# High-Pressure Density Measurements for the Binary System Ethanol + Heptane

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The density of the asymmetrical binary system composed of ethanol and heptane has been measured (630 points) for nine different compositions including the pure compounds at five temperatures in the range (293.15 to 333.15) K and 14 isobars up to 65 MPa with a vibrating-tube densimeter, The experimental uncertainty is estimated to be 0.5 kg·m$^{-3}$. The isothermal compressibility, the isobaric thermal expansion, and the excess molar volume have been derived from the experimental density data, revealing that a volume expansion occurs for this binary system. The results have been interpreted as due to changes in the molecular free-volume, disruption of the order molecular structure, and the breaking of hydrogen bonds within the self-associating alcohol.

## Introduction

Ethanol is a widely used compound in many industrial applications and is mostly synthetically produced by hydration of ethylene. It is, for example, used as solvent in paints or pharmaceuticals, as building blocks in the manufacture of high-molecular weight chemicals, and in the production of simple compounds such as acetic acid or ether. Recently, ethanol has become of interest as an additive to gasoline instead of methyl *tert*-butyl ether (MTBE), which had been introduced as the substitute for lead-containing compounds in gasoline but now has been found to have some environmental side effects due to its penetration through the soil and entering into the groundwater, which becomes polluted and undesirable for human consumption. As a consequence of this, ethanol is now (e.g., in the United States) added to gasoline. The common name for these gasoline blends is gasohol. As discussed by French and Malone,[1] the addition of ethanol to gasoline affects the production, storage, distribution, and use of the obtained gasoline blends because complex phase behavior is encountered.

To study the behavior of ethanol + petroleum fluids under various operating conditions, accurate mathematical models are required. Since these fluids are multicomponent mixtures involving paraffinic, naphthenic, and aromatic hydrocarbons as well as alcohols, it is impossible to determine experimentally all their properties under all conditions. However from a fundamental as well as a model developing point of view, experimental property studies of simplified mixtures can provide valuable information about the fluid behavior under various temperature and pressure conditions. One of these properties is the density or specific molar volume, which is an important property required in a wide range of engineering disciplines as well as in the determination of different fluid properties.

In this work, the focus is addressed to the binary system ethanol + heptane, which is part of a project related to the experimental measurements of the density and viscosity of ethanol + $C_7$ hydrocarbons. Previously, the density of ethanol + heptane has been measured by Ozawa et al.[2] for three compositions at three isotherms between (298.2 and 348.2) K and up to 196.2 MPa using a high-pressure piezometer with an uncertainty of 0.2 %. A vibrating-tube densimeter was used by Papaioannou et al.[3] to measure the density for 16 compositions at 298.15 K and up to 33.8 MPa with an uncertainty of 0.1 kg·m$^{-3}$. The same type of apparatus was used by Ulbig et al.,[4] who report the excess molar volume for eight mixtures at 298.15 K and three isobars up to 60 MPa with and uncertainty of 5·10$^{-3}$ cm$^3$·mol$^{-1}$. Recently, Dzida and Marczak[5] determined for eight compositions the density under pressure from experimental speed of sound measurements in the temperature range (293.2 to 318.2) K and up to 90 MPa, whereas the density at atmospheric was measured by a vibrating-tube densimeter.

In this work, new experimental densities of seven ethanol + heptane mixtures are measured up to 65 MPa and in the range (293.15 to 333.15) K using a vibrating-tube densimeter. These data along with those reported in the literature[2−5] are used to perform a comparison between ethanol + heptane densities determined by different techniques. In addition, the measured densities are used to derive the isothermal compressibility, isobaric thermal expansion, and excess molar volume in order to study the volumetric behavior of this binary system with respect to composition, temperature, and pressure.

## Experimental Procedure

An Anton-Paar DMA 60/512P high-pressure vibrating-tube densimeter was used to measure the density ($\rho$) as a function of pressure ($P$) and temperature ($T$). A schematic and detailed description of the experimental setup and procedures can be found in ref 6. To avoid using mercury as the pressurizing medium, a modification to the experimental setup described in ref 6 was made by removing the mercury pump and the high-pressure cell. Instead, a variable volume high-pressure piston cell was connected. At the front of the piston cell two entrances were located, which could be used for introducing the sample of interest. In our experimental setup, one entrance of the piston cell was connected with a tube to the densimeter, whereas a small tube with a valve was placed at the other entrance. This entrance was used as the outlet, when cleaning the densimeter, but it was also used to avoid any trapped bubbles during the

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filling of the densimeter and the piston cell. The piston was in direct contact with the sample, and the pressurization of the system was done by moving the piston forward.

The filling of the densimeter was performed in the following way. First, the piston was moved forward to the end of the cell in order to reduce the volume of the system that has to be evacuated. After evacuating the system, a funnel was connected as shown in ref 6 and filled with the sample to be studied. Then the valve connected to the funnel was opened, and the system was filled with the sample by gravity. To avoid any air being trapped in the piston cell, the outlet valve on the piston cell was opened and a few milliliters of the sample was allowed to run out before closing this valve. Moving the piston backward allowed a complete filling of the piston cell with the sample. The sample was brought to the desired temperature and pressure of interest and measured when the thermal and mechanical equilibrium were reached. The temperature of the vibrating tube was controlled by an external circulating temperature-controlled fluid and measured inside the density cell with an AOIP 5207 thermometer with an uncertainty of 0.05 K. The pressure was measured with a HBM manometer with an uncertainty of 0.05 MPa.

The calibration of the densimeter was performed with water and vacuum according to the procedure described by Lagourette et al.[7] In this method, the calibration was performed by measuring the temperature dependence of the period when the cell was under vacuum as well as the period at all considered *T*,*P* conditions for a chosen reference fluid, such as water, for which reliable and accurate densities are given at all *T*,*P* conditions.[8] Within the considered *T*,*P* conditions of this work, the density values of water[8] have a reported uncertainty of 0.003 %. The experimental device displays the oscillating period with seven figures, which according to the specification of Anton Paar for the used densimeter device corresponds to an uncertainty of the order of $10^{-5}$ kg·m$^{-3}$ related to the measured oscillating period.

The two chemicals used in this study are commercially available. Ethanol was from Riedel-de-Haën with a volume fraction purity > 99.8 % (gas chromatography), with a water volume fraction < 0.2 %, and a molecular weight $M_w = 46.07$ g·mol$^{-1}$. Heptane was from Riedel-de-Haën with a chemical purity > 99.5 % (gas chromatography) and $M_w = 100.20$ g·mol$^{-1}$. The chemicals were used without any further purification.

The binary mixtures composed of ethanol (1) + heptane (2) were prepared immediately before use by weighing at atmospheric pressure and ambient temperature using a Sartorius balance with an uncertainty of 0.001 g. For each mixture, a sample of 50 g was prepared, which taking into account the uncertainty of the balance resulted in an uncertainty in the mole fraction of less than $6 \cdot 10^{-5}$.

By applying the law of propagating errors, the overall experimental uncertainty in the reported density values is estimated to be 0.5 kg·m$^{-3}$. This uncertainty is similar to that reported in refs 9 and 10.

It should be mentioned that under certain circumstances (viscous fluids) the viscosity of the fluid can affect the density measured by a vibration tube densimeter, and a correction of the measured density value has to be done. It has been mentioned in ref 11 that for a DMA 512 and for samples with a viscosity higher than 15 mPa·s, the density correction would be around 0.055 kg·m$^{-3}$. For the considered fluids and mixtures in this work, the maximum viscosity is ~1.7 mPa·s found for ethanol at 293.15 K and 65 MPa. Furthermore, the correction value is also much lower than the experimental uncertainty of the densities reported in this work. Because of this, no correction of the measured densities has been performed.

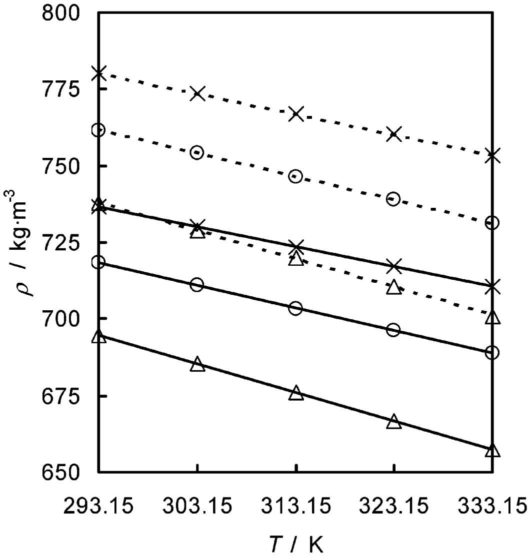

**Figure 1.** Density ($\rho$) vs temperature ($T$) at △, 0.1 MPa; ○, 30 MPa; and ×, 60 MPa for ethanol + heptane mixtures containing 25.0 mol % ethanol (—) and 75.0 mol % ethanol (- -). Lines are interpolated values.

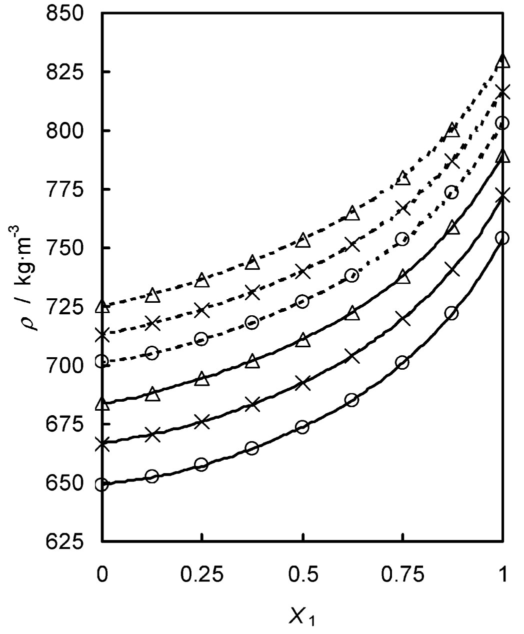

**Figure 2.** Density ($\rho$) vs mole fraction ($x_1$) for ethanol (1) + heptane (2) at 0.1 MPa (—) and 60 MPa (- -) for various isotherms: △, 293.15 K; ×, 313.15 K; and ○, 333.15 K. Lines are interpolated values.

## Results and Discussion

The measured densities of ethanol, heptane, and seven of their binary mixtures in the temperature range (293.15 to 333.15) K at intervals of 10 K and for pressures up to 65 MPa in steps of 5 MPa are reported in Table 1 as a function of temperature ($T$), pressure ($P$), and mole fraction of ethanol ($x_1$).

For all compositions, the density increases with increasing pressure and decreasing temperature. Within the considered temperature range (293.15 to 333.15) K the variation of the density versus temperature at constant pressure is practically linear as shown in Figure 1 for $x_1 = 0.250$ and $x_1 = 0.750$. In Figure 2, the variation of the density behavior versus composi-

**Table 1. Density $\rho$ versus Temperature ($T$), Pressure ($P$), and Mole Fraction ($x$) for Mixtures Composed of Ethanol (1) + Heptane (2)**

|  | $P$ | $T$/K |  |  |  |  | $P$ | $T$/K |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_1$ | MPa | 293.15 | 303.15 | 313.15 | 323.15 | 333.15 | MPa | 293.15 | 303.15 | 313.15 | 323.15 | 333.15 |
| 0 | 0.1 | 683.9 | 675.1 | 666.4 | 657.7 | 649.1 | 35.0 | 710.8 | 703.7 | 696.9 | 690.4 | 683.8 |
| 0 | 5.0 | 688.2 | 680.0 | 671.6 | 663.4 | 655.2 | 40.0 | 714.0 | 707.1 | 700.4 | 694.1 | 687.6 |
| 0 | 10.0 | 692.5 | 684.4 | 676.5 | 668.7 | 661.0 | 45.0 | 716.9 | 710.2 | 703.9 | 697.7 | 691.3 |
| 0 | 15.0 | 696.5 | 688.9 | 681.0 | 673.4 | 666.3 | 50.0 | 719.8 | 713.4 | 707.1 | 701.1 | 694.8 |
| 0 | 20.0 | 700.5 | 692.8 | 685.3 | 678.0 | 670.9 | 55.0 | 722.7 | 716.4 | 710.1 | 704.3 | 698.4 |
| 0 | 25.0 | 704.1 | 696.8 | 689.4 | 682.5 | 675.4 | 60.0 | 725.4 | 719.2 | 713.1 | 707.4 | 701.5 |
| 0 | 30.0 | 707.5 | 700.3 | 693.3 | 686.5 | 679.7 | 65.0 | 728.0 | 722.0 | 716.0 | 710.3 | 704.7 |
| 0.125 | 0.1 | 688.1 | 679.8 | 670.7 | 661.8 | 652.3 | 35.0 | 715.4 | 708.9 | 701.6 | 694.7 | 687.1 |
| 0.125 | 5.0 | 692.5 | 684.8 | 676.1 | 667.4 | 658.4 | 40.0 | 718.4 | 712.3 | 705.2 | 698.5 | 690.9 |
| 0.125 | 10.0 | 696.8 | 689.3 | 681.1 | 672.7 | 664.2 | 45.0 | 721.5 | 715.4 | 708.6 | 702.0 | 694.6 |
| 0.125 | 15.0 | 701.0 | 693.8 | 685.6 | 677.6 | 669.6 | 50.0 | 724.5 | 718.5 | 711.9 | 705.4 | 698.2 |
| 0.125 | 20.0 | 704.9 | 697.8 | 689.9 | 682.2 | 674.4 | 55.0 | 727.4 | 721.4 | 715.1 | 708.6 | 701.7 |
| 0.125 | 25.0 | 708.5 | 701.7 | 694.0 | 686.8 | 678.8 | 60.0 | 730.2 | 724.4 | 718.1 | 711.8 | 705.0 |
| 0.125 | 30.0 | 712.0 | 705.3 | 697.9 | 690.9 | 683.1 | 65.0 | 732.9 | 727.2 | 721.0 | 714.7 | 708.1 |
| 0.250 | 0.1 | 694.5 | 685.3 | 676.0 | 666.9 | 657.3 | 35.0 | 721.7 | 714.4 | 707.0 | 700.0 | 692.8 |
| 0.250 | 5.0 | 699.0 | 690.2 | 681.4 | 672.6 | 663.4 | 40.0 | 725.0 | 717.9 | 710.6 | 703.7 | 696.6 |
| 0.250 | 10.0 | 703.3 | 694.8 | 686.4 | 678.0 | 669.4 | 45.0 | 728.0 | 721.1 | 714.1 | 707.4 | 700.4 |
| 0.250 | 15.0 | 707.3 | 699.3 | 690.9 | 682.9 | 674.7 | 50.0 | 731.1 | 724.2 | 717.4 | 710.8 | 704.0 |
| 0.250 | 20.0 | 711.3 | 703.4 | 695.3 | 687.6 | 679.6 | 55.0 | 733.9 | 727.3 | 720.6 | 714.0 | 707.6 |
| 0.250 | 25.0 | 714.9 | 707.3 | 699.4 | 692.1 | 684.3 | 60.0 | 736.7 | 730.2 | 723.6 | 717.2 | 710.8 |
| 0.250 | 30.0 | 718.4 | 710.9 | 703.4 | 696.2 | 688.7 | 65.0 | 739.4 | 733.0 | 726.6 | 720.2 | 714.0 |
| 0.375 | 0.1 | 701.9 | 692.7 | 683.3 | 674.1 | 664.5 | 35.0 | 729.3 | 721.8 | 714.3 | 707.3 | 699.9 |
| 0.375 | 5.0 | 706.4 | 697.6 | 688.7 | 679.7 | 670.7 | 40.0 | 732.5 | 725.3 | 717.9 | 711.0 | 703.8 |
| 0.375 | 10.0 | 710.9 | 702.1 | 693.6 | 685.2 | 676.6 | 45.0 | 735.5 | 728.5 | 721.3 | 714.6 | 707.5 |
| 0.375 | 15.0 | 714.9 | 706.8 | 698.2 | 690.0 | 681.9 | 50.0 | 738.5 | 731.6 | 724.7 | 718.0 | 711.2 |
| 0.375 | 20.0 | 718.9 | 710.7 | 702.6 | 694.7 | 686.7 | 55.0 | 741.4 | 734.7 | 727.9 | 721.3 | 714.7 |
| 0.375 | 25.0 | 722.4 | 714.7 | 706.7 | 699.2 | 691.4 | 60.0 | 744.2 | 737.5 | 730.9 | 724.5 | 718.0 |
| 0.375 | 30.0 | 725.9 | 718.3 | 710.5 | 703.4 | 695.7 | 65.0 | 746.9 | 740.4 | 733.9 | 727.5 | 721.3 |
| 0.500 | 0.1 | 711.2 | 701.9 | 692.6 | 683.5 | 673.7 | 35.0 | 738.5 | 731.1 | 723.6 | 716.6 | 709.1 |
| 0.500 | 5.0 | 715.7 | 706.9 | 697.9 | 689.2 | 679.9 | 40.0 | 741.7 | 734.5 | 727.2 | 720.4 | 713.0 |
| 0.500 | 10.0 | 719.9 | 711.4 | 702.9 | 694.6 | 685.7 | 45.0 | 744.9 | 737.7 | 730.8 | 724.0 | 716.7 |
| 0.500 | 15.0 | 724.0 | 715.9 | 707.5 | 699.4 | 691.1 | 50.0 | 747.9 | 740.8 | 734.1 | 727.4 | 720.3 |
| 0.500 | 20.0 | 728.0 | 720.0 | 711.9 | 704.0 | 696.0 | 55.0 | 750.8 | 743.9 | 737.3 | 730.6 | 723.9 |
| 0.500 | 25.0 | 731.6 | 723.9 | 716.0 | 708.5 | 700.6 | 60.0 | 753.6 | 746.9 | 740.2 | 733.8 | 727.2 |
| 0.500 | 30.0 | 735.1 | 727.5 | 719.9 | 712.7 | 704.9 | 65.0 | 756.3 | 749.7 | 743.2 | 736.8 | 730.4 |
| 0.625 | 0.1 | 722.6 | 713.4 | 704.2 | 695.0 | 685.1 | 35.0 | 749.9 | 742.6 | 735.0 | 727.8 | 720.1 |
| 0.625 | 5.0 | 727.1 | 718.3 | 709.5 | 700.5 | 691.2 | 40.0 | 753.1 | 746.0 | 738.6 | 731.6 | 724.0 |
| 0.625 | 10.0 | 731.4 | 722.8 | 714.3 | 705.8 | 697.0 | 45.0 | 756.2 | 749.2 | 742.1 | 735.2 | 727.7 |
| 0.625 | 15.0 | 735.4 | 727.4 | 718.9 | 710.7 | 702.3 | 50.0 | 759.3 | 752.2 | 745.4 | 738.6 | 731.4 |
| 0.625 | 20.0 | 739.4 | 731.4 | 723.3 | 715.3 | 707.1 | 55.0 | 762.2 | 755.3 | 748.6 | 741.9 | 735.0 |
| 0.625 | 25.0 | 743.0 | 735.4 | 727.4 | 719.8 | 711.8 | 60.0 | 765.0 | 758.3 | 751.6 | 745.1 | 738.2 |
| 0.625 | 30.0 | 746.5 | 739.0 | 731.3 | 723.9 | 716.0 | 65.0 | 767.8 | 761.1 | 754.7 | 748.1 | 741.4 |
| 0.750 | 0.1 | 737.9 | 728.9 | 719.8 | 710.6 | 700.9 | 35.0 | 765.1 | 757.7 | 750.3 | 743.0 | 735.4 |
| 0.750 | 5.0 | 742.3 | 733.7 | 724.9 | 716.1 | 706.8 | 40.0 | 768.4 | 761.2 | 753.8 | 746.8 | 739.2 |
| 0.750 | 10.0 | 746.6 | 738.2 | 729.8 | 721.3 | 712.4 | 45.0 | 771.4 | 764.4 | 757.3 | 750.3 | 743.0 |
| 0.750 | 15.0 | 750.7 | 742.7 | 734.3 | 726.1 | 717.7 | 50.0 | 774.5 | 767.5 | 760.6 | 753.8 | 746.6 |
| 0.750 | 20.0 | 754.6 | 746.7 | 738.5 | 730.6 | 722.5 | 55.0 | 777.4 | 770.6 | 763.8 | 757.0 | 750.2 |
| 0.750 | 25.0 | 758.3 | 750.6 | 742.6 | 735.1 | 727.0 | 60.0 | 780.2 | 773.5 | 766.9 | 760.2 | 753.4 |
| 0.750 | 30.0 | 761.7 | 754.2 | 746.5 | 739.1 | 731.3 | 65.0 | 782.9 | 776.4 | 769.9 | 763.2 | 756.7 |
| 0.875 | 0.1 | 758.9 | 749.9 | 740.8 | 731.7 | 722.2 | 35.0 | 785.6 | 778.2 | 770.6 | 763.4 | 755.8 |
| 0.875 | 5.0 | 763.2 | 754.6 | 745.8 | 737.0 | 727.9 | 40.0 | 788.9 | 781.5 | 774.1 | 767.0 | 759.6 |
| 0.875 | 10.0 | 767.4 | 759.0 | 750.5 | 742.1 | 733.4 | 45.0 | 791.9 | 784.8 | 777.6 | 770.6 | 763.3 |
| 0.875 | 15.0 | 771.4 | 763.3 | 755.0 | 746.7 | 738.5 | 50.0 | 794.9 | 787.9 | 780.9 | 774.0 | 766.8 |
| 0.875 | 20.0 | 775.3 | 767.3 | 759.1 | 751.1 | 743.2 | 55.0 | 797.8 | 791.0 | 784.1 | 777.2 | 770.4 |
| 0.875 | 25.0 | 778.9 | 771.1 | 763.1 | 755.5 | 747.5 | 60.0 | 800.6 | 793.9 | 787.1 | 780.3 | 773.6 |
| 0.875 | 30.0 | 782.3 | 774.7 | 766.9 | 759.5 | 751.7 | 65.0 | 803.4 | 796.7 | 790.1 | 783.4 | 776.8 |
| 1 | 0.1 | 789.4 | 781.1 | 772.3 | 763.1 | 754.2 | 35.0 | 815.3 | 808.5 | 801.0 | 793.1 | 785.6 |
| 1 | 5.0 | 793.5 | 785.7 | 776.9 | 768.0 | 759.4 | 40.0 | 818.6 | 811.8 | 804.4 | 796.7 | 789.3 |
| 1 | 10.0 | 797.5 | 789.8 | 781.5 | 772.9 | 764.6 | 45.0 | 821.6 | 814.9 | 807.8 | 800.1 | 792.8 |
| 1 | 15.0 | 801.4 | 794.0 | 785.8 | 777.3 | 769.4 | 50.0 | 824.6 | 817.9 | 810.8 | 803.5 | 796.3 |
| 1 | 20.0 | 805.2 | 797.8 | 789.8 | 781.4 | 773.8 | 55.0 | 827.5 | 821.1 | 813.7 | 806.6 | 799.7 |
| 1 | 25.0 | 808.7 | 801.6 | 793.7 | 785.7 | 777.8 | 60.0 | 830.2 | 824.0 | 816.6 | 809.7 | 802.9 |
| 1 | 30.0 | 812.1 | 805.0 | 797.4 | 789.4 | 781.7 | 65.0 | 832.9 | 826.7 | 819.5 | 812.6 | 806.0 |

tion is shown for various isotherms at $P = 0.1$ MPa and $P = 60$ MPa, respectively. From Figure 2 and Table 1, it can be seen that the density behavior increases monotonically with increasing ethanol concentration.

The experimental density values ($\rho_{\text{exp}}$) have been compared with literature values ($\rho_{\text{lit}}$) previously reported[2,5] for ethanol + heptane and determined by different techniques. The literature data have been interpolated in order to obtain values corresponding to the pressures considered in this experimental work. Figure 3 shows the deviations obtained between the experimental ethanol densities of this work with the interpolated values by Ozawa et al.[2] at 323.2 K and up to 60 MPa. Furthermore, the deviations found between the ethanol densities of this work and those determined by Dzida and Marczak[5] at (293.15, 303.15,

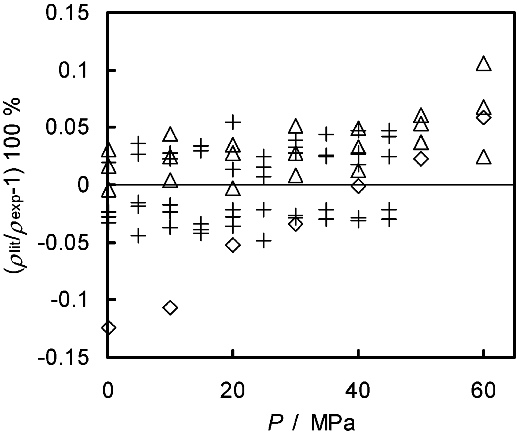

**Figure 3.** Comparison of densities for ethanol vs pressure ($P$) shown as the deviation ($\rho_{lit}/\rho_{exp} - 1$) between experimental values of this work ($\rho_{exp}$) and literature values ($\rho_{lit}$): ◇, by Ozawa et al.[2] at 323.2 K; △, by Dzida and Marczak[5] at (293.15, 303.15, and 313.15) K; and +, by Zéberg-Mikkelsen et al.[12] at (293.15, 303.15, 313.15, 323.15, and 333.15) K.

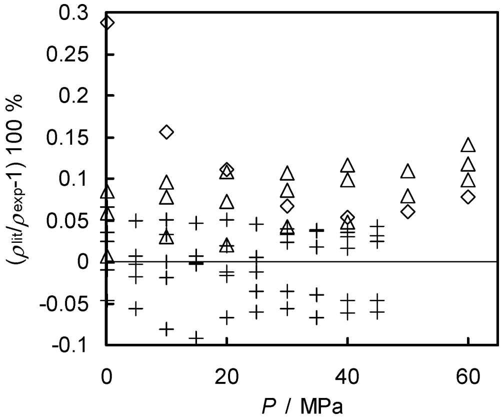

**Figure 4.** Comparison of densities for heptane vs pressure ($P$) shown as the deviation ($\rho_{lit}/\rho_{exp} - 1$) between experimental values of this work ($\rho_{exp}$) and literature values ($\rho_{lit}$): ◇, by Ozawa et al.[2] at 323.2 K; △, by Dzida and Marczak[5] at (293.15, 303.15, and 313.15) K; and +, by Fandiño et al.[11] at (293.15, 303.15, 313.15, 323.15, and 333.15) K.

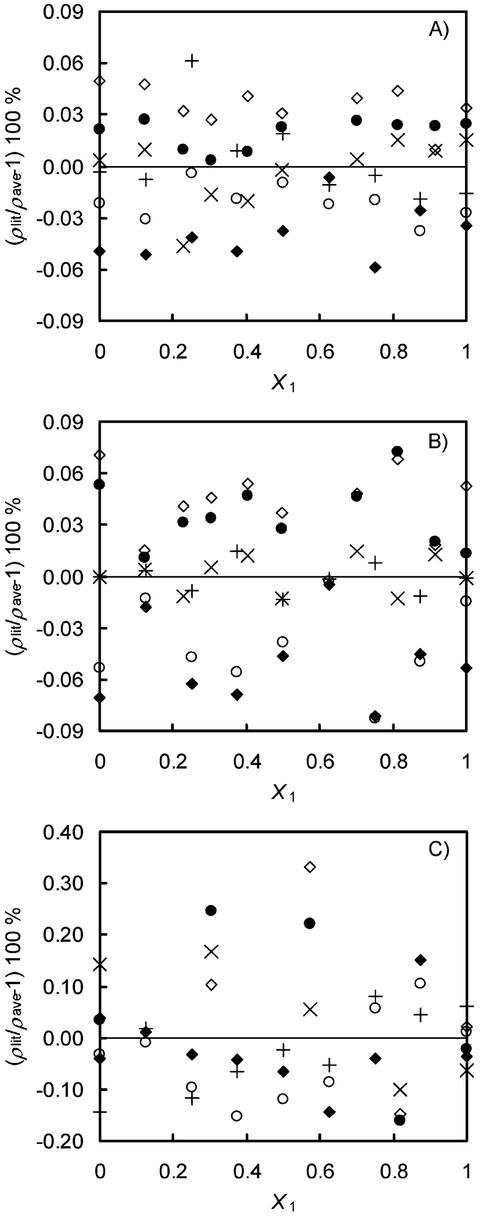

**Figure 5.** Comparison of densities for ethanol (1) + heptane (2) vs mole fraction ($x_1$) shown as the deviation ($\rho_{lit}/\rho_{ave} - 1$) between the average fitted values ($\rho_{ave}$) obtained from all data (this work and literature[2,5]) and the reported values ($\rho_{lit}$). (A) 293.15 K in this work at +, 0.1 MPa; ○, 30 MPa; and ◆, 60 MPa and by Dzida and Marczak[5] at ×, 0.1 MPa; ●, 30 MPa; and ◇, 60 MPa. (B) 313.15 K in this work at +, 0.1 MPa; ○, 30 MPa; ◆, and 60 MPa and by Dzida and Marczak[5] at ×, 0.1 MPa; ●, 30 MPa; and ◇, 60 MPa. (C) 323.15 K in this work at +, 0.1 MPa; ○, 30 MPa; ◆, and 60 MPa and by Ozawa et al.[2] at ×, 0.1 MPa; ●, 30 MPa; ◇, and 60 MPa.

and 313.15) K and up to 60 MPa are also shown in Figure 3. For heptane, a similar comparison has been performed between the experimental data of this work and the literature values obtained from refs 2 and 5. The obtained deviations are shown in Figure 4. For ethanol, an average absolute deviation (AAD $= (1/n)\sum_{i=1}^{n}|\rho_{lit,i}/\rho_{exp,i} - 1|$) of 0.06 % and a maximum absolute deviation (MxD $= |\rho_{lit,i}/\rho_{exp,i} - 1|$) of 0.12 % was found between the densities of this work and the interpolated values by Ozawa et al.[2], whereas the comparison with the density values of Dzida and Marczak[5] gave an AAD = 0.03 % and a MxD = 0.10 %. For heptane, the comparison between the densities of this work and the interpolated values by Ozawa et al.[2] resulted in an AAD = 0.12 % and a MxD = 0.29 %, whereas the comparison with the density values of Dzida and Marczak[5] resulted in an AAD = 0.08 % and a MxD = 0.14 %. Figure 5 shows the deviations obtained for ethanol + heptane densities of this work and those reported in the literature,[2,5] when these density data are compared with the average value obtained by fitting all density values at constant $T$,$P$ conditions as a function of the composition. Figures 3 through 5 reveal a good agreement between the measured data of this work and those determined by Dzida and Marczak,[5] which is within the reported uncertainty of 0.5 kg·m$^{-3}$. The deviations found with the Ozawa et al.[2] data are higher but around the uncertainty of 0.2 % reported by Ozawa et al.[2]

A comparison has also been performed between the measured values of the pure compounds and other recently reported densities, which have been measured using vibrating tube densimeters. For ethanol, the comparison with the density values[12] in the temperature range (293.15 to 333.15) K and up to 45 MPa resulted in an AAD of 0.03 % and a MxD of 0.05 %. The obtained deviations are shown in Figure 3. For heptane, the deviations obtained form the comparison with the measured values[11] in the temperature range (293.15 to 333.15) K and up to 45 MPa are shown in Figure 4, and the resultant AAD is 0.04 % with a MxD of 0.09 %. This comparison reveals (see Figures 3 and 4) that the deviations are within the experimental uncertainty reported for the measured densities.

In addition, a comparison of the measured density values of the pure compounds with the values calculated by the correlations of Cibulka and Ziková[13] and Cibulka and Hnědkovský[14] have been performed. The Cibulka correlations[13,14] have been derived for each of the pure compounds using experimental liquid densities covering wide ranges of temperature and pressure. The correlation method is based on the Tait-type relationship, and the general form of the Cibulka correlation is given as

$$\rho(T, P)/\text{kg·m}^{-3} = \frac{\rho_0(T)/\text{kg·m}^{-3}}{1 - C\ln[(B/\text{MPa} + P/\text{MPa})/(B/\text{MPa} + P_{\text{ref}}/\text{MPa})]} \tag{1}$$

where $B$ and $C$ are temperature-dependent functions defined in refs 13 and 14. Furthermore, $\rho_0(T)$ is the temperature dependence of the density of the fluid at a chosen reference pressure $P_{\text{ref}}$, which is generally chosen to be 0.1 MPa, unless the fluid is a gas at this condition. In this work, the required $\rho_0(T)$ values for ethanol and heptane, respectively, were obtained by an interpolation of the recommended density values given in the TRC tables[15,16] at 0.1 MPa. For ethanol, the comparison between the experimental values ($\rho_{\text{exp}}$) and those predicted by the Cibulka correlation ($\rho_{\text{calc}}$) results in an AAD of 0.04 % with a MxD of 0.10 %. For heptane, the AAD is 0.04 % with a MxD of 0.14 %.

In refs 11, 12, and 17−19, the Tait relationship given in eq 1 has been used to represent the $T,P,\rho$ surface of each mixture. In this work, the $T,P,\rho$ surface is represented in a similar way using the following temperature expression for $B$:

$$B/\text{MPa} = b_0 + b_1(T/\text{K}) + b_2(T/\text{K})^2 \tag{2}$$

and assuming that $C$ is temperature independent. The required $\rho_0(T)$ values are taken as the experimental densities at 0.1 MPa. The $b_i$ parameters in eq 2 and the $C$ parameter have been determined for each mixture by fitting eq 1 combined with eq 2 against the experimental density data. The obtained parameters are given in Table 2 along with the standard deviation for each composition.

## Derived Properties

The experimental densities can be used to derive other important quantities, such as the isothermal compressibility defined as

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial P}\right)_T \tag{3}$$

or the isobaric thermal expansivity defined as

$$\alpha_P = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_P \tag{4}$$

In this work, the isothermal compressibility of each mixture has been determined analytically by differentiating eq 1 using eq 2 along with the parameters given in Table 2. This results in the following expression for the isothermal compressibility:

$$\kappa_T = \frac{C(B/\text{MPa} + P/\text{MPa})^{-1}}{1 - C\ln[(B/\text{MPa} + P/\text{MPa})/(B/\text{MPa} + P_{\text{ref}}/\text{MPa})]} \tag{5}$$

The calculated isothermal compressibilities are estimated to have an uncertainty of 1 %.

**Table 2. Adjusted $C$, $b_0$, $b_1$, and $b_2$ Parameters for Equations 1 and 2 and the Standard Deviation ($s$) for Different Mole Fractions ($x$) of Ethanol (1) + Heptane (2) Mixtures**

| $x_1$ | $C$ | $b_0$ / MPa | $b_1$ / MPa·K$^{-1}$ | $b_2$ / MPa·K$^{-2}$ | $s$ / kg·m$^{-3}$ |
|---|---|---|---|---|---|
| 0 | 0.08593 | 408.2 | −1.774 | 0.002035 | 0.08 |
| 0.125 | 0.08540 | 446.6 | −2.044 | 0.002496 | 0.09 |
| 0.250 | 0.08602 | 395.1 | −1.680 | 0.001868 | 0.08 |
| 0.375 | 0.08578 | 390.6 | −1.650 | 0.001823 | 0.09 |
| 0.500 | 0.08597 | 382.1 | −1.588 | 0.001723 | 0.08 |
| 0.625 | 0.08617 | 367.6 | −1.486 | 0.001561 | 0.09 |
| 0.750 | 0.08677 | 353.1 | −1.374 | 0.001380 | 0.07 |
| 0.875 | 0.08666 | 331.1 | −1.206 | 0.001104 | 0.08 |
| 1 | 0.08632 | 325.4 | −1.168 | 0.001103 | 0.10 |

The isobaric thermal expansivity could also be obtained analytically by differentiating eq 1 taking into account the temperature dependence of $\rho_0(T)$. But as Cerdeiriña et al.[20] and Troncoso et al.[21] mention, the estimated isobaric thermal expansivities depend highly on the applied temperature-dependent functions for $B$ and $\rho_0(T)$, which lead to different isobaric thermal expansivities. Because of this, they recommend to derive the isobaric thermal expansivity numerically from the density values at constant pressure. However, since the densities at constant pressure of each mixture in this work decrease linearly with the temperature (see Figure 1), the slope of each isobar is equal to the derivative $(\partial\rho/\partial T)_P$ in eq 4. By inserting the determined $(\partial\rho/\partial T)_P$ values and the experimental densities into eq 4, the isobaric thermal expansivity at the different $T,P$ conditions of each mixture has been derived with an overall uncertainty estimated to be 0.5 % over the whole temperature and pressure range.

In the temperature range (293.15 to 333.15) K and from (5 to 40) MPa, a comparison of the estimated isothermal compressibility values for ethanol in this work with the reported values[12] shows a very good agreement with an AAD = 0.5 % and a MxD = 1.1 %. For the isobaric thermal expansivity in the range (303.15 to 323.15) K and (0.1 to 45) MPa, the agreement is also good, obtaining an AAD = 1.3 % and MxD = 3.2 %. These AADs are within the given uncertainties of the compared derived properties. For heptane, a comparison of the derived isothermal compressibilities with the estimated values obtained from ref 11 in the temperature range (293.15 to 333.15) K and from (5 to 40) MPa resulted in an AAD = 1.0 % and a MxD = 1.5 %. For the isobaric thermal expansivity, the comparison with the estimated values obtained from ref 11 in the range (303.15 to 323.15) K and from (0.1 to 40) MPa resulted in an AAD of 2.0 % and a MxD of 3.5 %. These deviations are within the uncertainties of the compared derived properties.

For all compositions within the considered $T,P$ range, the isothermal compressibility as well as the isobaric thermal expansion increases with increasing temperature and decreases with increasing pressure (see, for example, Figures 6 and 7). This may be related to changes in the molecular distance or the free-volume within the liquid, as discussed in for example refs 9, 12, and 22. Within the considered $T,P$ conditions, it is observed that heptane is more compressible than ethanol. Thus, ethanol is less expansive at low pressures, but with increasing pressure ethanol becomes more expansive than heptane. An explanation may be related to the formation of hydrogen bonds, which keep the ethanol molecules stronger together, making the fluid more rigid and less expansive, as discussed in ref 5. With increasing pressure, these hydrogen bonds become less important as compared with dispersive molecular interactions,

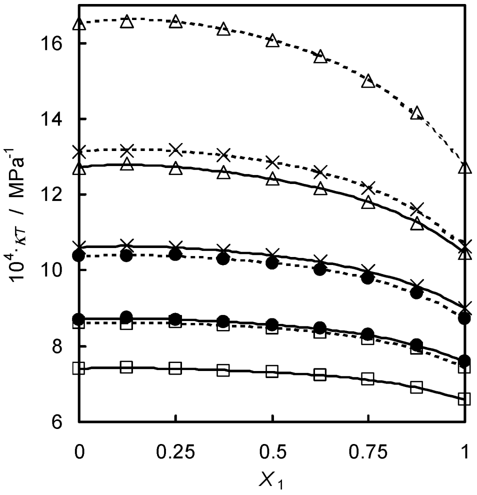

**Figure 6.** Isothermal compressibility ($\kappa_T$) vs mole fraction ($x_1$) for ethanol (1) + heptane (2) at 293.15 K (—) and 323.15 K (- -) for Δ, 5 MPa; ×, 20 MPa; ●, 40 MPa; and □, 60 MPa. Lines are interpolated values.

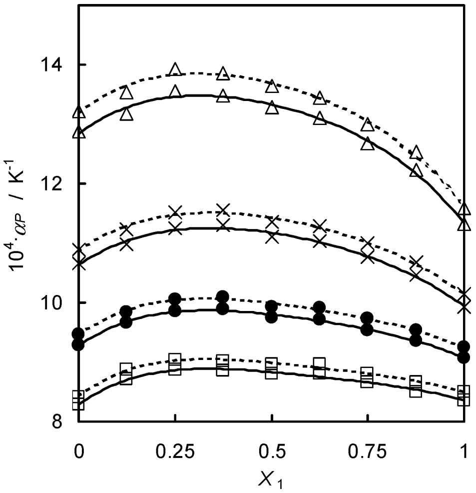

**Figure 7.** Isobaric thermal expansivity ($\alpha_P$) vs mole fraction ($x_1$) for ethanol (1) + heptane (2) at 303.15 K (—) and 323.15 K (- -) for Δ, 0.1 MPa; ×, 20 MPa; ●, 40 MPa; and □, 60 MPa. Lines are interpolated values.

making ethanol more expansive because, when only dispersive molecular interactions occur, the fluid with the lowest molecular weight will, in general, be the most expansive and compressible fluid, as mentioned in ref 12.

A monotonically decreasing behavior is found for the isothermal compressibility as a function of the ethanol concentration (see Figure 6) where the isothermal compressibility is plotted as a function of the ethanol concentration for various isobars at (293.15 and 323.15) K. In case of the isobaric thermal expansivity, its variation with the concentration of ethanol is shown in Figure 7 for various isobars at (303.15 and 323.15) K. This figure shows a non-monotonical behavior of the isobaric thermal expansivity as a function of the composition involving a maximum. A similar behavior has been found for other binary alcohol + hydrocarbon systems such as ethanol + toluene,[12] ethanol + methylcyclohexane,[22] and 1-propanol + toluene.[9] In refs 9, 12, and 22, the higher thermal expansivity of the mixtures is explained as the result of an increase in the free-volume and a more loosely packing of the molecules within the mixtures as a result of disruption of the ordered molecular structure within the liquid and the weakening or breaking of hydrogen bonds within the formed ethanol multimers.

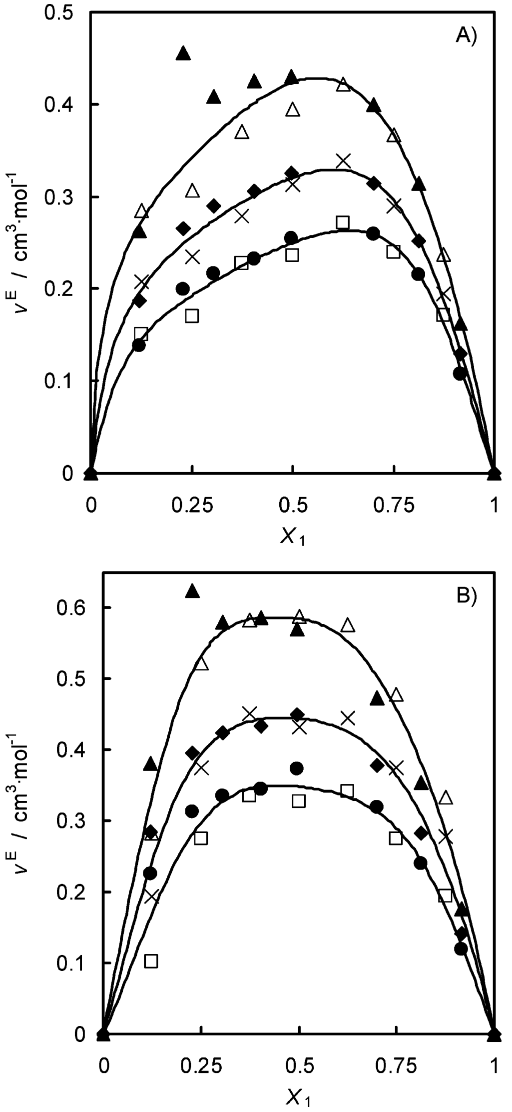

**Figure 8.** Excess molar volume ($V^E$) vs mole fraction ($x_1$) for ethanol (1) + heptane (2). (A) 293.15 K and (B) 313.15 K for △, 0.1 MPa; ×, 30 MPa; and □, 60 MPa of this work and ▲, 0.1 MPa; ◆, 30 MPa; and ●♀ 60 MPa of Dzida and Marczak.[5] Lines are interpolated values.

## Excess Molar Volume

Using the following expression, the excess molar volume ($V^E_{mix}$) of the binary mixtures at each $T,P$ condition has been calculated:

$$V^E_{mix} = (x_1 M_{w,1} + x_2 M_{w,2})/\rho_{mix} - ((x_1 M_{w,1}/\rho_1) + (x_2 M_{w,2}/\rho_2)) \tag{6}$$

where $x$ is the mole fraction and $M_w$ is the molecular weight. Furthermore, the subscript mix refers to the mixture, whereas subscripts 1 and 2 refer to the pure compounds, respectively.

For all the mixtures within the considered $T,P$ range, the excess molar volume is positive. Taking into account the uncertainty on the excess molar volume coming from the experimental densities, the excess molar volume increases with increasing temperature and decreases with increasing pressure (see Figure 8). The excess molar volume for the binary ethanol + heptane system is lower than for ethanol + methylcyclohexane[22] (positive excess values) but higher than for ethanol + toluene,[9] whose excess molar volume shows a sigmoid behavior involving positive and negative values as a function of the composition. The variation of the excess molar volume versus the composition for ethanol + heptane is shown for various isobars at $T$ = (293.15 and 313.15) K in Figure 8. Similar figures can be drawn for the other isotherms. Included in Figure 8 is the excess molar volume estimated from the densities reported by Dzida and Marczak.[5] Taking into account the uncertainty in the reported densities, a good agreement between the excess molar volumes of this work and those of Dzida and Marczak[5] is found (see Figure 8), especially in the ethanol-rich region.

The increase in the excess molar volumes with increasing temperature is a result of the higher thermal expansivity of the mixtures than of the pure compounds, which leads to a higher molar volume of the mixtures than for the pure compounds. This may be due to a more loosely molecular packing and an enlargement of the free-volume, which will result in the weakening or breaking of hydrogen bonds within the self-associating ethanol molecules. The explanation for the decrease in the excess molar volume with increasing pressure is mainly due to a decrease in the molecular distance and the free-volume of the mixtures and the pure compounds.

## Conclusion

The density of ethanol, heptane, and seven of their binary mixtures has been measured in the temperature range (293.15 to 333.15) K and up to 65 MPa with an overall uncertainty of 0.5 $kg \cdot m^{-3}$. These data have been used to derive other fluid properties, such as the isothermal compressibility and isobaric thermal expansivity, as well as the excess molar volume. A volume expansion occurs for this binary system when ethanol and heptane are mixed due to the disruption of the ordered molecular structure within the liquid and a weakening or breaking of the formed hydrogen bonds between ethanol molecules. A comparison of the density values of this work with previously reported values in the literature for this binary system revealed an agreement within the experimental uncertainty of 0.5 $kg \cdot m^{-3}$ with the density data determined by Dzida and Marczak[5] from experimental speed of sound measurements. The agreement with the data of Ozawa et al.[2] is also within the uncertainty of 0.2 % reported by Ozawa et al.

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