye.

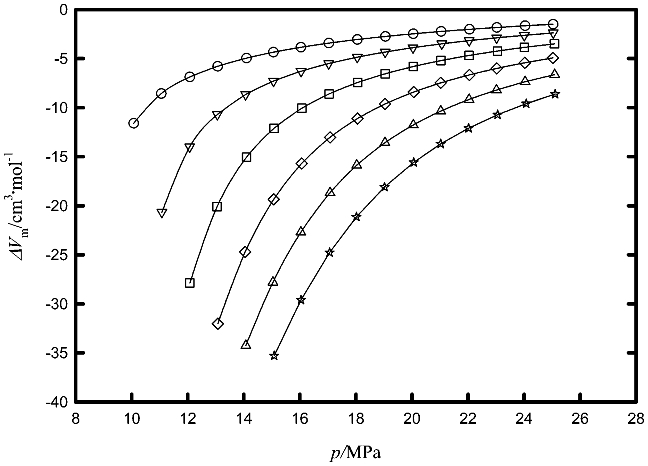

Figure 5. Volumes of mixing for CO_2 (1) + 1-butanol (2) mixtures at x_1 = 0.5965, at the following temperatures: ○, 313.16 K; ▽, 323.10 K; □, 333.00 K; ◇, 342.94 K; △, 352.88 K; ☆, 362.76 K; −, polynomial fitting for guiding the eye.

temperatures used in this study was selected taking into account the intended industrial application of CO_2 and binary mixtures (CO_2 + alcohol) as a supercritical solvent for extracting components from natural products.

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