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Density of Carbon Dioxide Expanded Ethanol at (313.2, 328.2, and 343.2) K

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The density of ethanol saturated and expanded with carbon dioxide (CO_2) was determined at (313.2, 328.2, and 343.2) K and up to pressures close to the mixture critical point using a novel device, consisting of a high-pressure view cell equipped with a sinker attached to a spring balance and a microscopic optical measuring device. The density of CO_2-expanded ethanol increased with pressure up to a maximum value at each temperature studied. A further increase in pressure caused a pronounced decrease in density until the mixture critical point was reached. The increase in density was temperature-dependent, with a less pronounced increase at higher temperatures. In the temperature and pressure range studied, the maximum increase in density of CO_2-expanded ethanol was (6.3, 4.8, and 3.7) % at (313.2, 328.2, and 343.2) K, respectively. At all temperatures investigated the density of CO_2-expanded ethanol exhibited the maximum value at pressures corresponding to a CO_2 density of about 190 $kg\cdot m^{-3}$, which translates into a reduced CO_2 density of 0.4. The experimental density data for CO_2-expanded ethanol were correlated to pressure and temperature; furthermore, a new correlation for CO_2-expanded ethanol density based on the reduced density of CO_2 and temperature was developed.

Introduction

Gas-expanded liquids have gained great attention in recent years because of their tunable solvent properties.[1] A gas-expanded liquid consists of an organic solvent equilibrated and expanded by dissolving a compressible gas such as CO_2 or ethane. CO_2, being nontoxic, nonflammable, and readily available at low cost, is preferably used to generate CO_2-expanded liquids. Thus, it is possible to obtain a wide range of solvent properties ranging from the neat organic solvent to supercritical CO_2 by adjusting the system pressure, temperature, and mixture composition. In this manner, a fairly polar solvent such as ethanol can be tuned by expanding it with pressurized CO_2. Thereby, its polarity can be altered and the solvent properties adjusted to solubilize or precipitate a specific compound. Furthermore, ethanol and CO_2 may be safely used in many processes and applications where a toxic solvent is not acceptable, such as in the food industry.

The density of CO_2-expanded ethanol is required for optimum process design. Density data of saturated CO_2-expanded ethanol are available in the literature.[2−8] However, there are discrepancies between and within some of the available density data. Besides being scattered, most of the published data fail to describe the maximum value of CO_2-expanded ethanol density and the pronounced decrease in the vicinity of the mixture critical point. Furthermore, even though correlations exist for specific temperatures,[9] on the basis of pressure, temperature, and compositional vapor−liquid equilibrium data using empirical equations or an equation of state approach,[7,10] it seems that a simple correlation based on pressure and temperature alone for the density of saturated CO_2-expanded ethanol covering the temperature range from (313.2 to 343.2) K has not been reported. Therefore, the objective of this study was to determine the density of saturated CO_2-expanded ethanol at (313.2, 328.2, and 343.2) K and pressures ranging from atmospheric pressure up to about (8 to 12) MPa, which is close to the mixture critical point. Another objective was to develop a correlation for saturated CO_2-expanded ethanol density covering the temperature range from (313.2 to 343.2) K and pressures up to the mixture critical point.

Experimental Section

Materials. For the density measurements food grade anhydrous ethanol (Commercial Alcohols, GreenField Ethanol, Inc., Winnipeg, MB, Canada) was used with a stated purity and water content of 99.99 % and 0.00008 volume fraction, respectively. Bone dry carbon dioxide with a purity of 99.9 % (Praxair, Edmonton, AB, Canada) was used for the density measurements. Both ethanol and carbon dioxide were used without further purification.

Apparatus. The experimental apparatus consisted of a high-pressure view cell equipped with a spring balance and has been described in detail elsewhere.[11] The main feature of the apparatus is a spring balance consisting of a glass sinker attached to an extension spring with a needle pointing at a microscopic glass scale. By means of a camera equipped with a microscopic lens, the position of the sinker submersed in the liquid can be determined precisely by locating the position of the needle pointing at the microscopic glass scale. Because of the magnification and high resolution of the images, the position of the sinker could be determined precisely by analyzing the images on the computer, so that density changes of about 0.1 $kg\cdot m^{-3}$ could be detected with this device. The view cell equipped with electric heaters was placed inside a temperature-controlled circulating air bath, which allowed maintaining the liquid circulated inside the view cell at a constant temperature to within ± 0.1 K. However, because of exothermic mixing effects following a stepwise increase in CO_2 pressure caused by the dissolution of CO_2 into ethanol, the liquid temperature fluctuated by about ± 0.5 K. Furthermore, a stepwise increase in CO_2 pressure of about (1 to 2) MPa also caused a spike in

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temperature due to the compression of CO_2, which along with the exothermic effects decayed over the time required for equilibration. Equilibration was achieved usually within 2 h by continuously pumping the liquid from the bottom of the view cell and spraying it into the pressurized CO_2 headspace at the top. The temperatures of the liquid inside the view cell and that of the air bath were measured by means of a custom-made data acquisition (DAQ) system calibrated against a precision digital thermometer (model 4000, Control Company, Friendswood, TX) with a resolution of 0.001 K using an insulated heating water bath (Haake H3, Karlsruhe, Germany). The DAQ system was connected to a computer and allowed continuous monitoring and recording of the temperatures with a resolution of 0.01 K. The overall estimated uncertainty in the reported temperature was about ± 0.15 K. The system was pressurized with CO_2 by means of a piston pump (ISCO model 250D, Isco Inc., Lincoln, NE). The pressure was monitored using a calibrated digital pressure indicator (Druck model DPI 104, General Electrics Sensing, Billerica, MA) with 0.05 % full scale accuracy and a maximum operating pressure of 35 MPa. The uncertainty in the pressure readings was ± 0.02 MPa.

Procedure. The apparatus was calibrated prior to each measurement by using pure CO_2 at various pressure levels ranging from about (20 to 30) MPa at the same temperature as the subsequent measurements. The density of CO_2 at each calibration point was calculated using the equation of state (EoS) of Span and Wagner.[12] According to the authors,[12] the estimated uncertainty in density is 0.03 % at pressures up to 30 MPa and temperatures up to about 350 K translating into the uncertainty in the calculated density of $\pm\, 0.25\ \mathrm{kg \cdot m^{-3}}$. With the uncertainty in the measured pressure and temperature in this study, the overall uncertainty of the calculated density used for calibration is about $\pm\, 0.75\ \mathrm{kg \cdot m^{-3}}$ or ± 0.1 %. The performance of the spring balance at elevated pressures was tested by measuring the density of a water–ethanol mixture under hydrostatic pressure up to 30 MPa which compared favorably to literature data with less than 0.1 % deviation, as described previously.[11] After calibration with CO_2 the apparatus was filled by injecting ethanol through the bottom port of the view cell using a syringe until the liquid level of ethanol was just above the window, ensuring that the sinker was completely submersed in liquid. Ethanol was warmed up to the desired temperature inside the view cell while being circulated using the circulation pump. Once the experimental temperature was reached, the circulation pump was switched off for a few seconds to avoid a downward flow of ethanol, which could cause vibrations and errors while measuring the position of the sinker. Then, as soon as the fluid inside the view cell came to rest, the position of the sinker was determined by taking an image of the needle attached to the hook holding the sinker pointing at the microscopic scale. After recording an image, the circulation pump was switched on again. During density measurements, images of the microscopic scale with the needle showing the position of the sinker were taken about every (15 to 30) min. The images were analyzed on the computer to determine the exact position of the sinker, which was translated into the density of the liquid using the calibration curve. The change in density could be followed in situ by observing the sinker position until a constant level was reached, which indicated equilibration. Usually, at least three images were taken and analyzed after equilibrium was reached at a given pressure setting for each replication. Three replications were performed for each density isotherm. A statistical analysis of the data was carried out using statistical software (SPSS version 17, SPSS Inc., Chicago, IL). Once equilibrium was reached and constant density observed, the pressure of the system was increased to the next desired level, and the liquid was circulated again to facilitate equilibration. The pressure was increased stepwise starting from atmospheric pressure up to about 12 MPa, until the density dropped and the mixture critical point was reached. Throughout the entire measurement cycle the temperature of the liquid phase was continuously monitored, ensuring that enough time was allowed for thermal equilibration after temperature fluctuations caused by the pressure increase. The increase in CO_2 pressure caused the liquid phase consisting of ethanol saturated with CO_2 to expand substantially, which can be more than 300 % in volume at elevated CO_2 pressures, as reported by Kordikowski et al.[2] Therefore, the liquid level was adjusted and kept constant just above the window of the view cell during experiments by carefully bleeding ethanol out of the bottom of the view cell after every stepwise pressure increase. Thereby, enough headspace inside the view cell was maintained for the ethanol to expand while reaching equilibrium.

Table 1. Comparison Between Experimental (exptl) and Literature Data (lit.) for the Density of Anhydrous Ethanol ($\rho_{\mathrm{EtOH}}{}^{0}$) at Atmospheric Pressure and T = (313.2, 328.2, and 343.2) K

	$\rho_{\mathrm{EtOH}}{}^{0}/\mathrm{kg \cdot m^{-3}}$			
T/K	exp	lit	ref	100 $\Delta\rho/\rho^{a}$
313.2	768.9 ± 1.73	768.0	13	0.12
		772.3	14	−0.43
		771.7	18	−0.36
		772.1	19	−0.41
328.2	752.7 ± 0.60	750.5	13	0.30
		758.1	14	−0.71
		758.4	18	−0.75
		758.5	19	−0.77
343.2	740.2 ± 0.12	732.3	13	1.08
		743.3	14	−0.41
		744.9	18	−0.63
		744.5	19	−0.57

[a] $100\ \Delta\rho/\rho = 100(\rho_{\mathrm{EtOH}}{}^{\mathrm{exp}} - \rho_{\mathrm{EtOH}}{}^{\mathrm{lit}})/(\rho_{\mathrm{EtOH}}{}^{\mathrm{lit}})$.

Results and Discussion

Density of CO_2-Expanded Ethanol. The accuracy of the system was first tested at atmospheric pressure by measuring the density of anhydrous ethanol at (313.2, 328.2, and 343.2) K. The average densities of ethanol determined after triplicate measurements with the spring balance after calibration with CO_2 were compared to literature data, as shown in Table 1. The density of anhydrous ethanol at atmospheric pressure agreed reasonably well with literature data[13,14] even though there were some inconsistencies in the literature data. However, the data obtained by using the following so-called Rackett equation for the density of pure ethanol at atmospheric pressure (eq 1) from ref 14 agree well with other literature data:[15−19]

$$\rho_{\mathrm{EtOH}}{}^{0} = \frac{M_{\mathrm{EtOH}} \cdot C_1}{C_2{}^{1+\left(1-\frac{T}{C_3}\right)^{C_4}}} \qquad (1)$$

where T is the temperature in K, M is the molecular weight of ethanol ($46.069\ \mathrm{kg \cdot kmol^{-1}}$), and the model parameters are $C_1 = 1.648$, $C_2 = 0.27627$, $C_3 = 513.92$, and $C_4 = 0.2331$. The deviations between the literature values reported for pure ethanol density and those found in this study could be attributed to the purity of the ethanol used. Ethanol of 99.99 % purity and water content of 0.00008 volume fraction as stated by the manufacturer was used in this study without any further treatment, whereas the reported purities of ethanol used in the literature were as follows: 0.99 mole fraction in ref 2, 0.998 in ref 5, ≥ 0.998

Table 2. Experimental Results[a] for the Density of CO_2-Expanded Ethanol (ρ_{EtOH}^{CX}) at T = (313.2, 328.2, and 343.2) K and up to Pressures near the Mixture Critical Point

T/K = 313.2				T/K = 328.2				T/K = 343.2			
P		ρ_{EtOH}^{CX}		P		ρ_{EtOH}^{CX}		P		ρ_{EtOH}^{CX}	
MPa	N	$kg \cdot m^{-3}$	Δ%[b]	MPa	N	$kg \cdot m^{-3}$	Δ%[b]	MPa	N	$kg \cdot m^{-3}$	Δ%[b]
0.10	9	768.9 ± 1.73	0.23	0.11	9	752.7 ± 0.60	0.08	0.16	9	740.2 ± 0.12	0.02
2.05	9	785.8 ± 1.65	0.21	2.20	9	766.2 ± 0.81	0.11	2.27	9	749.8 ± 0.33	0.04
4.40	9	802.6 ± 1.17	0.15	4.38	9	777.2 ± 0.21	0.03	4.36	9	758.3 ± 0.40	0.05
5.86	9	813.0 ± 1.04	0.13	5.86	9	784.2 ± 0.53	0.07	5.82	12	764.5 ± 0.64	0.08
6.56	9	817.2 ± 1.18	0.14	6.44	3	786.5 ± 0.13	0.02	7.17	9	766.5 ± 0.29	0.04
7.27	15	813.7 ± 1.59	0.20	7.13	9	788.3 ± 0.30	0.04	7.85	9	767.8 ± 0.45	0.06
7.84	8	793.5 ± 5.87	0.74	7.81	6	789.2 ± 0.19	0.02	8.54	9	767.0 ± 0.49	0.06
8.17	3	762.5 ± 0.10	0.01	8.17	9	788.7 ± 0.12	0.01	9.24	9	765.2 ± 0.46	0.06
8.51	11	734.3 ± 5.69	0.77	8.52	9	786.6 ± 0.35	0.04	9.93	9	760.7 ± 0.85	0.11
				8.86	6	782.4 ± 0.16	0.02	10.61	9	750.1 ± 1.42	0.19
				9.21	9	774.6 ± 0.17	0.02	11.22	11	734.2 ± 1.97	0.27
				9.56	6	755.2 ± 0.74	0.10				
				9.90	6	730.1 ± 2.12	0.29				

[a] The uncertainties were determined from the standard deviation of the mean of N observations at a confidence interval of 95 %. [b] Δ% denotes the variability as a percentage determined from the standard deviation of the mean of N observations at a confidence interval of 95 %.

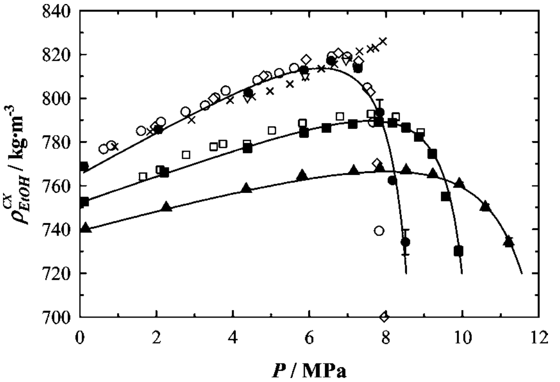

Figure 1. Measured density of saturated CO_2-expanded ethanol (ρ_{EtOH}^{CX}) versus pressure of CO_2 at various temperatures from this study: ●, 313.2 K; ■, 328.2 K; ▲, 343.2 K. Error bars represent confidence interval of 95 % for N observations (see Table 2). Lines were calculated using eq 2. Literature data at T = 313.2 K: ○, ref 6; ×, ref 4; ▽, ref 8; ◇, ref 9. T = 328.2 K: □, ref 6.

with water of < 0.002 mass fraction in ref 15, 0.995 volume fraction in ref 16, > 0.998 in refs 3 and 4, and 0.997 with water of 0.003 mass fraction in ref 17. In some reports the purity of ethanol was not specified.[7] Furthermore, for the ethanol used in this study the manufacturer stated a density of 788.4 $kg \cdot m^{-3}$ at 293.15 K, which is slightly lower than the value obtained by using eq 1 (790.4 $kg \cdot m^{-3}$), indicating that, as expected, the density of ethanol was affected by purity. In addition, using pressurized CO_2 for the calibration of the spring balance added uncertainty to the measured density data as described above. Nevertheless, the agreement with literature data seemed acceptable considering the differences in ethanol purities between different studies.

The isotherms for the density of CO_2-expanded ethanol were measured in triplicate at (313.2, 328.2, and 343.2) K up to about 12 MPa. The results for density of CO_2-expanded ethanol are listed in Table 2 and illustrated in Figure 1, with the corresponding confidence intervals of 95 % based on the standard deviation of the mean of N observations at each pressure level. The precision of the apparatus at elevated pressures was acceptable considering that the variability in the measured data was less than 0.25 % for pressures up to a level where the maximum density was reached (Table 2). The pressure where the maximum density was reached was temperature-dependent. At pressures above the maximum density in the vicinity of the mixture critical point, the variability in the measured density data increased.

Table 3. Parameters for the Correlation Given in Equation 2

i	A_i
1	$-8.6337 \cdot 10^{-1}$
2	$1.0355 \cdot 10^{3}$
3	$3.6834 \cdot 10^{-3}$
4	-1.5085
5	$2.7000 \cdot 10^{1}$
6	$5.1143 \cdot 10^{-3}$
7	9.7372
8	$-4.7748 \cdot 10^{3}$
9	$9.1586 \cdot 10^{-3}$
10	-6.3279
11	$1.0985 \cdot 10^{3}$

CO_2-Expanded Ethanol Density: Correlation to Temperature and Pressure. The measured density of saturated CO_2-expanded ethanol (ρ_{EtOH}^{CX} in $kg \cdot m^{-3}$) was correlated to CO_2 pressure (P in MPa) and temperature (T in K) by using the following empirical equation:

$$\rho_{EtOH}^{CX} = \frac{k_1(T) + k_2(T) \cdot P}{1 + k_3(T) \cdot P + k_4(T) \cdot P^2} \qquad (2)$$

with the temperature-dependent coefficients k_1 to k_4 defined as follows:

$$k_1(T) = A_1 T + A_2 \qquad (3)$$

$$k_2(T) = A_3 T^2 + A_4 T + A_5 \qquad (4)$$

$$k_3(T) = (A_6 T^2 + A_7 T + A_8) \cdot 10^{-4} \qquad (5)$$

$$k_4(T) = (A_9 T^2 + A_{10} T + A_{11}) \cdot 10^{-4} \qquad (6)$$

The parameters A_1 to A_{11} for eqs 3 to 6 are listed in Table 3. The correlation is valid within the temperature range of T = (313.2 to 343.2) K. The deviations between the experimental density values and the correlated density using eq 2 are illustrated in Figure 2. The deviation between calculated and experimental values is less than about 0.5 % for pressures up to the maximum density. Above the maximum density the deviation is slightly more pronounced (< 1.5 %) because of the much greater sensitivity of the measured density to small pressure variations in the vicinity of the mixture critical point, which causes greater uncertainty. The deviations between correlated density values of CO_2-expanded ethanol using eq 2 and values found in the literature[2,4−7] in the range of T = (298.2 to 355.0) K are illustrated in Figure 3. To test the performance of the correlation outside of the temperature range of T = (313.2

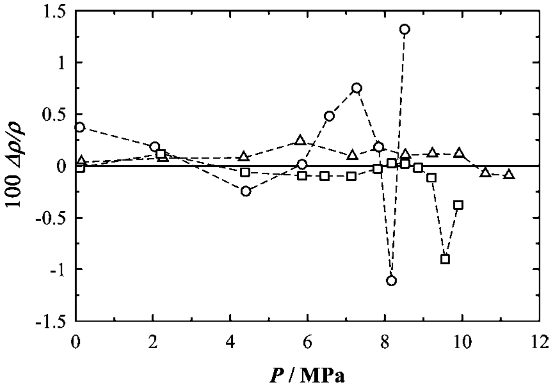

Figure 2. Deviation, $\Delta\rho/\rho = (\rho_{\mathrm{exp}} - \rho_{\mathrm{calc}})/\rho_{\mathrm{calc}}$, between the experimental density values found in this study and calculated density values obtained by using eq 2 for CO_2-expanded ethanol at various temperatures: ○, 313.2 K; □, 328.2 K; △, 343.2 K.

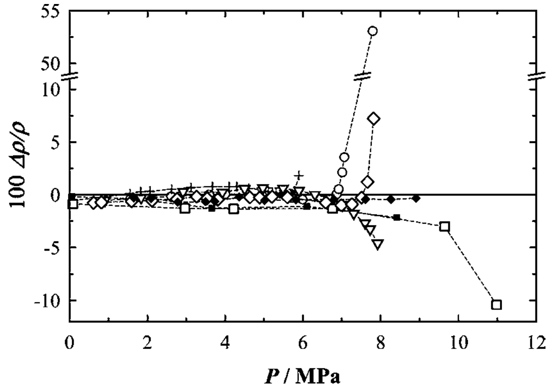

Figure 3. Deviation, $\Delta\rho/\rho = (\rho_{\mathrm{calc}} - \rho_{\mathrm{lit}})/\rho_{\mathrm{lit}}$, between the density values calculated using the correlation (eq 2) and available literature data at various temperatures: +, 298.2 K, ref 2; ○, 308.2 K, ref 7; ▽, 313.2 K, ref 4; ◇, 313.2 K, ref 6; □, 336.0 K, ref 5; ◆, 338.2 K, ref 6; ■, 355.0 K, ref 5.

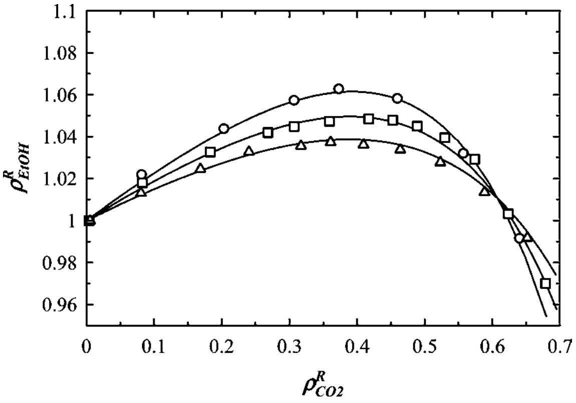

Figure 4. Relative density of saturated CO_2-expanded ethanol ($\rho_{\mathrm{EtOH}}{}^{\mathrm{R}}$) versus the reduced density of CO_2 ($\rho_{\mathrm{CO2}}{}^{\mathrm{R}}$) from this study at various temperatures: ○, 313.2 K; □, 328.2 K; △, 343.2 K. Lines were calculated using eq 10.

to 343.2) K of this study, the density of CO_2-expanded ethanol was also correlated at $T = (298.2, 308.2, \text{and } 355.0)$ K using eq 2. The deviations were less than 5 % at pressures up to about 7.5 MPa for all temperatures. However, the literature data of comparison are quite scattered. Also, because not all literature data exhibit the sharp decrease in density at elevated pressure, some of the data may not be reliable in the vicinity of the mixture critical point, such as those reported in refs 3 to 5. The data of ref 3 have been omitted in our comparison because the reported values are about 18 % below comparable literature data. The data for CO_2-expanded ethanol density reported in refs 2, 6, and 7 seem to be more accurate at pressures above the maximum density, since they follow a pronounced decrease close to the mixture critical point. As anticipated, the deviation between the correlation (eq 2) and literature values outside of the recommended temperature range can be rather large especially at elevated pressures. Therefore, the correlation (eq 2) should preferably be used within the temperature limit of $T = (313.2 \text{ to } 343.2)$ K from atmospheric pressure up to pressure levels close to the mixture critical point. The pressures required to reach the mixture critical point of the system CO_2–ethanol were reported by Joung et al.[20] for the temperature range from (313.4 to 344.75) K. The reported pressures[20] for the mixture critical point compare fairly well with the pressures obtained in this study where the isotherms exhibit a sudden decrease. Within the pressure region between that corresponding to the density maximum and the mixture critical point the uncertainty in the measured data and therefore in the correlation is larger. Therefore, the suggested upper pressure limit (P_{limit} in MPa), which is temperature-dependent, for the correlation (eq 2) can be evaluated using the following empirical equation (eq 7), which was derived by correlating the pressures for the mixture critical point from ref 20 to temperature (T in K):

$$P_{\mathrm{limit}} = 0.1233T - 30.5 \tag{7}$$

CO_2-Expanded Ethanol Density: Correlation to Reduced CO_2 Density. The density of CO_2-expanded ethanol ($\rho_{\mathrm{EtOH}}{}^{\mathrm{CX}}$) was further analyzed by plotting the relative density of ethanol ($\rho_{\mathrm{EtOH}}{}^{\mathrm{R}}$) against the reduced density of CO_2 ($\rho_{\mathrm{CO2}}{}^{\mathrm{R}}$), which were calculated as follows:

$$\rho_{\mathrm{EtOH}}{}^{\mathrm{R}} = \frac{\rho_{\mathrm{EtOH}}{}^{\mathrm{CX}}(P, T)}{\rho_{\mathrm{EtOH}}{}^{0}(P_0, T)} \tag{8}$$

where $\rho_{\mathrm{EtOH}}{}^{0}$ is the density of ethanol at atmospheric pressure P_0 and temperature T and $\rho_{\mathrm{EtOH}}{}^{\mathrm{CX}}$ is the density of CO_2-expanded ethanol at elevated pressure P and temperature T. The reduced density of CO_2 was calculated using the density of CO_2 at the critical point ($\rho_{\mathrm{CO2}}{}^{\mathrm{C}} = 467.6\ \mathrm{kg\cdot m^{-3}}$) from literature[21] and calculating the density of CO_2 (ρ_{CO2}) at pressure P and temperature T using the EoS from Span and Wagner[12] according to:

$$\rho_{\mathrm{CO2}}{}^{\mathrm{R}} = \frac{\rho_{\mathrm{CO2}}(P, T)}{\rho_{\mathrm{CO2}}{}^{\mathrm{C}}} \tag{9}$$

The results are presented in Figure 4, which shows a distinct trend for the density of CO_2-expanded ethanol with the reduced density of CO_2. The maximum density of CO_2-expanded ethanol was observed at a reduced CO_2 density of about 0.4 at all temperatures investigated. Furthermore, the curves intersected at $\rho_{\mathrm{CO2}}{}^{\mathrm{R}} = 0.6$, where the density of the CO_2-expanded ethanol reached a value close to $\rho_{\mathrm{EtOH}}{}^{0}$. Because of the striking relationship between the reduced density of CO_2 ($\rho_{\mathrm{CO2}}{}^{\mathrm{R}}$) and the reduced density of CO_2-expanded ethanol ($\rho_{\mathrm{EtOH}}{}^{\mathrm{R}}$), the following correlation was developed:

$$\rho_{\mathrm{EtOH}}{}^{\mathrm{R}} = \frac{1 + h_1(T)\cdot\rho_{\mathrm{CO2}}{}^{\mathrm{R}}}{1 + h_2(T)\cdot\rho_{\mathrm{CO2}}{}^{\mathrm{R}} + h_3(T)\cdot(\rho_{\mathrm{CO2}}{}^{\mathrm{R}})^2} \tag{10}$$

with the temperature-dependent parameters $h_i(T)$, with $i = 1$ to 3 being defined as:

$$h_i(T) = B_i + C_iT \tag{11}$$

using the temperature T in K and the parameters B_i and C_i listed in Table 4.

Table 4. Parameters for the Correlation Given in Equation 10

i	B_i	C_i
1	−2.2890	$3.9840 \cdot 10^{-3}$
2	−3.3291	$6.5564 \cdot 10^{-3}$
3	1.7185	$-4.2896 \cdot 10^{-3}$

With this correlation the density of CO_2-expanded ethanol (ρ_{EtOH}^{CX}) can be calculated up to pressures corresponding to a reduced CO_2 density of $\rho_{CO2}^{R} = 0.7$. The deviations between the calculated values for density of CO_2-expanded ethanol obtained by using eq 10 together with experimental values for ρ_{EtOH}^{0} listed in Table 1, and the experimental values listed in Table 2 are illustrated in Figure 5. The deviations are less than about 0.5 % over the entire pressure range for which $\rho_{CO2}^{R} < 0.7$. The performance of this correlation is superior to that given in eq 2. However, it requires the calculation of ρ_{CO2}^{R} using the Span and Wagner EoS.[12] The correlation (eq 10) was also tested against literature data[2,6,7] at temperatures of T = (293.2, 308.2, 313.2, and 328.2) K. For this purpose, the density of ethanol at atmospheric pressure ρ_{EtOH}^{0} was first calculated using eq 1 at T = (293.2, 308.2, 313.2, and 328.2) K. Then, the reduced density of CO_2 (ρ_{CO2}^{R}) was computed at the pressure and temperature conditions T = (293.2, 308.2, 313.2, and 328.2) K for which densities of CO_2-expanded ethanol were reported in refs 2, 6, and 7 using the Span and Wagner EoS.[12] Finally, the density of CO_2-expanded ethanol was calculated using eq 10 with the values of ρ_{EtOH}^{0} obtained from eq 1 and compared to the density values reported in refs 2, 6, and 7. The results are plotted in Figure 6, which shows that the correlation (eq 10 with eq 1) was able to predict the density of CO_2-expanded ethanol both inside and outside of the temperature range of this study quite well, with deviations of less than 1 % up to the maximum density. Furthermore, it is remarkable that the correlation based on the reduced density of CO_2 also predicted reasonably well the density of CO_2-expanded ethanol at temperatures below the critical temperature of CO_2 (T_c = 304.25 K). However, as mentioned above, the correlation (eq 10) should only be used up to a reduced CO_2 density of 0.7 ($\rho_{CO2}^{R} < 0.7$), if the temperature is above the critical temperature of CO_2 ($T > T_c$). However, if the temperature is below the critical temperature ($T < T_c$), the correlation works well only up to pressures where CO_2 is still in the form of vapor and not liquefied. For example, at T = 293.2 K the maximum density of CO_2-expanded ethanol could be calculated at a pressure of 5.7 MPa coinciding with the transition from vapor to liquid. At that point (T = 293.2 K and P = 5.7 MPa) the reduced density of CO_2 is close to 0.4, the same value as that found for temperatures above the critical temperature of CO_2. A further increase in pressure leads to the decrease in CO_2-expanded ethanol density as reported in ref 2. At T = 293.2 K and P = 5.73 MPa, the vapor to liquid phase transition of CO_2 has occurred, leading to a liquid CO_2 density of 773.4 kg·m^{-3}, which translates into a reduced density of $\rho_{CO2}^{R} = 1.6$. Therefore, the upper limit for the correlation (eq 10) was exceeded ($\rho_{CO2}^{R} > 0.7$), and CO_2-expanded ethanol density could not be calculated beyond that pressure using eq 10. Nevertheless, as evidenced in Figure 6, the correlation performed well up to the maximum density of CO_2-expanded ethanol at all temperatures. The deviations between the density values reported in refs 2, 6, and 7 and the correlated values for CO_2-expanded ethanol using eqs 10 and 1 to compute ρ_{EtOH}^{CX} and ρ_{EtOH}^{0}, respectively, were generally less than 1 % up to pressures corresponding to the maximum density. However, at pressures above the maximum density closer to the mixture critical point the deviations between the correlation (eq 10 with eq 1) and the literature data were larger, which in the case of data from ref 7 at a temperature of 308.2 K reached up to 37 % for pressures above 7 MPa. Moreover, the deviations may be attributed to the larger variability in the available experimental values in the pressure region close to the mixture critical point potentially due to the increased pressure sensitivity for the density of CO_2-expanded ethanol.

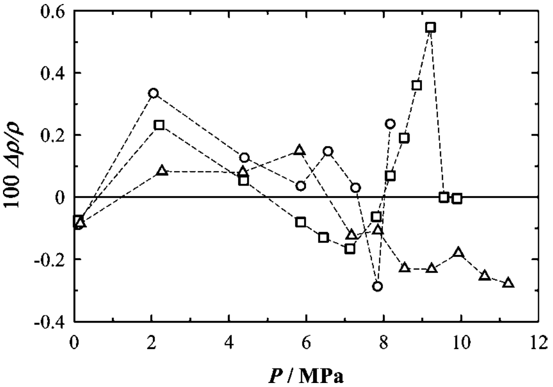

Figure 5. Deviation, $\Delta\rho/\rho = (\rho_{exp} - \rho_{calc})/\rho_{calc}$, between the experimental density values found in this study and the calculated density values obtained by using eq 10 for CO_2-expanded ethanol at various temperatures: ○, 313.2 K; □, 328.2 K; △, 343.2 K.

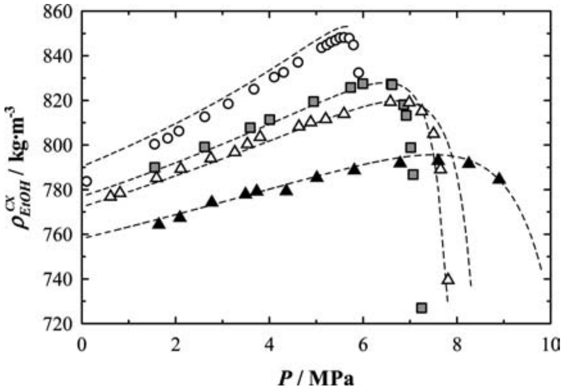

Figure 6. Comparison between the density values of CO_2-expanded ethanol (ρ_{EtOH}^{CX}) calculated using the correlation based on the reduced density of CO_2 (eq 10) and the values available in the literature at various pressures and temperatures: ○, 293.2 K, ref 2; □, 308.2 K, ref 7; △, 313.2 K, ref 6; ▲, 328.2 K, ref 6. The dashed lines were calculated using eqs 1 and 10 to obtain ρ_{EtOH}^{0} and ρ_{EtOH}^{CX}, respectively.

Conclusions

The density of saturated CO_2-expanded ethanol (ρ_{EtOH}^{CX}) was measured in triplicate along isotherms at T = (313.2, 328.2, and 343.2) K and pressures up to the mixture critical point using a spring balance equipped with a glass sinker. The density was first correlated to pressure and temperature using an empirical equation, which described ρ_{EtOH}^{CX} well within the temperature limits of this study and up to pressures in the vicinity of the mixture critical point. Furthermore, a novel correlation was presented on the basis of the reduced density of CO_2 (ρ_{CO2}^{R}) and temperature. The correlation based on reduced CO_2 density, along with correlations from literature for the density of ethanol at atmospheric conditions, can be used to calculate the density of saturated CO_2-expanded ethanol satisfactorily up to a reduced CO_2 density of about 0.7 ($\rho_{CO2}^{R} < 0.7$). Furthermore, it was shown that the correlation based on ρ_{CO2}^{R} was able to predict the density of CO_2-expanded ethanol outside of the temperature range of this study as well. Even at temperatures below the critical temperature of CO_2 ($T < T_c = 304.25$ K) the correlation performed reasonably well up to the maximum density of CO_2-expanded ethanol with deviations of less than 1 %. At all temperatures investigated and at those evaluated outside of the temperature range of this study, the maximum density of CO_2-expanded ethanol was observed at a pressure corresponding to a reduced CO_2 density of about 0.4 ($\rho_{CO2}^R = 0.4$).

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