# High-Pressure Vapor−Liquid Equilibria, Liquid Densities, and Excess Molar Volumes for the Carbon Dioxide + 2-Propanol System from (308.10 to 348.00) K

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Vapor−liquid equilibrium data and volumetric properties (density and excess molar volumes) of the carbon dioxide (1) + 2-propanol (2) system have been determined for seven molar compositions, $z_1$, close to 0.15, 0.20, 0.42, 0.60, 0.80, 0.95, and 0.97, using a vibrating tube densimeter, which takes advantage of a forced path mechanical calibration model. The Peng−Robinson equation of state including Panagiotopoulos and Reid mixing rules is used to correlate the data. Comparison of the new data with selected literature data and correlated results shows good consistency agreement, demonstrating the reliability of the data presented herein.

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## 1. Introduction

Supercritical fluid extraction (SFE) is a more and more used technology. It is receiving increasing attention from both industry and academic researchers. The basic steps of a SFE process are the following:

(1) The material (solid or liquid) containing the compound to be extracted is put in contact with a high-pressure supercritical fluid (SF) (pure or mixed with a cosolvent for selectivity purposes),[1] and the compound is partially dissolved selectively into the supercritical phase.

(2) The compound can be recovered by a pressure or temperature change of the system. SFE has several advantages as many substances are more soluble in high-pressure supercritical fluids than in liquids at ambient conditions. As diffusion coefficients are higher in supercritical fluids than in liquids, mass transfers are consequently faster. The viscosity of SF is much lower than that of liquids, which is also clearly advantageous.

The most common compound used as a SF in SFE is carbon dioxide: $CO_2$ is a very attractive compound because it is cheap, nontoxic, and its critical temperature (304.21 K) is close to the ambient temperature, which allows smaller heating−cooling costs. $CO_2$ at high pressure is also a good sterilizer for food products. Industry needs very accurate thermodynamic models for designing and optimizing SFE separation processes. Among the important properties used in SFE are the volumetric properties.

$CO_2$ cannot be universally used, as it is a nonpolar compound. Then, it has no strong interaction with polar components and consequently no favored selectivity. To solve this problem, cosolvents are generally added to $CO_2$. Cosolvents change the SF fluid density and critical properties. In addition, they can produce strong interactions with solutes, i.e., hydrogen bonds, dipole interactions, etc. In this paper, the studied cosolvent is isopropanol. It is a polar compound able to create H bonds with solutes to be extracted selectively.

The use of cosolvents (such as alcohols) in combination with one supercritical solvent (e.g., carbon dioxide) has motivated new phase equilibrium measurements. Process design and optimization of operating conditions relies strongly on accurate thermodynamic data in large temperature and pressure ranges. In this paper, we have considered 2-propanol as the cosolvent to $CO_2$. Limited information is available about vapor−liquid equilibrium data, and even less is available about $P\rho T$ properties in the liquid phase for the carbon dioxide (1) + 2-propanol (2) binary system as indicated in refs 2 and 3.

A “synthetic open circuit method” taking advantage of a vibrating tube densimeter is used to determine, at and outside saturation conditions, volumetric properties in isothermal conditions of either pure compounds or mixtures in vapor, liquid, and supercritical conditions. The Peng−Robinson equation of state[4] (PR EoS) is used to correlate the data at saturation.

## 2. Experimental Section

***Apparatus.*** A detailed description of the typical apparatus is available elsewhere (Bouchot and Richon[5]). Its flow diagram is presented in Figure 1. The apparatus used in this work utilizes an Anton Paar DMA 512P vibrating tube (Figure 1). The vibrating tube is made of Hastelloy and can work up to 70 MPa. It has already provided data for the ethane and hydrogen sulfide binary mixture.[6] The period of the vibration, $\tau$, in seconds, is recorded with a HP53131A data acquisition unit (12). The uncertainty of vibrating period values is $\pm\ 10^{-8}$ s. The temperature of the vibrating tube is controlled by a regulated liquid bath (LAUDA RE206) with stability within ± 0.01 K. The temperature of the remaining parts of the circuit is regulated by a (HUBER Variostat P1C50P) liquid bath. Temperatures are measured by two Pt100 probes (11 and 14) connected to the HP34970A data acquisition unit (13). These Pt100 probes are periodically calibrated against a 25 Ω reference thermometer (TINSLEY Precision Instrument) certified by the Laboratoire National d’Essais (Paris, France). Resulting uncertainties in temperatures are within ± 0.01 K. A vacuum was achieved by means of a vacuum pump (AEG type LN38066008). Pressures are measured using three pressure transducers (Druck PTX611) of three complementary ranges: (0 to 0.2) MPa, (0 to 5) MPa, and (0 to 40) MPa. These sensors were calibrated against a dead weight pressure balance (Desgranges & Huot model 5202S) for the (0.3 to 40) MPa pressure range and against an electronic balance (fundamental digital pressure standard, Desgranges & Huot model 24610, France) for pressures below 0.3 MPa. The

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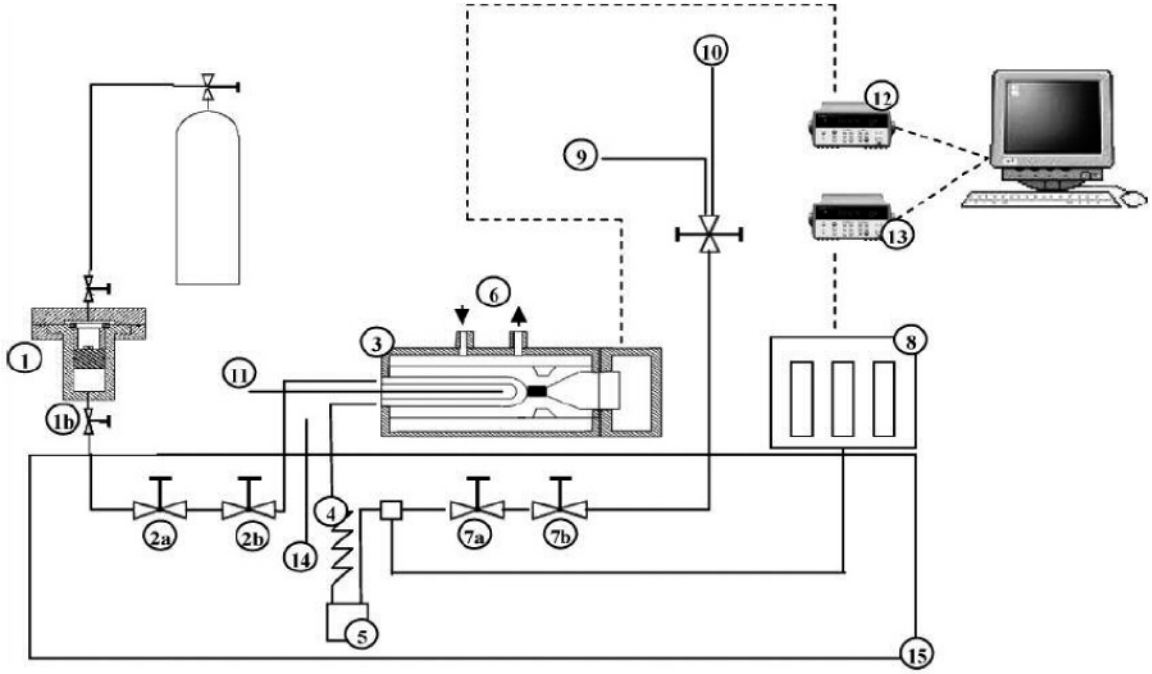

**Figure 1.** Flow diagram of the equipment: 1, loading cell; 2a and 2b, regulating and shut-off valves; 3, DMA 512 P densimeter (Anton Paar); 4, heat exchanger; 5, bursting disk; 6, inlet of the temperature regulating fluid; 7a and 7b, regulating and shut-off valves; 8, pressure sensors maintained at constant temperature (373.15 K); 9, vacuum pump; 10, vent; 11, vibrating cell temperature sensor; 12, HP 53131A unit; 13, HP34970A unit; 14, bath temperature sensor; 15, liquid bath.

**Table 1. Pure Compound Properties (from Ref 12)**

| compd | formula | CAS No. | $M$<br>kg·mol$^{-1}$ | $P_C$<br>MPa | $T_C$<br>K | $v_C \cdot 10^{-5}$<br>m$^3$·mol$^{-1}$ | $\rho_C$<br>kg·m$^{-3}$ |
|---|---|---|---|---|---|---|---|
| carbon dioxide | $CO_2$ | 124-38-9 | 0.04401 | 7.374 | 304.12 | 9.4 | 468.2 |
| 2-propanol | $C_3H_8O$ | 67-63-0 | 0.0601 | 4.762 | 508.3 | 22 | 273.2 |

pressure transducers are connected to the HP34970A data acquisition unit. Real time data are recorded every 3 s by a computer linked to both HP units. Knowledge of the composition of the mixtures prepared inside the loading cell (1) is deduced from its double weighing before and after introducing each component through a previously evacuated line. A CC3000 analytical balance, from Sartorius AG Göttingen, was used to get accurate mass values. Uncertainties of mass determinations are $\pm\ 10^{-4}$ g.

***Materials.*** Carbon dioxide is from Air Liquide with a certified purity higher than 99.99 % volume fraction. 2-Propanol is from Prolabo with a certified purity higher than 99 % volume fraction (see Table 1).

***Experimental Procedure.*** First, the baths are programmed at constant temperatures with a small temperature difference corresponding to the requested measurements: bubble or dew pressures (see ref 5 for details). The whole circuit was evacuated using the vacuum pump (with the 9, 7a, and 7b valves open while valves 10 and 2b are closed). During this time, the mixture was prepared into the loading cell (1) according to the method described by Bouchot and Richon[5] and Galicia-Luna et al.[7] A few period values are recorded to have a reference vibrating period at the lowest accessible pressure ($< 5 \cdot 10^{-4}$ MPa) with classical vacuum pumps. After connecting the loading cell to the circuit through valve 1b, a vacuum is achieved up to 1b by opening valves 2a and 2b. The loading cell is also connected to a high-pressure cylinder to pressurize the mixture to a pressure much higher than its bubble point pressure, maintaining it in the homogeneous liquid state even when loading the vibrating tube. Then, valves 7a and 2b are closed and valve 1b is opened. Small amounts of fluid (small flow rates controlled by regulating valve 2b) can be continuously introduced into the vibrating tube. Then, the pressure increases continuously up to the dew point at a controlled rate with a maximum of 0.005 MPa·s$^{-1}$. During this process, the fluid is assumed to be in equilibrium, and pressure, period, and temperature ($P\tau T$) are recorded every 2 s. After recording the dew point (determined through the drastic slope change observed in the $P\tau$ or $P\rho$ curves) behavior going from single phase to diphasic properties (as described by Bouchot and Richon[5]), the fluid is fully condensed in the whole circuit by increasing pressure up to the chosen maximum pressure of the study (approximately from (10 to 15) MPa in this work). Valves 9 and 10 were closed, and valve 7a was opened. The condensation over a pressure range leads to a composition gradient inside the vibrating tube and circuit. It should be noted that it is necessary to introduce a fresh mixture from the loading cell to purge the circuit. By opening valve 10, the fluid was allowed to circulate (it is assumed that the liquid inside the vibrating tube is representative of the fluid from the loading cell when the measured period remains constant and is not dependent on further purging). The liquid phase is studied from the chosen upper pressure limit down to the bubble point determined through the drastic change in the $P\tau$ (or $P\rho$) behaviors going from single phase to diphasic properties as described by Bouchot and Richon.[5] The pressure decreases continuously at a controlled rate of a maximum of 0.005 MPa·s$^{-1}$ using regulating valve 7a. During this process, the fluid is assumed to be in equilibrium, and pressure, period ($\tau$), and temperature ($P\tau T$) are recorded every 2 s. Periods are converted into density values using the forced path mechanical calibration model (FPMC, Bouchot and Richon[8]), whose parameters were calculated from (PFT) data of a reference fluid (R134a), whose thermodynamic properties are well described by Tillner-Roth and Baehr.[9]

***Estimation of Uncertainties (Taking into Account Expanded Uncertainties and Co*v*erage Factors as Described in http://physics.nist.go*v*/cuu/Uncertainty/index.html).*** The global un-

**Table 2. Liquid Densities and Excess Molar Volumes of the Carbon Dioxide (1) + 2-Propanol (2) Binary System for Seven Mole Fractions and Five Temperatures at Various Pressures**

| $P$ / MPa | $\rho$ / kg·m$^{-3}$ | $v^E$ / cm$^3$·mol$^{-1}$ | $P$ / MPa | $\rho$ / kg·m$^{-3}$ | $v^E$ / cm$^3$·mol$^{-1}$ | $P$ / MPa | $\rho$ / kg·m$^{-3}$ | $v^E$ / cm$^3$·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| $x_1 = 0.139_6$; $T$/K = 308.11 | | | $x_1 = 0.139_6$; $T$/K = 313.09 | | | $x_1 = 0.139_6$; $T$/K = 323.05 | | |
| 1.814 | 786.2 | −173.5 | 2.502 | 781.7 | −122.1 | 2.995 | 771.3 | −103.2 |
| 2.252 | 786.8 | −135.1 | 3.002 | 782.3 | −97.8 | 3.503 | 771.9 | −84.9 |
| 3.003 | 787.7 | −95.2 | 3.513 | 782.9 | −80.0 | 4.003 | 772.6 | −71.4 |
| 3.206 | 787.9 | −87.5 | 4.008 | 783.5 | −67.0 | 4.494 | 773.2 | −61.1 |
| 3.427 | 788.2 | −80.2 | 4.501 | 784.1 | −56.8 | 5.074 | 773.9 | −51.3 |
| 3.607 | 788.4 | −74.9 | 5.001 | 784.7 | −48.5 | 5.511 | 774.5 | −45.3 |
| 4.089 | 788.9 | −62.9 | 5.497 | 785.3 | −41.5 | 6.033 | 775.2 | −39.2 |
| 5.013 | 789.9 | −46.1 | 6.023 | 785.9 | −35.3 | 7.021 | 776.4 | −29.9 |
| 5.503 | 790.5 | −39.3 | 6.504 | 786.5 | −30.3 | 7.514 | 777.1 | −26.1 |
| 6.019 | 791.0 | −33.0 | 7.026 | 787.1 | −25.5 | 8.002 | 777.6 | −22.7 |
| 6.518 | 791.7 | −27.7 | 7.489 | 787.6 | −21.5 | 8.527 | 778.3 | −19.4 |
| 7.009 | 792.2 | −22.8 | 7.998 | 788.2 | −17.2 | 9.033 | 778.8 | −16.5 |
| 7.512 | 792.7 | −17.6 | 8.509 | 788.8 | −12.9 | 9.519 | 779.4 | −14.0 |
| 8.016 | 793.3 | −10.5 | 8.995 | 789.3 | −9.4 | | | |
| 8.530 | 793.9 | −7.2 | 9.503 | 789.8 | −7.6 | | | |
| 8.990 | 794.3 | −6.3 | | | | | | |
| 9.498 | 794.8 | −5.7 | | | | | | |
| $x_1 = 0.139_6$; $T$/K = 332.99 | | | $x_1 = 0.139_6$; $T$/K = 347.95 | | | $x_1 = 0.2003_4$; $T$/K = 308.11 | | |
| 2.861 | 759.8 | −114.1 | 3.317 | 742.5 | −102.2 | 3.514 | 792.7 | −110.5 |
| 3.000 | 760.0 | −107.9 | 3.516 | 742.7 | −95.3 | 4.006 | 793.4 | −92.1 |
| 3.297 | 760.4 | −96.3 | 4.002 | 743.5 | −81.4 | 4.510 | 794.0 | −77.2 |
| 3.495 | 760.7 | −89.6 | 4.464 | 744.3 | −71.0 | 5.028 | 794.7 | −64.8 |
| 4.008 | 761.5 | −75.4 | 5.008 | 745.1 | −61.2 | 5.504 | 795.3 | −55.2 |
| 4.509 | 762.2 | −64.6 | 5.502 | 745.9 | −53.9 | 6.006 | 795.9 | −46.4 |
| 5.030 | 762.8 | −55.7 | 6.011 | 746.7 | −47.7 | 6.517 | 796.5 | −38.5 |
| 6.502 | 764.9 | −38.0 | 6.501 | 747.5 | −42.6 | 7.029 | 797.2 | −31.1 |
| 7.005 | 765.6 | −33.6 | 7.037 | 748.3 | −37.9 | 7.516 | 797.7 | −23.9 |
| 7.501 | 766.3 | −29.8 | 7.523 | 749.1 | −34.2 | 8.001 | 798.3 | −14.1 |
| 8.010 | 766.9 | −26.4 | 8.023 | 749.8 | −30.8 | 8.511 | 798.9 | −9.0 |
| 8.521 | 767.6 | −23.4 | 8.497 | 750.5 | −28.0 | 9.019 | 799.5 | −7.6 |
| 9.040 | 768.3 | −20.6 | 8.993 | 751.3 | −25.4 | 10.003 | 800.7 | −6.3 |
| 9.511 | 768.8 | −18.4 | 9.568 | 752.1 | −22.7 | 10.047 | 800.8 | −6.3 |
| 9.974 | 769.5 | −16.4 | 10.032 | 752.8 | −20.8 | | | |
| $x_1 = 0.2003_4$; $T$/K = 313.10 | | | $x_1 = 0.2003_4$; $T$/K = 323.07 | | | $x_1 = 0.2003_4$; $T$/K = 333.05 | | |
| 3.601 | 786.8 | −110.3 | 4.004 | 775.4 | −101.5 | 4.210 | 763.4 | −100.6 |
| 4.007 | 787.4 | −95.3 | 4.307 | 775.8 | −91.9 | 4.492 | 763.8 | −92.2 |
| 4.523 | 788.1 | −79.9 | 4.497 | 776.1 | −86.5 | 4.799 | 764.3 | −84.2 |
| 5.069 | 788.7 | −67.0 | 4.802 | 776.6 | −78.8 | 5.001 | 764.6 | −79.4 |
| 5.497 | 789.3 | −58.5 | 5.014 | 776.9 | −73.9 | 5.470 | 765.3 | −69.8 |
| 6.027 | 790.0 | −49.4 | 5.510 | 777.5 | −63.9 | 5.996 | 766.1 | −60.7 |
| 6.504 | 790.7 | −42.3 | 6.029 | 778.3 | −55.1 | 6.511 | 766.9 | −53.1 |
| 7.010 | 791.3 | −35.5 | 6.513 | 779.0 | −48.1 | 7.008 | 767.7 | −46.9 |
| 7.494 | 791.9 | −29.5 | 7.000 | 779.7 | −41.9 | 7.519 | 768.4 | −41.3 |
| 7.989 | 792.6 | −23.5 | 7.519 | 780.5 | −36.1 | 8.008 | 769.2 | −36.6 |
| 8.557 | 793.2 | −16.6 | 8.013 | 781.1 | −31.1 | 8.503 | 769.9 | −32.3 |
| 9.017 | 793.8 | −11.9 | 8.543 | 781.8 | −26.3 | 9.019 | 770.6 | −28.3 |
| 9.636 | 794.6 | −9.1 | 9.139 | 782.5 | −21.5 | 9.506 | 771.3 | −25.0 |
| | | | 9.497 | 783.0 | −18.9 | 9.994 | 772.1 | −22.0 |
| | | | 10.068 | 783.8 | −15.2 | | | |
| $x_1 = 0.2003_4$; $T$/K = 347.97 | | | $x_1 = 0.4248_1$; $T$/K = 308.12 | | | $x_1 = 0.4248_1$; $T$/K = 313.10 | | |
| | | | 4.780 | 807.5 | −150.5 | 5.812 | 801.4 | −108.2 |
| 5.098 | 745.6 | −86.8 | 5.038 | 808.2 | −132.9 | 6.012 | 801.7 | −101.2 |
| 5.302 | 746.1 | −80.1 | 5.326 | 808.8 | −120.3 | 6.200 | 802.1 | −95.0 |
| 5.533 | 746.5 | −75.6 | 5.517 | 809.2 | −112.6 | 6.395 | 802.6 | −88.9 |
| 6.025 | 747.4 | −67.0 | 6.029 | 810.3 | −93.8 | 6.602 | 803.1 | −82.7 |
| 6.609 | 748.4 | −58.4 | 6.505 | 811.3 | −78.1 | 6.803 | 803.5 | −77.0 |
| 7.005 | 749.2 | −53.4 | 6.515 | 811.4 | −77.8 | 7.055 | 804.1 | −70.1 |
| 7.508 | 750.1 | −47.9 | 6.714 | 811.8 | −71.6 | 7.208 | 804.3 | −66.0 |
| 8.010 | 751.0 | −43.0 | 7.035 | 812.4 | −61.8 | 7.409 | 804.8 | −60.7 |
| 8.501 | 751.7 | −38.8 | 7.207 | 812.8 | −56.6 | 7.611 | 805.2 | −55.5 |
| 8.915 | 752.4 | −35.6 | 7.501 | 813.4 | −47.2 | 7.802 | 805.7 | −50.7 |
| 9.581 | 753.5 | −31.1 | 7.700 | 813.8 | −34.0 | 7.998 | 806.1 | −45.7 |
| 9.706 | 753.7 | −30.3 | 8.024 | 814.4 | −24.8 | 8.201 | 806.5 | −40.4 |
| 10.014 | 754.2 | −28.5 | 8.606 | 815.6 | −14.4 | 8.597 | 807.3 | −30.1 |
| | | | 8.802 | 816.0 | −13.2 | 8.797 | 807.6 | −25.4 |
| | | | 9.002 | 816.4 | −12.2 | 9.024 | 808.1 | −21.2 |
| | | | 9.529 | 817.3 | −10.5 | 9.602 | 809.3 | −15.5 |
| | | | 9.898 | 818.0 | −9.6 | 10.055 | 810.1 | −13.2 |
| $x_1 = 0.4248_1$; $T$/K = 323.03 | | | $x_1 = 0.4248_1$; $T$/K = 333.02 | | | $x_1 = 0.4248_1$; $T$/K = 347.93 | | |
| 6.842 | 786.9 | −88.7 | 7.301 | 770.1 | −87.9 | 7.801 | 744.8 | −90.2 |
| 7.010 | 787.3 | −84.4 | 7.408 | 770.5 | −85.5 | 7.908 | 745.1 | −88.1 |
| 7.302 | 788.1 | −77.2 | 7.506 | 770.6 | −83.3 | 7.999 | 745.5 | −86.3 |

**Table 2 (Continued)**

| $P$/MPa | $\rho$/kg·m$^{-3}$ | $v^E$/cm$^3$·mol$^{-1}$ | $P$/MPa | $\rho$/kg·m$^{-3}$ | $v^E$/cm$^3$·mol$^{-1}$ | $P$/MPa | $\rho$/kg·m$^{-3}$ | $v^E$/cm$^3$·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| $x_1 = 0.4248_1$; $T$/K = 323.03 | | | $x_1 = 0.4248_1$; $T$/K = 333.02 | | | $x_1 = 0.4248_1$; $T$/K = 347.93 | | |
| 7.530 | 788.6 | −72.0 | 7.613 | 771.0 | −81.0 | 8.130 | 745.9 | −83.8 |
| 8.004 | 789.7 | −62.0 | 7.806 | 771.4 | −77.0 | 8.239 | 746.2 | −81.8 |
| 8.302 | 790.4 | −56.1 | 8.005 | 772.0 | −73.1 | 8.408 | 746.8 | −78.8 |
| 8.401 | 790.6 | −54.2 | 8.209 | 772.6 | −69.2 | 8.501 | 747.2 | −77.2 |
| 8.500 | 790.8 | −52.4 | 8.394 | 773.2 | −65.9 | 8.600 | 747.4 | −75.6 |
| 8.603 | 791.2 | −50.5 | 8.802 | 774.1 | −59.1 | 8.712 | 747.8 | −73.7 |
| 8.710 | 791.4 | −48.6 | 8.916 | 774.5 | −57.2 | 8.801 | 748.2 | −72.3 |
| 8.821 | 791.7 | −46.7 | 9.000 | 774.7 | −55.9 | 8.890 | 748.4 | −70.9 |
| 9.000 | 792.1 | −43.6 | 9.100 | 775.0 | −54.4 | 9.033 | 748.8 | −68.7 |
| 9.209 | 792.5 | −40.2 | 9.205 | 775.3 | −52.9 | 9.105 | 749.1 | −67.7 |
| 9.309 | 792.8 | −38.6 | 9.304 | 775.6 | −51.4 | 9.244 | 749.4 | −65.6 |
| 9.401 | 793.1 | −37.2 | 9.410 | 775.8 | −49.9 | 9.410 | 750.0 | −63.3 |
| 9.502 | 793.3 | −35.7 | 9.506 | 776.1 | −48.6 | 9.501 | 750.2 | −62.1 |
| 9.601 | 793.4 | −34.2 | 9.607 | 776.4 | −47.2 | 9.608 | 750.7 | −60.7 |
| 9.728 | 793.7 | −32.4 | 9.809 | 776.8 | −44.6 | | | |
| $x_1 = 0.6086_1$; $T$/K = 308.11 | | | $x_1 = 0.6086_1$; $T$/K = 313.12 | | | $x_1 = 0.6086_1$; $T$/K = 323.05 | | |
| 6.002 | 812.2 | −133.2 | 6.801 | 802.8 | −107.8 | 7.506 | 779.7 | −101.1 |
| 6.221 | 813.0 | −122.6 | 7.000 | 803.5 | −100.0 | 7.703 | 780.7 | −94.9 |
| 6.400 | 813.7 | −114.3 | 7.203 | 804.4 | −92.2 | 7.803 | 781.1 | −91.9 |
| 6.606 | 814.5 | −105.0 | 7.402 | 805.2 | −84.8 | 7.910 | 781.7 | −88.7 |
| 6.807 | 815.2 | −96.1 | 7.602 | 806.0 | −77.5 | 8.009 | 782.2 | −85.8 |
| 7.019 | 815.9 | −86.9 | 7.804 | 806.8 | −70.1 | 8.208 | 783.1 | −80.1 |
| 7.203 | 816.7 | −78.9 | 8.010 | 807.7 | −62.6 | 8.404 | 784.1 | −74.8 |
| 7.401 | 817.4 | −69.9 | 8.197 | 808.3 | −55.7 | 8.607 | 785.0 | −69.5 |
| 7.607 | 818.3 | −59.9 | 8.400 | 809.1 | −48.2 | 8.800 | 785.8 | −64.6 |
| 7.804 | 818.9 | −48.9 | 8.602 | 809.8 | −40.7 | 9.004 | 786.7 | −59.6 |
| 8.005 | 819.7 | −34.6 | 8.812 | 810.5 | −33.6 | 9.301 | 788.0 | −52.8 |
| 8.209 | 820.4 | −24.9 | 9.000 | 811.3 | −28.7 | 9.501 | 788.9 | −48.4 |
| 8.600 | 821.7 | −18.4 | 9.213 | 812.0 | −24.6 | 9.702 | 789.8 | −44.3 |
| 8.810 | 822.4 | −16.6 | 9.392 | 812.6 | −22.1 | 9.805 | 790.2 | −42.3 |
| 9.000 | 823.1 | −15.3 | 9.600 | 813.3 | −19.9 | | | |
| 9.101 | 823.3 | −14.7 | 9.802 | 814.0 | −18.2 | | | |
| 9.200 | 823.8 | −14.3 | 10.001 | 814.6 | −16.9 | | | |
| $x_1 = 0.6086_1$; $T$/K = 333.02 | | | $x_1 = 0.6086_1$; $T$/K = 347.94 | | | $x_1 = 0.7943_1$; $T$/K = 308.11 | | |
| 8.226 | 753.6 | −74.5 | 9.809 | 716.0 | −78.2 | 6.824 | 793.7 | −122.1 |
| 8.305 | 754.3 | −76.6 | 9.815 | 717.0 | −78.2 | 7.001 | 795.6 | −111.0 |
| 8.400 | 754.8 | −78.9 | 9.822 | 718.1 | −78.2 | 7.206 | 797.4 | −99.4 |
| 8.504 | 755.5 | −81.1 | 9.831 | 719.1 | −78.1 | 7.400 | 799.2 | −88.0 |
| 8.610 | 756.0 | −83.4 | 9.840 | 719.7 | −78.0 | 7.607 | 801.1 | −74.9 |
| 8.701 | 756.6 | −85.6 | 9.850 | 720.0 | −77.9 | 7.810 | 803.0 | −60.0 |
| 8.802 | 757.3 | −88.1 | 9.861 | 720.0 | −77.7 | 8.007 | 804.6 | −41.9 |
| 8.900 | 757.9 | −90.7 | 9.873 | 720.2 | −77.5 | 8.197 | 806.2 | −29.9 |
| 9.005 | 758.5 | −93.1 | 9.885 | 720.2 | −77.3 | 8.414 | 807.8 | −24.0 |
| 9.103 | 759.0 | −95.6 | 9.897 | 720.3 | −77.1 | 8.618 | 809.6 | −20.8 |
| | | | 9.910 | 720.4 | −76.8 | 8.796 | 810.8 | −18.8 |
| | | | 9.949 | 720.8 | −76.2 | 9.017 | 812.5 | −17.0 |
| | | | 10.004 | 721.1 | −75.2 | 9.203 | 813.9 | −15.7 |
| | | | 10.052 | 721.5 | −74.4 | 9.400 | 815.3 | −14.6 |
| | | | 10.104 | 721.9 | −73.6 | 9.607 | 816.6 | −13.6 |
| | | | 10.152 | 722.2 | −72.8 | 9.807 | 818.0 | −12.8 |
| | | | | | | 9.902 | 818.6 | −12.5 |
| $x_1 = 0.7943_1$; $T$/K = 313.08 | | | $x_1 = 0.7943_1$; $T$/K = 323.06 | | | $x_1 = 0.7943_1$; $T$/K = 332.97 | | |
| 7.544 | 777.4 | −102.0 | | | | 9.739 | 686.8 | −76.1 |
| 7.601 | 778.5 | −97.2 | | | | 9.804 | 689.2 | −74.7 |
| 7.810 | 780.8 | −87.3 | 8.724 | 745.3 | −82.8 | 9.901 | 691.4 | −72.6 |
| 8.013 | 783.0 | −77.7 | 8.802 | 746.6 | −79.6 | 10.001 | 693.5 | −70.5 |
| 8.205 | 784.9 | −68.6 | 8.905 | 747.9 | −76.4 | 10.101 | 695.6 | −68.4 |
| 8.410 | 786.8 | −58.7 | 9.005 | 749.2 | −73.3 | 10.201 | 697.8 | −66.4 |
| 8.593 | 788.4 | −49.8 | 9.204 | 751.6 | −67.4 | 10.302 | 699.9 | −64.4 |
| 8.800 | 790.3 | −40.7 | 9.410 | 753.9 | −61.5 | 10.404 | 701.7 | −62.4 |
| 8.999 | 792.2 | −33.9 | 9.606 | 756.2 | −56.2 | 10.507 | 703.7 | −60.5 |
| 9.208 | 794.0 | −28.8 | 9.792 | 758.2 | −51.5 | 10.606 | 705.4 | −58.6 |
| 9.405 | 795.7 | −25.2 | 10.001 | 760.2 | −46.6 | 10.808 | 708.9 | −55.0 |
| 9.619 | 797.5 | −22.5 | 10.310 | 763.1 | −40.2 | 11.007 | 712.0 | −51.7 |
| 9.803 | 799.0 | −20.6 | | | | 11.204 | 715.0 | −48.6 |
| 10.061 | 800.9 | −18.5 | | | | 11.404 | 717.8 | −45.6 |
| 10.515 | 804.0 | −15.7 | | | | 11.607 | 720.5 | −42.8 |
| 11.013 | 807.3 | −13.5 | | | | 11.805 | 722.9 | −40.2 |
| 11.507 | 810.6 | −11.9 | | | | 12.004 | 725.3 | −37.8 |
| 11.994 | 813.5 | −10.6 | | | | | | |
| 12.199 | 814.6 | −10.2 | | | | | | |
| 12.410 | 815.6 | −9.7 | | | | | | |
| 12.606 | 816.7 | −9.3 | | | | | | |

**Table 2 (Continued)**

| $P$/MPa | $\rho$/kg·m$^{-3}$ | $v^E$/cm$^3$·mol$^{-1}$ | $P$/MPa | $\rho$/kg·m$^{-3}$ | $v^E$/cm$^3$·mol$^{-1}$ | $P$/MPa | $\rho$/kg·m$^{-3}$ | $v^E$/cm$^3$·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| $x_1 = 0.7943_1$; $T$/K = 347.95 | | | $x_1 = 0.9492_0$; $T$/K = 308.12 | | | $x_1 = 0.9492_0$; $T$/K = 313.09 | | |
| 11.400 | 647.2 | −63.0 | 7.302 | 699.6 | −103.2 | 7.960 | 642.1 | −82.6 |
| 11.604 | 653.3 | −60.3 | 7.402 | 704.9 | −96.6 | 8.001 | 648.3 | −80.9 |
| 11.812 | 658.7 | −57.6 | 7.605 | 713.8 | −82.0 | 8.200 | 666.4 | −71.2 |
| 12.007 | 663.0 | −55.1 | 7.802 | 720.9 | −65.3 | 8.400 | 677.7 | −60.7 |
| 12.201 | 666.8 | −52.8 | 8.002 | 728.0 | −43.8 | 8.606 | 688.5 | −49.7 |
| 12.502 | 672.6 | −49.3 | 8.204 | 734.5 | −29.0 | 8.803 | 697.0 | −40.1 |
| 12.802 | 677.6 | −46.1 | 8.404 | 740.3 | −22.8 | 9.002 | 704.0 | −32.5 |
| 13.202 | 684.0 | −42.1 | 8.605 | 745.7 | −19.3 | 9.201 | 710.9 | −27.1 |
| 13.504 | 688.5 | −39.5 | 8.802 | 750.6 | −16.9 | 9.408 | 717.1 | −23.1 |
| 13.802 | 692.8 | −36.9 | 9.004 | 755.4 | −15.1 | 9.604 | 722.7 | −20.3 |
| 14.109 | 696.9 | −34.5 | 9.201 | 759.7 | −13.7 | 9.800 | 728.1 | −18.2 |
| 14.406 | 700.5 | −32.4 | 9.408 | 764.0 | −12.5 | 10.003 | 733.1 | −16.5 |
| 14.703 | 703.9 | −30.4 | 9.610 | 768.0 | −11.6 | 10.201 | 737.5 | −15.1 |
| 15.000 | 707.4 | −28.6 | 9.805 | 771.5 | −10.8 | 10.405 | 741.5 | −13.8 |
| 15.207 | 709.6 | −27.4 | 10.003 | 774.9 | −10.1 | 10.605 | 744.7 | −12.8 |
| 15.407 | 711.9 | −26.4 | 10.202 | 778.0 | −9.4 | 10.803 | 747.4 | −11.8 |
| 15.610 | 714.0 | −25.4 | 10.405 | 780.9 | −8.9 | | | |
| 15.813 | 716.1 | −24.4 | 10.617 | 783.7 | −8.3 | | | |
| 16.004 | 717.9 | −23.5 | 10.807 | 785.9 | −7.9 | | | |
| 16.303 | 720.7 | −22.3 | | | | | | |
| 16.501 | 722.4 | −21.5 | | | | | | |
| 16.808 | 725.0 | −20.3 | | | | | | |
| $x_1 = 0.9492_0$; $T$/K = 323.05 | | | $x_1 = 0.9492_0$; $T$/K = 332.99 | | | $x_1 = 0.9492_0$; $T$/K = 347.96 | | |
| 9.107 | 526.2 | −58.2 | 10.561 | 502.4 | −42.0 | 10.989 | 348.5 | −26.3 |
| 9.400 | 575.3 | −55.0 | 10.601 | 506.6 | −41.8 | 11.505 | 382.4 | −27.0 |
| 9.710 | 607.0 | −48.9 | 10.709 | 517.4 | −41.1 | 12.004 | 415.7 | −27.1 |
| 10.015 | 628.2 | −42.4 | 10.810 | 526.9 | −40.4 | 12.507 | 448.4 | −26.6 |
| 10.301 | 644.3 | −36.8 | 10.910 | 536.2 | −39.7 | 13.000 | 477.1 | −25.4 |
| 10.600 | 658.2 | −31.8 | 11.209 | 560.9 | −37.2 | 13.503 | 503.0 | −23.8 |
| 10.904 | 670.3 | −27.5 | 11.503 | 580.0 | −34.4 | 14.006 | 527.8 | −22.3 |
| 11.211 | 681.1 | −24.0 | 11.803 | 596.0 | −31.4 | 14.511 | 550.1 | −20.7 |
| 11.508 | 689.9 | −21.3 | 12.102 | 611.4 | −28.9 | 15.011 | 569.6 | −19.1 |
| 11.807 | 698.3 | −19.1 | 12.404 | 624.7 | −26.5 | 15.495 | 586.6 | −17.7 |
| 12.106 | 705.9 | −17.2 | 12.705 | 635.9 | −24.2 | 15.997 | 602.4 | −16.3 |
| 12.404 | 712.6 | −15.6 | 13.010 | 645.6 | −22.1 | 16.514 | 617.0 | −15.0 |
| 12.703 | 719.2 | −14.3 | 13.302 | 654.5 | −20.4 | 17.014 | 629.5 | −13.8 |
| 13.006 | 725.5 | −13.2 | 13.603 | 663.6 | −18.9 | 17.513 | 640.4 | −12.7 |
| 13.309 | 731.4 | −12.2 | 13.906 | 671.7 | −17.5 | 17.988 | 648.6 | −11.6 |
| 13.608 | 736.7 | −11.3 | 14.213 | 678.9 | −16.2 | | | |
| 13.907 | 742.0 | −10.5 | 14.513 | 684.7 | −15.0 | | | |
| 14.210 | 746.8 | −9.8 | | | | | | |
| 14.504 | 751.1 | −9.2 | | | | | | |
| 14.804 | 755.1 | −8.6 | | | | | | |
| $x_1 = 0.9715_6$; $T$/K = 308.13 | | | $x_1 = 0.9715_6$; $T$/K = 313.12 | | | $x_1 = 0.9715_6$; $T$/K = 323.05 | | |
| 7.456 | 611.7 | −86.8 | 8.124 | 526.2 | −66.1 | 8.528 | 303.9 | −21.7 |
| 7.502 | 636.2 | −84.5 | 8.526 | 627.3 | −49.7 | 9.031 | 381.9 | −31.2 |
| 7.992 | 680.6 | −41.7 | 9.002 | 662.5 | −29.7 | 9.535 | 467.3 | −34.2 |
| 8.522 | 706.8 | −18.0 | 9.522 | 689.0 | −19.3 | 10.046 | 540.0 | −31.2 |
| 8.997 | 724.3 | −13.0 | 10.021 | 708.1 | −14.6 | 10.501 | 577.6 | −25.4 |
| 9.508 | 739.8 | −10.3 | 10.520 | 722.7 | −11.8 | 11.011 | 612.9 | −20.4 |
| 10.027 | 752.9 | −8.5 | 10.993 | 734.9 | −10.0 | 11.512 | 638.9 | −16.8 |
| 10.521 | 763.7 | −7.3 | 11.514 | 746.8 | −8.5 | 12.028 | 660.4 | −14.0 |
| 11.017 | 773.2 | −6.3 | 12.038 | 757.3 | −7.4 | 12.516 | 677.0 | −12.0 |
| 11.500 | 781.6 | −5.6 | 12.512 | 765.8 | −6.6 | 13.014 | 691.5 | −10.5 |
| 12.008 | 789.6 | −4.9 | 13.003 | 773.6 | −5.8 | 13.558 | 705.3 | −9.1 |
| 12.520 | 797.2 | −4.4 | 13.500 | 781.1 | −5.2 | 14.003 | 715.4 | −8.2 |
| 13.012 | 803.8 | −3.9 | 13.998 | 788.2 | −4.7 | 14.516 | 725.9 | −7.3 |
| 13.520 | 810.4 | −3.5 | 14.495 | 794.8 | −4.2 | 15.024 | 735.4 | −6.6 |
| 14.014 | 816.4 | −3.2 | 15.008 | 801.1 | −3.8 | 15.506 | 743.6 | −6.0 |
| 14.520 | 822.1 | −2.9 | | | | | | |
| 15.000 | 827.3 | −2.6 | | | | | | |

certainty of density data in the liquid phase is estimated to be within ± 0.05 % with a minimum value of ± 0.2 kg·m$^{-3}$, due to the uncertainties of the mechanical parameters used in the FPMC model. Global temperature uncertainties are estimated to be about ± 0.02 K, which includes the temperature uncertainty of the bath regulation. Global uncertainties of pressure measurements after calibration are (± 0.00015, ± 0.001, and ± 0.002) MPa, respectively, to the sensor's ranges: (0.2, 5, and 40) MPa. Uncertainties of mixture compositions are within ± 2·10$^{-4}$ in mole fraction.

## 3. Experimental Results and Modeling

Table 2 presents the experimental liquid density data sets for six compositions of the carbon dioxide + 2-propanol binary system at five temperatures. Our experimental liquid density data are compared with those of Yaginuma et al.,[3] who used the variable volume cell to measure the density for different compositions, and presented in Figure 2. Deviations, calculated using eqs 6 and 7, are presented in Table 3. As can be seen, they are in relative agreement with the selected literature data.

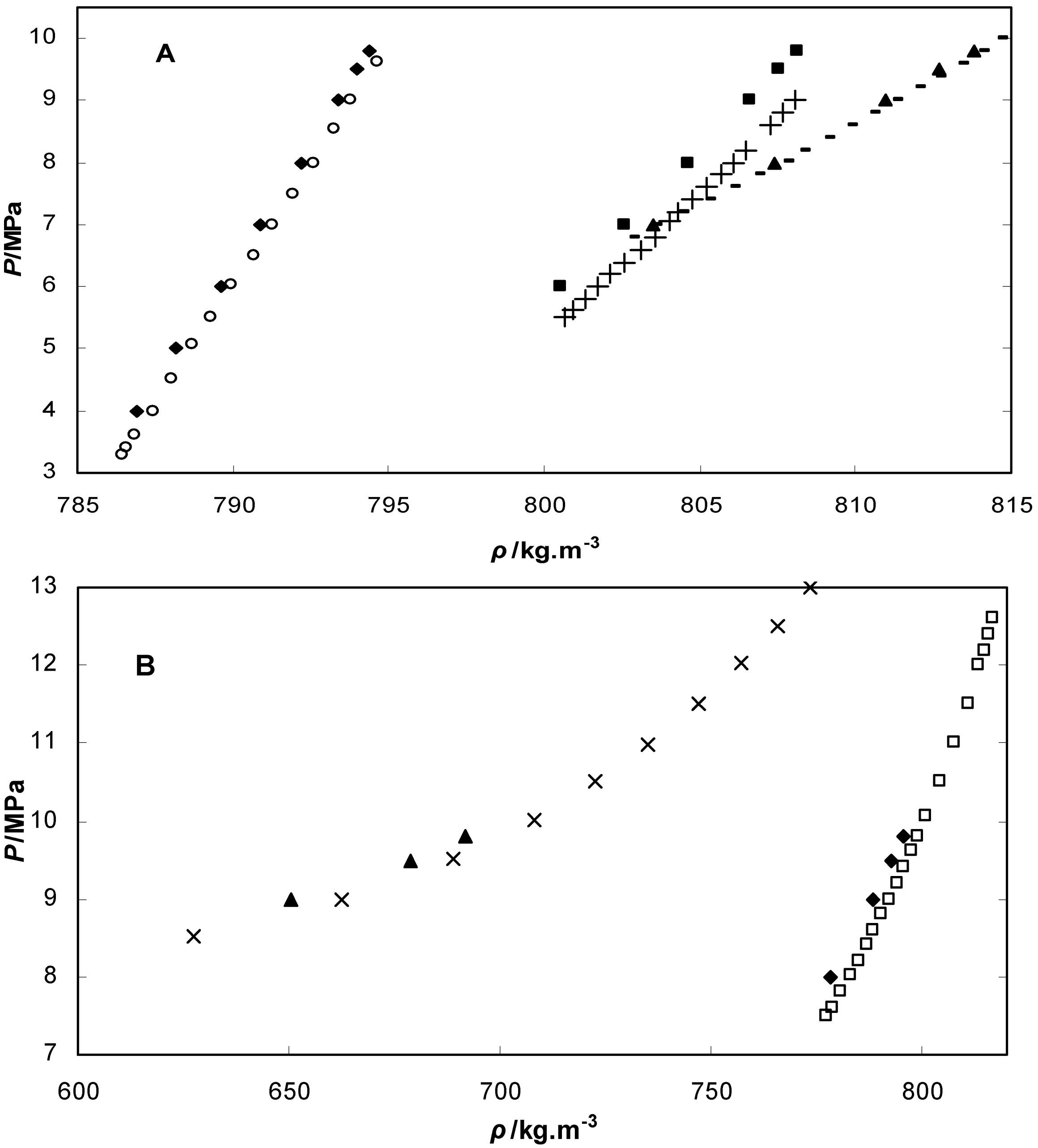

**Figure 2.** *PρT* data of the carbon dioxide (1) + 2-propanol (2) binary system. (A) Experimental data of Yaginuma et al.[3] at 313.15 K: ♦, $z_1 = 0.20$; ■, $z_1 = 0.40$; ▲, $z_1 = 0.60$. Our work at 313.10 K: ○, $z_1 = 0.2003$; +, $z_1 = 0.4248$; -, $z_1 = 0.6086$. (B) Experimental data of Yaginuma et al.[3] at 313.15 K: ♦, $z_1 = 0.80$; ▲, $z_1 = 0.97$. Our work at 313.10 K: □, $z_1 = 0.7943$; ×, $z_1 = 0.9715$.

**Table 3. Density Deviations between Our Data and Those from Yaginuma et al.[3]**

| our work | Yaginuma et al.[3] | deviations (eqs 6 and 7) | |
|---|---|---|---|
| $T$/K = 313.10 | $T$/K= 313.15 | absolute | relative |
| $x_1$ | $x_1$ | kg·m$^{-3}$ | % |
| 0.2003 | 0.20 | −0.41 | 0.05 |
| 0.6086 | 0.60 | −0.18 | 0.02 |
| 0.7943 | 0.80 | −3.98 | 0.51 |
| 0.9715 | 0.97 | −11.73 | 1.75 |

In addition to simultaneous measurement of density, the vibrating tube densimeter allows estimation of bubble points as shown by Bouchot and Richon.[5] Figure 3 shows how these points are determined. Table 4 presents the results. To evaluate the accuracy of our experimental method, a comparison with literature data was done.

Bamberger and Maurer[10] have previously studied this system at three temperatures, (293, 313, and 333) K. They developed a model to correlate their experimental data. They considered a symmetric approach to calculate *PTxy* properties involving the Peng−Robinson equation of state (PR EoS) (eq 1).

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \tag{1}$$

where $P$ is the pressure (Pa); $T$ represents the temperature (K); $R$ stands for the molar gas constant (8.314 J·mol$^{-1}$·K$^{-1}$); $a$ is the attractive parameter of the EoS; $b$ is the molar covolume; and $v$ is the molar volume of the mixture (m$^3$·mol$^{-1}$). The pure component properties are indicated in Table 1.

The Panagiotopoulos and Reid[11] mixing rules are used to extend the PR EoS to mixtures.

$$b = \sum_i x_i b_i \tag{2}$$

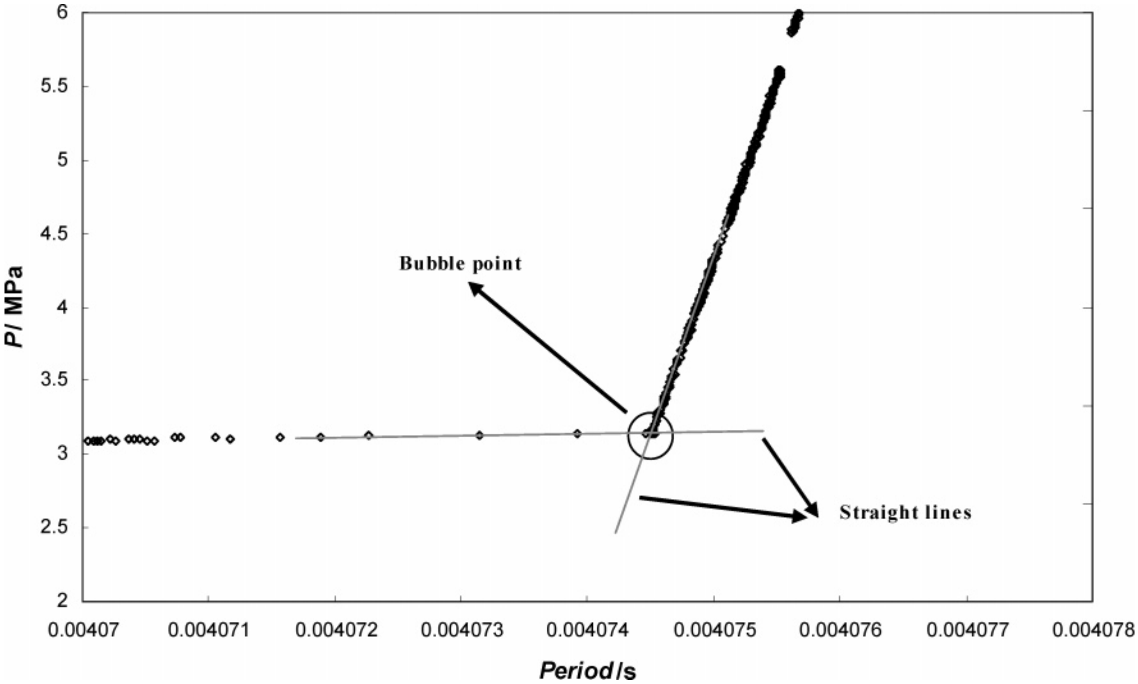

**Figure 3.** Graphical determination of bubble points on the pressure−period diagram.

**Table 4. Comparison between the Bubble Point Experimental Data Determined for the $CO_2$ (1) + 2-Propanol (2) Binary System and the Calculated Value Obtained with the Model Developed by Bamberger and Maurer**

| calcd with the model developed by Bamberger and Maurer | | | experimental work | |
|---|---|---|---|---|
| $x_1$ | $y_{1\text{calcd}}$ | $P_{\text{calcd}}$ MPa | $P_{\text{exptl}}$ MPa | deviation % |
| $T$/K = 313.10 | | | | |
| 0.1390 | 0.9904 | 2.26 | 2.28 | 0.73 |
| 0.2003 | 0.9918 | 3.13 | 3.64 | 14.13 |
| 0.4248 | 0.9918 | 5.56 | 5.85 | 4.90 |
| 0.6086 | 0.9902 | 6.68 | 6.78 | 1.43 |
| 0.7943 | 0.9890 | 7.19 | 7.54 | 4.68 |
| 0.9492 | 0.9876 | 7.85 | 7.96 | 1.35 |
| 0.9715 | 0.9865 | 8.08 | 8.10 | 0.30 |
| $T$/K = 308.10 | | | | |
| 0.1390 | 0.9924 | 2.15 | 1.76 | −22.17 |
| 0.2003 | 0.9935 | 2.96 | 2.75 | −7.64 |
| 0.4248 | 0.9936 | 5.19 | 4.78 | −8.64 |
| 0.6086 | 0.9927 | 6.16 | 5.95 | −3.46 |
| 0.7943 | 0.9921 | 6.56 | 6.82 | 3.75 |
| 0.9492 | 0.9922 | 7.18 | 7.27 | 1.23 |
| 0.9715 | 0.9928 | 7.41 | 7.45 | 0.54 |
| $T$/K = 323.07 | | | | |
| 0.1390 | 0.9852 | 2.49 | 2.66 | 6.51 |
| 0.2003 | 0.9873 | 3.45 | 4.05 | 14.77 |
| 0.4248 | 0.9870 | 6.3 | 6.81 | 7.44 |
| 0.6086 | 0.9835 | 7.77 | 7.87 | 1.33 |
| 0.7943 | 0.9791 | 8.5 | 8.72 | 2.50 |
| $T$/K = 333.00 | | | | |
| 0.1390 | 0.9779 | 2.71 | 2.82 | 4.05 |
| 0.2003 | 0.9810 | 3.77 | 4.21 | 10.45 |
| 0.4248 | 0.9805 | 7.03 | 7.23 | 2.78 |
| 0.6086 | 0.9736 | 8.85 | 8.23 | −7.58 |
| 0.7943 | 0.9613 | 9.87 | 9.72 | −1.52 |
| $T$/K = 348.00 | | | | |
| 0.1390 | 0.9619 | 3.03 | 3.32 | 8.76 |
| 0.2003 | 0.9674 | 4.23 | 5.10 | 17.00 |
| 0.4248 | 0.9665 | 8.07 | 7.72 | −4.56 |
| 0.6086 | 0.9530 | 10.43 | 10.00 | −4.32 |
| 0.7943 | 0.9148 | 11.87 | 11.35 | −4.61 |

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad (3)$$

For a binary system, $a_{ij}$ is determined using a specific function involving the binary interaction parameter and attractive parameter $a$ for components $i$ and $j$

$$a_{ij} = (1 - k_{ij} - (k_{ij} - k_{ji})x_i)\sqrt{a_i a_j} \qquad (4)$$

The attractive parameter contain two terms ($a = \alpha(T,T_C)a_C$). $\alpha$ is called the alpha function which takes into account temperature dependence of $a$. In their paper, Bamberger and Maurer used the following alpha function (Mehlem et al.[13])

$$\ln(\alpha_i(T,T_{Ci})) = m\left[1 - \frac{T}{T_{Ci}}\right] + n\left[1 - \sqrt{\frac{T}{T_{Ci}}}\right]^2 \qquad (5)$$

where $x_i$ is the molar fraction of the component $i$ ($i = 1$ or 2, $CO_2$ and 2-propanol, respectively), and $T_{Ci}$ and $P_{Ci}$ are, respectively, the critical temperature and pressure of component $i$. The parameters $m$, $n$, $k_{12}$, and $k_{21}$, determined by Bamberger and Maurer,[10] are given in Table 5.

Deviations (see Table 4) between calculated and experimental data are expressed by expressions 6 and 7.

$$\text{relative deviation: dev } \% = \frac{100}{N}\sum_N \left(\frac{|U_{\text{exptl}} - U_{\text{calcd}}|}{U_{\text{calcd}}}\right) \qquad (6)$$

$$\text{absolute deviation: dev} = \frac{100}{N}\sum_N (U_{\text{exptl}} - U_{\text{calcd}}) \qquad (7)$$

## 4. Comparison with Literature Data and Discussion

***Isothermal PρT and Excess Volume Data of the Mixture.*** To compare the capability of the previous model to calculate volumetric properties, we have considered the excess volume for all the mixtures (see Table 2). They are calculated using eq 8

$$v^E = v - (x_1 v_1 + x_2 v_2) \qquad (8)$$

where $v_1$ and $v_2$ are the experimental pure component molar volumes calculated with the PR EoS; $x_1$ and $x_2$ represent the

**Table 5. Component Parameters from Bamberger and Maurer[13]**

| | alpha function parameters (eq 5) | | Panagiotopoulos and Reid mixing rules binary interaction parameters | |
|---|---|---|---|---|
| compd | *m* | *n* | $k_{12}$ | $k_{21}$ |
| carbon dioxide | 0.6877 | 0.3813 | 0.1467 | |
| 2-propanol | 1.1979 | 0.8456 | | 0.1005 |

mole fractions of carbon dioxide and of 2-propanol, respectively; and $v$ is the molar volume of the mixture.

Figure 4 shows the experimental excess volume data compared to the excess volumes calculated using the Peng−Robinson equation of state and some literature data. Our experimental data seem to be in good agreement with the literature data and the calculated data except for the composition of 0.9492 where the mixture is near its critical temperature.

According to Figure 4, it can be seen that excess molar volume is negative particularly for the high concentration of $CO_2$. It is probably due to a packing effect between the two molecules. Moreover, the PR EoS gives a good representation of excess molar volume. Observed deviations are within (± 2.1) $cm^3 \cdot mol^{-1}$. Figure 5 shows the experimental excess volume data compared to the excess volumes calculated using the Peng−Robinson equation of state. Our experimental data seem to be in good agreement with data calculated using the PR EoS except for at the temperature of 308.10 K where the model results are slightly out of the deviation's range.

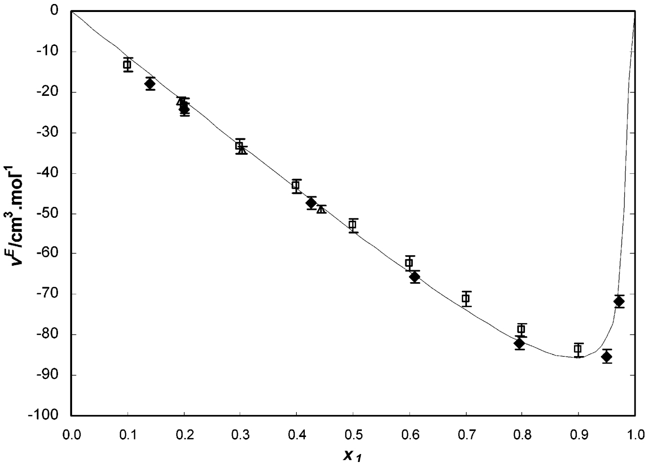

**Figure 4.** Excess molar volumes of the carbon dioxide (1) + 2-propanol (2) binary system as a function of composition at 313 K and 8 MPa. △, Zuniga-Moreno et al.;[4] □, Yaginuma et al.;[3] ♦, this work. Solid line, calculated with the model developed by Bamberger and Maurer.

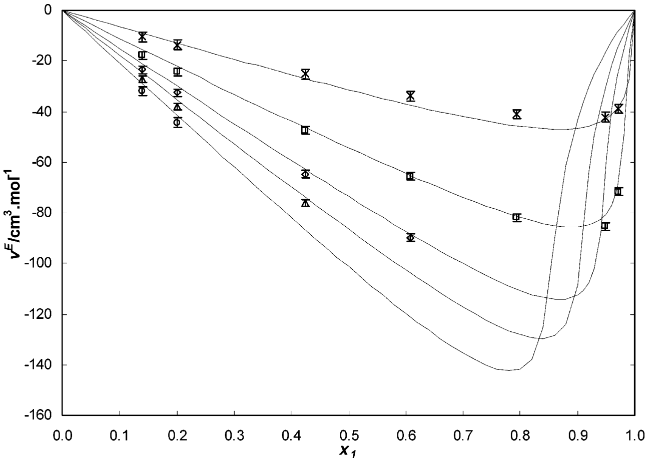

**Figure 5.** Excess molar volumes of the carbon dioxide (1) + 2-propanol (2) binary system as a function of $CO_2$ composition at 8 MPa and five temperatures. This work at: ×, 308.10 K; □, 313.10 K; ◊, 323.06 K; △, 333.06 K; ○, 348.00 K. Solid line, calculated with the model developed by Bamberger and Maurer.

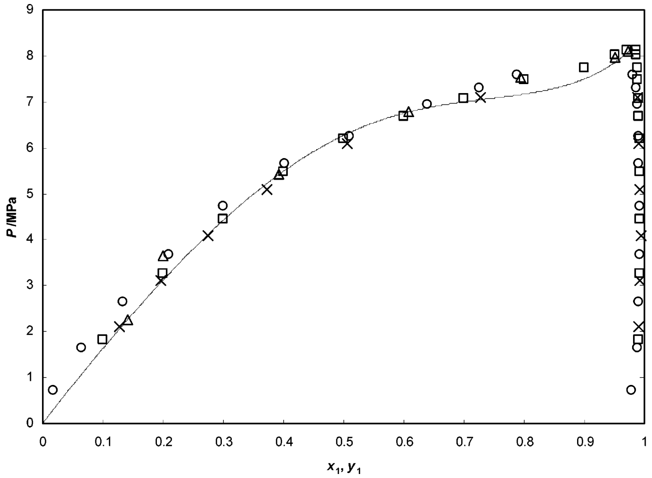

**Figure 6.** Vapor−liquid equilibrium data for temperatures around 313 K concerning the binary system $CO_2$ (1) + 2-propanol (2). ×, Bamberger and Maurer data at 313.2 K; □, Yaginuma et al. at 313.15 K; ○, Lazzaroni et al.[14] at 313 K; △, this work at 313.10 K. Solid line: bubble point curve calculated with the PR EoS at 313.11 K.

***Vapor−Liquid Equilibrium (VLE).*** The experimental VLE data and their deviations are given in Table 4, and some of them are shown in Figure 6 and are compared with selected literature data. To predict our VLE data, we have used the PR EoS and the Panagiotopoulos and Reid mixing rules. According to Table 4, we can see that our experimental data are in relatively good agreement with predicted VLE data by the PR EoS. The deviations are probably due to the difficulty in determining very accurately the break point and also due to the fact that Bamberger and Maurer gave temperature-independent binary interaction parameters. Consequently, we can consider that the presented technique is convenient to get accurate *PVT* data and satisfactory to estimate bubble pressures. In fact, bubble pressure measurements are really more accurate using the variable volume cell technique (Fontalba et al.[15]) or static analytic method (Laugier and Richon[16]).

## 5. Conclusion

A vibrating tube densimeter, taking advantage of a forced path mechanical calibration model, was used for generating new volumetric properties, and the experimental data were generated in a large range of carbon dioxide compositions, particularly for new compositions close to one in carbon dioxide (i.e., 0.15, 0.20, 0.42, 0.61, 0.80, 0.95, and 0.97), and at temperatures between (308.15 and 348.15) K. The reliability of the data was finally tested with the results of a model based on the Melhem et al. modification of the Peng−Robinson equation of state with the Panagiotopoulos and Reid mixing rules as well as with some selected data from the literature. The determination of the bubble point from density data shows satisfactory agreement with VLE data from the literature.

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