

PVT properties of oxygenated compounds DIPE and DBE for the development of new biofuels

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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-isopropylether (DIPE) and Di-butylether (DBE) are used as blending agents in reformulated gasoline. The DBE acts as 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. The DIPE is chemically similar to hydrocarbons and presents low solubility in water. Concerning the solubility in water, DIPE is the less contaminant ether amongst those fuels oxygenates of high molecular mass and branched structure. Finally, the high boiling point of DIPE allows incorporation of more light feedstocks in gasoline, especially light cyclic alkanes which are also used as octane enhancers. The knowledge of several properties, including densities at different temperatures and pressures, is required for engineering design and for subsequent operations. The test of the existent models and the development of new methods for prediction of the thermodynamic functions, is of particular significance because it is the only way to ensure accurate results. Moreover, for the optimized design of several industrial processes (storage, transport, separation, and mixing processes), reliable experimental pVT data are needed. For these reasons, this work aims to provide experimental information on the volumetric properties which should be useful for modelling purposes. A review on density of DIPE and DBE published data under pressure and reported in this work. Comparison between both sets of data is presented.

Keywords:

Bio-fuels, Density, DIPE, DBE.

1. Ethers as components of second generation biofuels

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. First generation biofuels are made from the sugars and vegetable oils found in arable crops, which can be easily extracted using conventional technology. First generation biofuel processes are useful but limited in most cases: there is a threshold above which they cannot produce enough biofuel without threatening food supplies and biodiversity. Second generation biofuels can help solve these problems and can supply a larger proportion of global fuel supply sustainably, affordably, and with greater environmental benefits. The goal of second generation biofuel processes is to extend the amount of biofuel that can be produced sustainably by using biomass consisting of the residual non-food parts of current crops, such as stems, leaves and husks that are left behind once the food crop has been extracted, as well as other crops that are not used for food purposes (non-food crops), such as switchgrass, grass, jatropha, whole crop maize, miscanthus and cereals that bear little grain, and also industry waste such as woodchips, skins and pulp from fruit pressing, etc. The problem that

second generation biofuel processes are addressing is to extract useful feedstocks from this woody or fibrous biomass, where the useful sugars are locked in by lignin, hemicellulose and cellulose. All plants contain lignin, hemicellulose and cellulose. These are complex carbohydrates (molecules based on sugar). The following second generation biofuels are under development, although most or all of these biofuels are synthesized from intermediary products, like alcohols (i.e., mixture of mostly ethanol, propanol, and butanol, with some pentanol, hexanol, heptanol, and octanol).

Various ethers have been suggested as fuel additives that, either alone or in mixture with other ethers or alcohols, can enhance the octane rating and reduce pollution effects arising out of the combustion process [1]. Thus, the ethers increase the amount of oxygen in gasoline in order to reduce the CO content in the exhaust gas of automobiles. Over past years, many researchers have directed their attention to branched alkyl ethers (MTBE, ETBE, TAME and DIPE), because of their excellent applications as additives in fuels and bio-fuels.

Di-isopropyl ether (DIPE), $C_6H_{14}O$, is secondary ether, which can be obtained industrially as a by-product in the production of isopropanol by hydration of propene. From the environmental point of view, di-isopropyl ether (DIPE) presents some important advantages compared to other branched alkyl ethers. Concerning the solubility in water, DIPE is the less contaminant ether amongst those fuels oxygenates of high molecular mass and branched structure [2]. In addition, the DIPE is non-toxic and non-polluting chemical [3,4]. The high boiling point of DIPE allow incorporation of more light feedstocks in gasoline, especially light cyclic alkanes which are also used as octane enhancers.

Dibutyl ether (DBE), $C_8H_{18}O$, is also used as blending agent in reformulated gasoline and has been included in recent international regulations [5] on the promotion of the use of energy from renewable sources for transport. The DBE acts as non-polluting, high octane number blending agent. DBE could be also used as cetane enhancer in bio-diesel fuel [6], and can be obtained as an added valued additive to second generation bio-fuels. Industrially, dibutyl ether can be obtained by dehydration of 1-butanol on alumina.

Table 1 presents a summary of thermophysical data of DIPE and DBE.

Table 1. Summary of thermophysical data of DIPE and DBE.

Compound	Molecular Formula	CAS Number	Molar Mass (g.mol ⁻¹)	Boiling Point (°C/K)
DIPE	$C_6H_{14}O$	108-20-3	102.17	68.5 °C / 341.6 K
DBE	$C_8H_{18}O$	142-96-1	130.23	142.4 °C / 415.5 K

This work concerns DIPE and DBE. A review on density of DIPE and DBE published data under pressure and reported in this work. Comparison between both sets of data is presented. As both ethers are frequently mixed with bio-alcohols, a list of available density data on DIPE + alcohol and DBE + alcohol mixtures is also presented.

2. Review on PVT properties of DIPE and DBE

PVT data have great importance from theoretical and practical approaches. In practical context, the equations of state are instrumental for *PVT* calculation in process engineering problems and especially in petroleum gas/liquid equilibrium calculations. A successful *PVT* model based on a fitting equation of state can be helpful to determine the state of the flow regime, the parameters for handling the reservoir fluids, piping and sizing. Moreover, for the optimized design of several industrial processes (storage, transport, separation and mixing processes), reliable experimental data are needed. Reliability of molecular based equations of state are often analysed by comparing their predictions with *PVT* experimental values.

Compressed liquid densities for DIPE at high pressure and high temperature has been measured successively by Schornack and Eckert [7] (14 data points at 303.15 K and 323.15 K up to 504.6 MPa), Govender et al. [8] (50 data points from 288.15 K to 328.15 K up to 8.0 MPa), Ulbig et al. [9-11] (12 data points from 278.15 K to 323.15 K up to 60.0 MPa), Ihmels and Gmehling [12] (328 data points from 273.21.15 K to 473.13 K up to 35 MPa), Meng et al. [13] (70 data points from 243.15 K to 373.15 K up to 21.68 MPa). Very recently, our group has published new data, Dakkach et al. [14] (158 points from 293.15 K to 393.29 K up to 140 MPa). From the pressure range point of view, except for the data from Schornack and Eckert [7] and Dakkach et al. [14], all the measurements were carried out under a pressure lower than 60 MPa. On the hand of temperature, except data from references [12], [13] and [14], all published density data for the liquid phase were measured well below the normal boiling point of DIPE, 341.6 K. Table 2 shows the summary of the literature review.

Table 2. High pressure density literature data for DIPE. N corresponds to the number of data points.

Reference	Year	T _{min} /K	T _{max} /K	p _{min} /MPa	p _{max} /MPa	N
Schornack and Eckert [7]	1970	303.15	323.15	1.0	511.3	14
Govender et al. [8]	1996	288.15	328.15	0.1	8	50
Ulbig et al. [9-11]	1997	278.15	323.15	0.1	60	12
Ihmels and Gmehling [12]	2002	273.21	473.13	0.34	35	328
Meng et al. [13]	2009	243.15	373.15	0.1	21.68	70
Dakkach et al. [14]	2015	293.15	393.29	0.1	140	158

To the extent we know, compressed liquid densities for DBE, that are rather scarce, have been measured only by Meng et al. [13], (70 data points between 243.15 K and 373.15 K, and from 0.1 to 21.1 MPa) and by our research group, Alaoui et al. [15], (90 points from 293.15 K to 393.15 K, up to 140 MPa).

3. Comparison of PVT properties of DIPE and DBE

For the purpose of comparison of *PVT* data between DIPE and DBE, homogeneous set of data from references [14] and [15] have been used. Data over the temperature range 293.15 K to 393.15 K and pressure range from 0.1 MPa to 140 MPa are correlated using the following Tait-like equation:

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

where

$$\rho_0(T) = A_0 + A_1T + A_2T^2 + A_3T^3 \quad (2)$$

$$B(T) = B_0 + B_1T + B_2T^2 \quad (3)$$

Mention here that the A_i , B_i and C parameters values were determined by correlating simultaneously all the experimental densities values versus pressure and temperature. ρ_0 is the density at a reference

pressure p_0 , usually 0.1 MPa. The Tait-correlation parameters taken from [14] and [15] are given in Table 3 for DIPE and DBE.

Table 3. Parameters of (1) for density correlation for DIPE and DBE in the ranges (293.15 K - 393.15 K) and (0.1 MPa - 140 MPa), following [14-15].

Equation (1) parameters	DIPE	DBE
$A_0 / \text{g cm}^{-3}$	1.0867	0.9395
$A_1 / \text{g cm}^{-3} \text{K}^{-1}$	$-1.914 \cdot 10^{-3}$	$-2.794 \cdot 10^{-4}$
$A_2 / \text{g cm}^{-3} \text{K}^{-2}$	$3.873 \cdot 10^{-6}$	$-1.221 \cdot 10^{-6}$
$A_3 / \text{g cm}^{-3} \text{K}^{-3}$	$-5.360 \cdot 10^{-9}$	$6.054 \cdot 10^{-10}$
B_0 / MPa	312.2	348.7
$B_1 / \text{MPa K}^{-1}$	-1.269	-1.282
$B_2 / \text{MPa K}^{-2}$	$1.307 \cdot 10^{-3}$	$1.221 \cdot 10^{-3}$
C	0.08865	0.08861

Figure 1 shows the variation of density as a function of pressure at $T = (298.15, 333.15 \text{ and } 393.15 \text{ K})$ for DIPE and DBE calculated using (1), and DIPE and DBE parameters from Table 3. As usual, density increases when pressure increases.

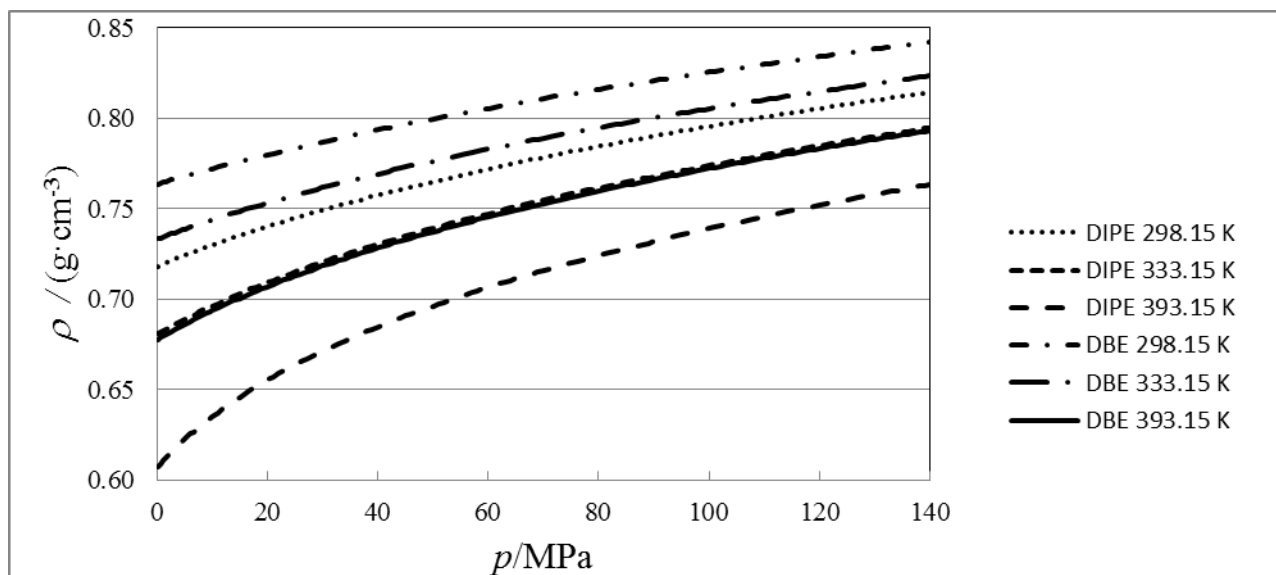


Fig. 1. Density versus pressure behaviour of DIPE and DBE for $T = (298.15, 333.15 \text{ and } 393.15 \text{ K})$

At constant temperature the curves are concave, which is associated with a negative second order derivative. 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. Moreover, for both fluids, density decreases when temperature increases. This figure shows 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 (1).

DBE presents higher density values than DIPE for the same temperature and pressure. At a first sight, this behaviour could be expected due to the fact that molar mass of DBE is 1.275 (27.5%) times the one of DIPE, following Table 1. However, density data of DBE are greater than those of DIPE by 4.5%, 5.0% and 6.1% in average at 298.15 K, 333.15 K and 393.15 K respectively. As

ethers are non-self-associating compounds, no hydrogen bonds between molecules are expected. Then volumetric compactness of DIPE due to its branched structure (see Fig. 2) with respect to the linear structure of DBE, could explain the differences.

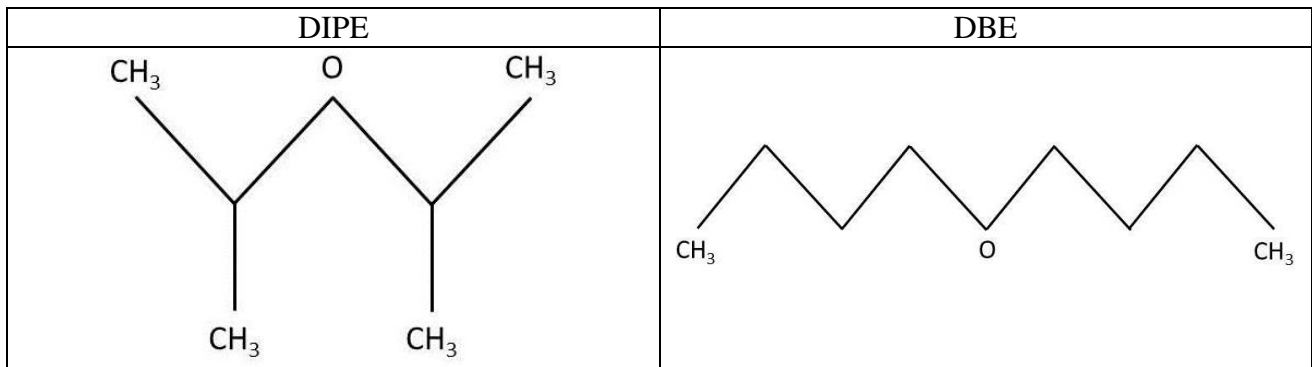


Fig. 2. Molecular structure of DIPE and DBE

4. The derived thermodynamic properties of DIPE and DBE

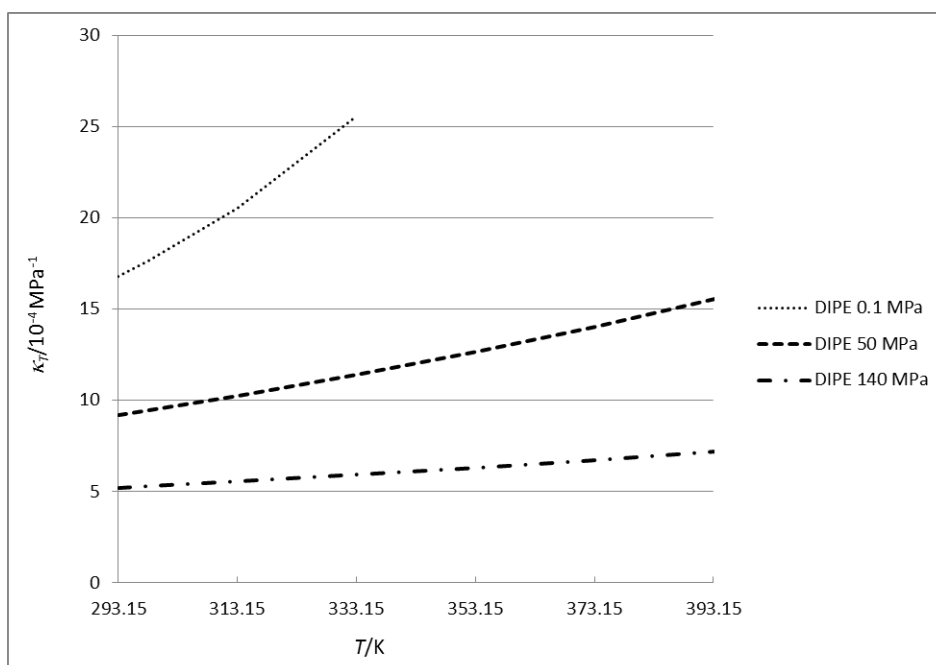
The experimental densities were used to derive other important properties such as isothermal compressibility and isobaric expansivity which can give valuable information on the dependence of the volumetric properties on temperature and pressure. The isothermal compressibility, κ_T , can describe the effect of pressure on the density based on the equation, and is obtained by differentiating equation (1)

$$\kappa_T = \left(\frac{1}{\rho} \right) \left(\frac{\partial \rho}{\partial p} \right)_T \quad (4)$$

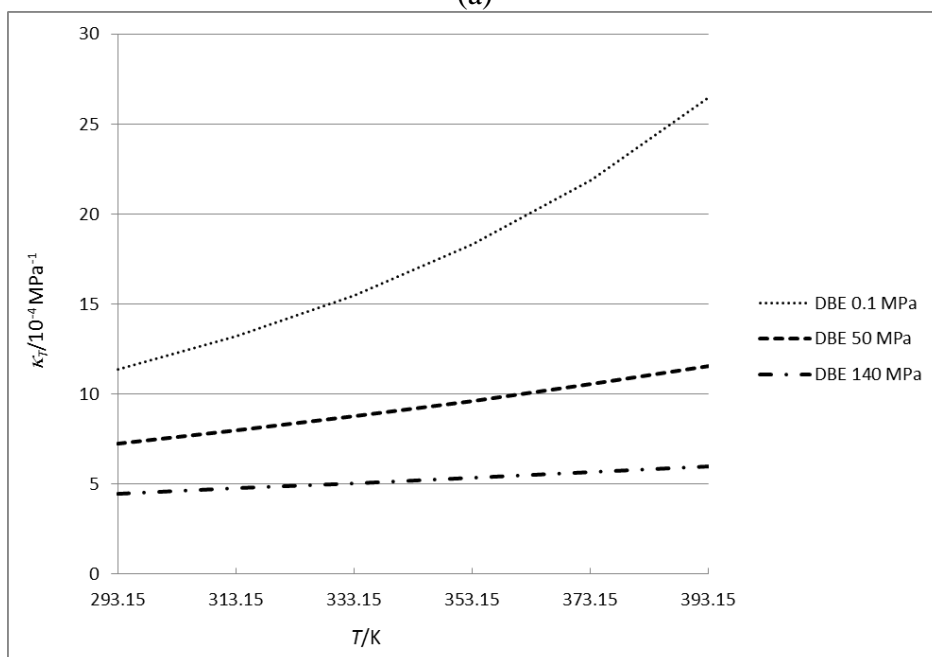
Similarly the isobaric thermal expansivity, α_p , describes the effect of temperature on the density, and could also be obtained analytically by differentiating equation (1)

$$\alpha_p = \left(\frac{1}{\rho} \right) \left(\frac{\partial \rho}{\partial T} \right)_p \quad (5)$$

The isothermal compressibility, κ_T , and the isobaric thermal expansivity, α_p , were calculated from the above procedures, and reported in Fig. 3 and Fig 4.



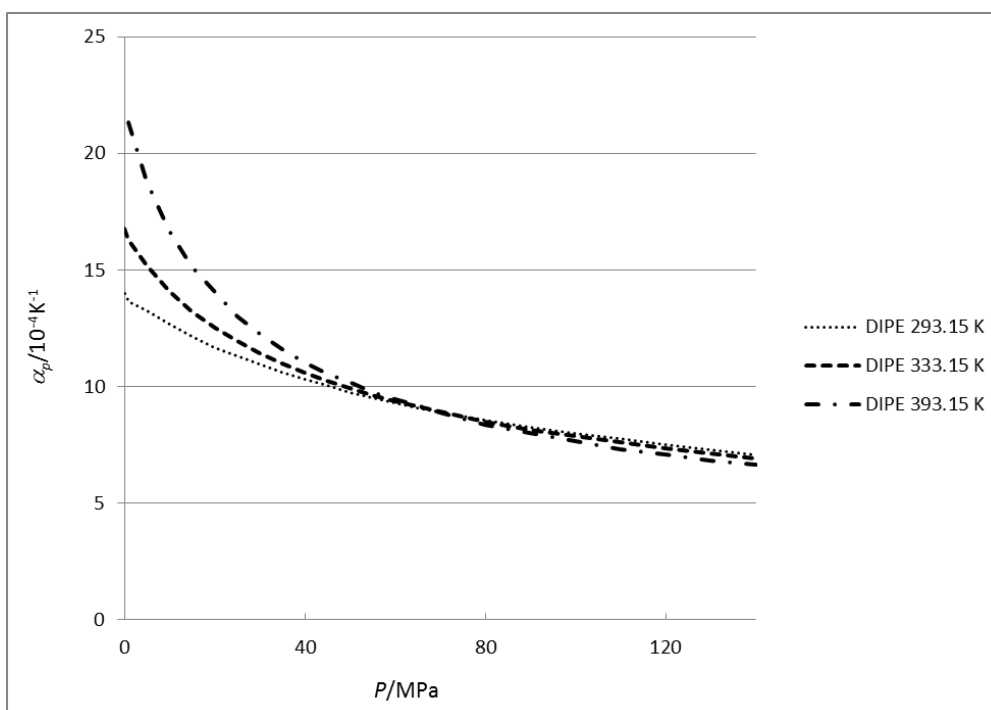
(a)



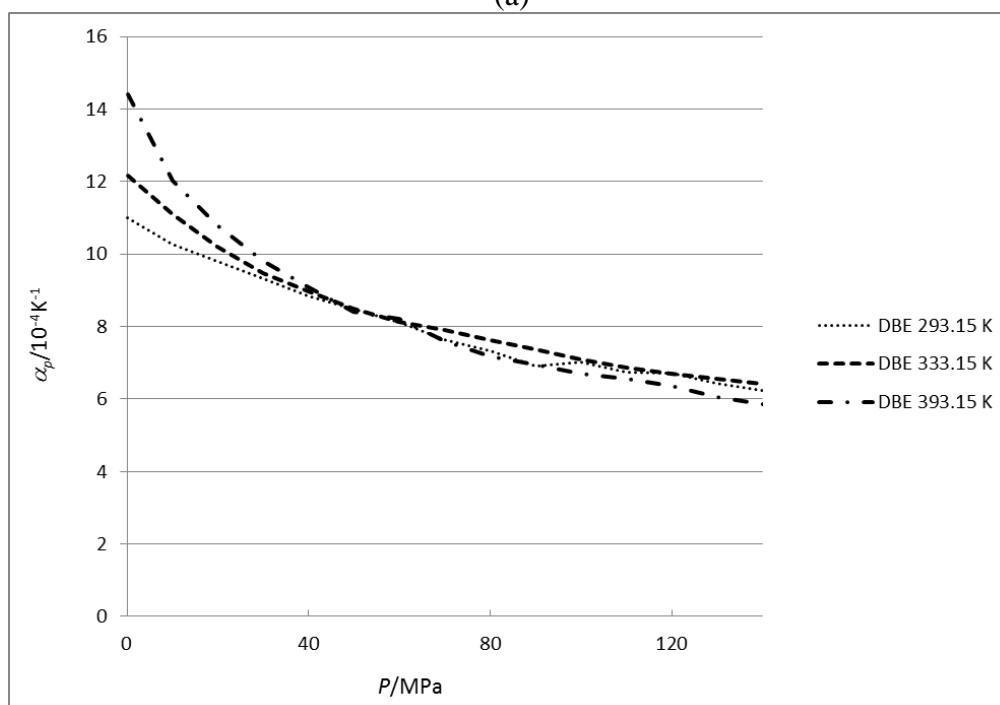
(b)

Fig. 3. Values of the isothermal compressibility, κ_T , for DIPE (a) and DBE (b) at 0.1, 50 and 140 MPa as a function of temperature.

Within the pressure range, it has been observed that curvilinear forms of α_P and κ_T are characteristic. In general, an increase in density implies a decrease in the molar volume with a corresponding decrease in the free intermolecular space. As a result, the ability of the liquid to expand or compress decreases as well, which corresponds to lower values of α_P as the pressure increases. This effect is more pronounced for DIPE. Concerning the isothermal compressibility, the effect of high pressure leads to a more linear behaviour of κ_T than at low pressures.



(a)



(b)

Fig. 4. Values of the isobaric thermal expansivity, α_p , for DIPE (a) and DBE (b) 293.15, 333.15 and 393.15 K as a function of pressure.

5. Conclusions

Diisopropyl ether (DIPE) and dibutyl ether (DBE) are considered as potential oxygenated additives for second generation biofuels. A literature review on densities in the compressed liquid state is presented for DIPE and DBE for temperatures between 243.15 K and 473.15 K and pressures up to 511 MPa. These measurements represent a wide range of the *PVT* data available for DIPE and

DBE. Data from 293.15 K to 393.15 K and up to 140 MPa were correlated with a Tait-type equation to allow reliable interpolation of data. The derived thermodynamic properties isothermal compressibility and isobaric expansivity, which can give valuable information on the dependence of the volumetric properties on temperature and pressure, are also presented.

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Nomenclature

A_i, B_i, C	coefficients of density correlation
p	pressure, MPa
p_0	reference pressure, MPa
T	temperature, K

Greek symbols

α_p	isobaric thermal expansivity, K ⁻¹
ρ	density, g·cm ⁻³
ρ_0	density at a reference pressure p_0 , g·cm ⁻³
κ_T	isothermal compressibility, MPa ⁻¹

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