RENEWABLE OXYGENATED ADDITIVES IN BIOFUELS: HIGH PRESSURE DENSITIES OF MIXTURES DIBUTYL-ETHER + HEPTANE AT HIGH TEMPERATURE AND PRESSURE.

Alaoui, F.1,2, González-Fernández, M. J.1, Muñoz, N.1, Aguilar F.1 and Montero E.1,

*Author for correspondence

1Department of Electromechanical Engineering, Escuela Politécnica Superior
University of Burgos,
Burgos, 09006,
Spain,

2Ecole Nationale des Sciences Appliquées d'El Jadida
Université Chouaib Doukkali-El Jadida,
El Jadida 24002,
Morocco,
E-mail: emontero@ubu.es

ABSTRACT

The increasing worldwide use of bio-fuels constitutes one of the measures considered to reduce greenhouse gas emissions. Bio-fuels also have an important part to play in promoting the security of energy supply, and promoting technological development and innovation. Di-butyl ether (DBE) is used as blending agent in reformulated gasoline and has been included in recent international regulations on the promotion of the use of energy from renewable sources for transport. The DBE is a non-polluting, high octane number blending agent. DBE could be also used as cetane enhancer in bio-diesel fuel, and can be obtained as an added valued additive to second generation bio-fuels. Second generation bio-fuels could be obtained from ligno-cellulosic biomass and waste materials.

Ether + alkane mixtures are of interest as model mixtures for gasoline in which the ether act as renewable, high octane number blending agent. From this point of view the study of the binary mixtures dibutyl ether + heptane, are very interesting. Heptane has been chosen as a representative of the linear alkanes that contain real gasoline. Density of the binary mixtures DBE + heptane and its pure compounds have been measured under pressure and reported in this work using a vibrating tube densitometer. Accurate PVT properties of pure ethers and its mixtures are required to develop and test equations of state, because equations of state are critical to design storage and transport systems in the fuel industry. Moreover, high temperature and pressure data serve to validate equations of state which are reliable for the increasingly use of industrial and engine processes under hard conditions.

Experimental densities (826 points) for the compressed liquid phase of the binary systems DBE + heptane have been measured at 298.15, 313.15, 333.15, 353.15, 373.15 and 393.15 K and at pressures up to 140 MPa, with an absolute uncertainty of 0.7 kg·m⁻³. For each composition, the experimental values were correlated using a Tait-type equation. Results show non-linear behaviour of the mixture.

INTRODUCTION

Increasing global concern due greenhouse gas emissions has generated much interest in the environmental friendly alternative bio-fuels. Bio-fuels for internal combustion engines as oxygenated compounds are also becoming important because of diminishing petroleum reserves and increasing air pollution [1, 2].

The oxygenated compounds used worldwide like simple alcohols and ethers, are used as gasoline additives to reduce pollutants from vehicle exhaust gases. Di-butyl ether (DBE) is used as blending agent in reformulated gasoline and has been included in recent international regulations on the promotion of the use of energy from renewable sources for transport. The DBE is a non-polluting, high octane number blending agent. DBE could be also used as cetane enhancer in bio-diesel fuel, and can be obtained as an added valued additive to second generation bio-fuels. Second generation bio-fuels could be obtained from ligno-cellulosic biomass and waste materials.

This work continues previous works of our group on the density of mixtures of oxygenates additives with fuel and biofuel components at high pressure and high temperature [3-6].

By means of a vibrating-tube densitometer, experimental densities (826 points) for the compressed liquid phase of the binary systems DBE + heptane have been measured at 298.15,
313.15, 333.15, 353.15, 373.15 and 393.15 K and at pressures up to 140 MPa, with an absolute uncertainty of 0.7 kg·m⁻³. For each composition, the experimental values were correlated using a Tait-type equation. Results show non-linear behaviour of the mixture.

**NOMENCLATURE**

| AA, Bi, C | [%] | Absolute Average Deviation |
| Bias | [%] | Average Deviation |
| MD | [%] | Maximum Deviation |
| N | Number of experimental data points |
| p | [MPa] | Pressure |
| p₀ | [MPa] | Reference pressure |
| T | [K] | Temperature |

Special characters

| σ | [g cm⁻³] | Standard deviation |
| ρ | [g cm⁻³] | Density |
| ρ₀ | [g cm⁻³] | Density at a reference pressure p₀ |

Superscripts, subscripts
calc | Calculated |
| exp | Experimental |
| i | Constituent identification |

**EXPERIMENTAL**

**Materials**

Dibutyl Ether (C₁₂H₂₄O, molar mass 130.228 g·mol⁻¹, CAS. 142-96-1) and heptane (C₇H₁₆, molar mass 100.2 g·mol⁻¹, CAS. 142-82-5) were obtained from Sigma-Aldrich with mole fraction purity of respectively 0.993 and 0.995. These chemicals were subject to no further purification and directly injected into the high pressure cell as soon as the bottles were opened.

Measurement Technique. Experimental Procedure

An Anton-Paar DMA HPM high-pressure vibrating-tube densitometer was used to measure the density ρ as a function of pressure p (up to 140 MPa) and temperature T between 293.15 and 393.15 K. The experimental setup was similar to the one described in a previous paper [5]. This type of densitometer can be used to perform measurements in a broad range of temperature intervals [10].

Pure fluids used in binary mixtures were degasified prior to the preparation of the samples. Degassing is carried out using an ultrasonic bath PSelecta, model Ultrason-H. Each mixture was prepared immediately before measuring, by weighing in glass vials sealed to prevent evaporation. For weighing, a Sartorius balance model BP 221S has been used, with resolution of 10⁻⁴ g, uncertainty ±0.0001 g. The estimated uncertainty in the composition of the mixture is ±0.00004 in mole fraction.

Prior to any measurement, the densitometer is evacuated using a vacuum pump Leybold Trivac D8B, protected by vacuum trap filled with liquid nitrogen. The system can get a vacuum pressure of 2 Pa, measured with a vacuum-meter Leybold.Vakuum Thermovac TTR91. After evacuation, filling of the densitometer is produced by suction of the substance from the sealed glass vial.

**Calibration procedure**

The calibration of the densitometer was performed according to the new procedure described by Comuñas et al. [7] which is modification of the procedure previously proposed by Lagourette et al. [8]. The calibration of the vibrating-tube densitometer has been performed using three reference fluids (water, vacuum and decane).

At 0.1 ≤ p ≤ 140 MPa and 293.15 ≤ T ≤ 363.15 K. The calibration of the densitometer over these ranges of temperature and pressure has been carried out using the procedure previously proposed by Lagourette et al. [8]. The pair of substances of calibration used are water and vacuum. The density values of water values have been taken from the equation of State (EoS) reported by Wagner and Pruss [9]. The uncertainty in density of this EoS is 0.0001% at 0.1 MPa in the liquid phase, 0.001% at other liquid states at pressures up to 10 MPa and temperatures to 423 K, and 0.003% at pressures in the interval 10 to 100 MPa and temperature up to 423 K. The uncertainty is of the order of 0.02% at 1000 MPa.

At p = 0.1 MPa and T ≥ 373.15 K. The limitation of this procedure occurs when the measurements are carried out at 0.1 MPa and temperatures greater or equal to the boiling point of water (373.15 K). This is the case of the present work because the study is done up to temperatures above 373.15 K. In this work decane has been selected as substance of reference at conditions p = 0.1 MPa and T ≥ 373.15 K, because its density is well known at the atmospheric pressure over wide temperature intervals [10].

At p > 0.1 MPa and T ≥ 373.15 K. In the interval 0 to 1 MPa, as the pressure expansion coefficient of the cell is very low, the volume of the cell does not significantly change with pressure. Following the new procedure proposed in [7] the reference pressure for water density is 1 MPa instead of 0.1 MPa. It is necessary to know the oscillation period of the evacuated cell (over the entire temperature interval) and the period of the cell full of water and the density of water (for p > 0.1 MPa and for T ≥ 373.15 K). Over the above T, p intervals, only one reference fluid is necessary (water) together with the period of the evacuated cell.
After the densitometer was filled with the sample to be studied, the sample was brought to the desired temperature and pressure of interest and measured when thermal and mechanical equilibriums were reached.

Taking into account the accuracy of the temperature, the pressure, the period of oscillation measurement for water, vacuum, the studied systems, and the water density accuracy, the overall experimental uncertainty in the reported density values is estimated to be ±0.7 kg-m⁻³ (i.e., around ±0.07% for density close to water density). However, for measurements at atmospheric pressure at \( T = 373.15 \) and 393.15 K we used decane as reference fluid. The uncertainty of the decane density data reported in [10] (of the order of 0.0001 g·cm⁻³) is greater than that of water and consequently for the 2 data points at 373.15 K and 393.15 K, at \( p = 0.1 \) MPa the uncertainty is estimated to be less than 0.5%.

**RESULTS AND DISCUSSION**

For the purpose of comparing the experimental density values with those obtained with the two correlations considered in this work, we have used the Absolute Average Deviation (AAD), the Maximum Deviation (MD), the Average Deviation (Bias), and the standard deviation (\( \sigma \)) which are defined as follows:

\[
\text{AAD} = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{\rho_i^{\text{exp}} - \rho_i^{\text{calc}}}{\rho_i^{\text{exp}}} \right|
\]

\[
\text{MD} = \text{Max} \left( \frac{100}{N} \sum_{i=1}^{N} \left| \frac{\rho_i^{\text{exp}} - \rho_i^{\text{calc}}}{\rho_i^{\text{exp}}} \right| \right)
\]

\[
\text{Bias} = \frac{100}{N} \sum_{i=1}^{N} \left( \frac{\rho_i^{\text{exp}} - \rho_i^{\text{calc}}}{\rho_i^{\text{exp}}} \right)
\]

\[
\sigma = \sqrt{\frac{\sum_{i=1}^{N} \left( \frac{\rho_i^{\text{exp}} - \rho_i^{\text{calc}}}{\rho_i^{\text{exp}}} \right)^2}{N-1}}
\]

where \( N \) is the number of experimental data (\( N = 138 \) for each composition) and \( m \) the number of parameters (we will see below that with our correlation \( m = 7 \)).

The measured densities of pure DBE and heptane, and the four binary mixtures DBE (1) + heptane (2) (mole fraction \( x_1 = 0.3526, 0.5007, 0.6735, 0.8469 \)) are reported in Table 1 along six isotherms between 298.15 K to 393.15 K and at pressures up to 140 MPa (23 isobars). No measurements were made at \( p = 0.1 \) MPa and at 373.15 K and 393.15 K for pure heptane, because the boiling point of heptane is 373.15 K.

**Table 1.** Experimental Densities, \( \rho \) (kg·m⁻³), for \( x \) DBE + \((1-x)\) heptane at various Temperatures \( T \) and Pressures \( p \).  

\[
\begin{array}{cccccccc}
\text{mole fraction} & \text{0.0000} & \text{0.1} & \text{0.3526} & \text{0.5007} & \text{0.6735} & \text{0.8469} & \\
\text{mole fraction } x_1 & 298.15 & 313.15 & 333.15 & 353.15 & 373.15 & 393.15 & \\
\text{298.15} & 313.15 & 333.15 & 353.15 & 373.15 & 393.15 & \\
\text{298.15} & 313.15 & 333.15 & 353.15 & 373.15 & 393.15 & \\
\end{array}
\]

Where \( \rho^i \) is the density of component \( i \) at temperature \( T \), calculated for \( p = \text{atmospheric} \).
mixtures at high pressure or high temperature.

No data were found in the literature for the same binary
temperature is non-linear (more particularly at low pressure)
considered here is sufficiently large, the density versus
maximum deviation occurs at (\(T = 393.15\) K and \(p = 1\) MPa)
for \(x_i = 0.8469\).

<table>
<thead>
<tr>
<th>(x_i)</th>
<th>(g)</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>0.9643</td>
<td>0.8377</td>
</tr>
<tr>
<td>0.05</td>
<td>0.01</td>
<td>0.06</td>
</tr>
</tbody>
</table>

**Table 2.** Obtained Parameters and Deviations for Density Correlation by using equation 5 for \(x\) DBE + (1-x) heptane.

\[
\rho(T,p) = \frac{\rho_0(T)}{1 - C \ln \left( \frac{B(T) + p}{B(T) + 0.1 \text{MPa}} \right)}
\]

where

\[
\rho_0(T) = A_0 + A_1 T + A_2 T^2
\]

\[
B(T) = B_0 + B_1 T + B_2 T^2
\]

Notice that the AAD and the standard deviations are lower
than the experimental uncertainty; consequently equations 5 to
7 make it possible to interpolate the density at any \(T, p\)
conditions. Figures 1(a) and (b) show the variation of density as
a function of temperature at \(p = 0.1\) and 140) MPa at different
mole fractions of DBE: \(x_i = 0.0, 0.3526, 0.5007, 0.6735, 0.8469\)
and 1.0. As usual, density decreases when temperature
increases. This figure show that, as the temperature interval
considered here is sufficiently large, the density versus
temperature is non-linear (more particularly at low pressure)
which justifies the use of equation 5.
mole fractions of DBE: \( x_1 = 0.0, 0.3526, 0.5007, 0.6735, 0.8469 \) and 1.0. Following the same behavior, density increases when pressure increases. The shape of the isothermal curves of the density versus pressure is compatible with the logarithmic relationship used in the Tait-type density relation used to model the influence of pressure on density.

**CONCLUSION**

826 experimental density data for the compressed liquid phase of the binary systems DBE + heptane have been measured at 298.15, 313.15, 333.15, 353.15, 373.15 and 393.15 K and at pressures up to 140 MPa (23 isobars), with an absolute uncertainty of 0.7 kg·m\(^{-3}\). Pure compounds and four intermediate mole fractions, \( x_1 = 0.3526, 0.5007, 0.6735 \) and 0.8469, are reported. For each composition, the experimental values were correlated using a Tait-type equation. As the temperature interval considered here is sufficiently large, the density versus temperature is non-linear. Also the shape of the isothermal curves of the density versus pressure shows a logarithmic relationship. High temperature and pressure data could serve to validate equations of state which are reliable for the increasingly use of industrial and engine processes.

**ACKNOWLEDGEMENT**

Support for this work came from the Ministerio de Ciencia e Innovación. Spain. Project ENE2009-14644-C02-02

**REFERENCES**


[10] TRC, Thermodynamic Tables, Texas A&M University, College Station, 1996.