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Speed of sound, density and derivative properties of binary mixtures HFE-7500 + Diisopropyl ether under high pressure

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ABSTRACT

Speeds of sound for the binary system HFE-7500 + Diisopropyl ether have been measured at pressures up to 100 MPa and within a temperature interval from (293.15 to 353.15) K. High pressure density measurements were carried out by using a U-tube densimeter up to 140 MPa and at temperatures from (293.15 to 393.15) K. Additionally, the density and the isentropic compressibility were evaluated from integration of speed of sound data in the pressure range from (0.1 to 100) MPa and in the temperature interval from (293.15 to 353.15) K. This work also reports a correlation for both the density and the speed of sound within their estimated uncertainties to evaluate the volume and its derivatives with respect to pressure and temperature.

1. Introduction

Since the decade of the '70 s, concern on stratospheric ozone layer depletion [1] and later on climate change [2] has led to plan a phase-out of halogenated hydrocarbons by setting limits in emissions and production of these substances in order to reduce its impact on the atmosphere. Perfluorocarbons (PFCs) and perfluoropolyethers (PFPEs) were introduced as alternatives to ozone depleting substances and were intended to be used as propellants, cleaning solvents, lubricants, as refrigerants of some specialized refrigeration systems or as heat transfer media due to its stability, low viscosity, low surface tension and excellent dielectric properties. Although these properties made them widely used in industry processes, PFCs were demonstrated to have extraordinary long atmospheric lifetimes and to be some of the most potent greenhouse gases [3]. The Kyoto Protocol, adopted on December 1997 implemented the objective to reduce these anthropogenic greenhouse gas emissions, stablishing a structure of emission reduction commitment periods, in which the first period included the PFCs as one of the fluids whose use and production had to be diminished during the period (2008 – 2012). The Paris Agreement, which was adopted on December 2015, and signed in April 2016, provided a proposal to mitigate the greenhouse gas emissions that will start in the year 2020, focusing high GWP substances on the spotlight. This situation urged to search environmentally friendly alternatives to these commonly used fluorocarbons but with the same or similar properties. Some fluids, as fluorinated ethers, fluoroamines, alcohols and sulphur compounds were proposed and investigated [4] but the knowledge about their thermophysical properties, toxicity and stability is sometimes scarce.

Hydrofluoroether fluids (HFEs) are a type of fluorinated ethers investigated since the decade of the '90 s as substitutes of CFCs, HCFCs and PFCs among other fluorocarbons, due to their desirable environmental properties, that is, zero ozone depletion potential (ODP), low global warming potential (GWP) and short atmospheric lifetimes (ALT) and due to their thermophysical properties. HFEs show low toxicities, compatibility with a large range of materials including most metals and plastics, stability and low diffusive and drag-out losses [5].

2-Trifluoromethyl-3-ethoxydodecafluorohexane, known as HFE-7500, is proposed to be a good alternative to PFCs and PFPEs replacement because it is a dielectric fluid with low viscosity, high liquid density, low surface tension, being almost non-toxic and showing favorable environmental properties such as zero ODP, a very low GWP and an ALT of 2.2 years.

Diisopropyl ether (DIPE) is used in a wide variety of applications, for example it is used as solvent or as cleaning agent. The

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addition of the fluorinated compound HFE-7500 implies a reduction on the flammability of Diisopropyl ether, making this binary mixture a good option to be used in high precision cleaning, or as solvent as oil-based solutions dissolve in it.

In this work the physical properties speed of sound and density of the binary mixture x HFE-7500 + (1 − x) Diisopropyl ether have been determined experimentally at high pressures and at high temperatures at five mole fractions, x = (0.250, 0.375, 0.500, 0.625 and 0.750). Density was also calculated by integration of speed of sound data, and the derivative properties isentropic compressibility, isothermal compressibility and isobaric expansion were also determined from speed of sound measurements.

2. Experimental section

2.1. Materials

Hydrofluoroether fluid HFE-7500, also known by its chemical name, 2-trifluoromethyl-3-ethoxydodecafluorohexane or 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-trifluoromethylhexane (CAS: 297730-93-9) was obtained from the 3 M company with a stated mass fraction purity greater than 0.995. Diisopropyl ether (DIPE), also known as 2,4-dimethyl-3-oxapentane, was supplied by Sigma-Aldrich (CAS: 108-20-3), with a purity greater than 0.995. Neither one of the fluids was subject to further purification. Table 1 shows the specifications of both chemicals.

2.2. Speed of sound measurement

To determine the speed of sound at high pressure in compressed liquids, a cylindrical acoustic cell using a pulse-echo technique working in transmission mode was used. The operating principle is based on the determination of the time delay between the transmitted pulse and the first echo of an acoustic wave that spreads through the fluid. The apparatus, which has been described previously [6], was made to measure speeds of sound in liquids and was designed for working up to 210 MPa using a pulse-echo method working at 3 MHz with a path length fixed to L_0 = 30 mm. It has two electromechanical transducers in direct contact with the fluid facing each other inside a hollow cylindrical support in which one acts as a transmitter, and the other as the receiver. The acoustic sensor is placed inside a stainless-steel vessel closed at one end by a plug with three electric connectors. Prior to make the measurements, and in order to bring the path length needed for calculating speed of sound, the apparatus was calibrated with two reference fluids, purified water [7,8] and heptane [9] at different pressures and temperatures.

To ensure a constant temperature, the acoustic cell is immersed in a thermoregulated bath filled with silicone oil so that the stability in temperature is of 0.02 K in the range investigated. The temperature is measured thanks to a Pt100 probe in contact with the liquid sample with an uncertainty of ±0.1 K. With respect to the pressure, it is generated by a high pressure volumetric pump that reaches the cell by the liquid itself and is measured by using a pressure gauge calibrated between (0.1 and 100) MPa so the uncertainty is of 0.01 MPa in our pressure range. The expanded uncertainty for speed of sound in the pressure and temperature ranges investigated according to the law of propagation of standard uncertainties [10] is estimated to be 2 m·s^{-1}.

2.3. Density measurement

Since density is one of the most important physical properties because other important properties can be determined from its knowledge, high pressure densities for the binary mixture x HFE-7500 + (1 − x) Diisopropyl ether were determined experimentally in this work. For this purpose, an Anton Paar DMA HPM vibrating tube densitometer operating in the ranges (293.15–393.15) K for the temperature and (0.1–140) MPa for the pressure was used. The density is determined by the oscillation period of a U-tube made of Hastelloy in the presence of damping and under an external periodic force. This oscillation period differs for each fluid and it depends also on temperature and on pressure, being density related to the square of the period by a linear law. The calibration of the vibrating-tube densitometer has been performed according to the procedure described by Comuñas et al. [11] using three reference fluids: vacuum, water [12] and decane [13], being decane the choice as reference liquid for temperatures higher than the boiling point of water (373.15 K) at 0.1 MPa.

The estimated uncertainty given in temperature by the Pt100 probe placed inside the densitometer was ±0.1 K in the temperature range investigated, (293.15–393.15) K while the estimated uncertainty given in pressure by the HBM pressure gauge was 0.01 MPa for the pressure interval considered (0.1–140) MPa. The expanded uncertainty in density was then obtained from the uncertainties in temperature, in pressure, and taking into account the uncertainty in measurements of oscillation period, as well the error in the calibration method, giving an estimated value of ±0.5 kg·m^{-3} (0.06%) in the pressure range investigated. The mixtures were prepared immediately before use by weighing the corresponding amount of each component for every mole fraction, filling stoppered bottles of 250 cm^3 in volume at atmospheric pressure using a high precision Sartorius balance with an uncertainty of ±0.001 g. Taking into account the uncertainty of the balance, and considering a coverage factor k = 2, the expanded uncertainty in the composition of the mixtures results to be 5·10^{-4} in mole fraction.

2.4. Micro differential scanning calorimetry (μDSC)

In order to calculate high pressure density data from speed of sound measurements by following the procedure described on Section 3. Results and Discussion, heat capacity values C_p, are needed. For this purpose, a SETARAM Micro DSC 7 evo calorimeter was used to measure this property at atmospheric pressure and in different temperature ranges for the pure compounds and for the five mole compositions of the binary mixture x HFE-7500 + (1 − x) Diisopropyl ether. This calorimeter is based on the Calvet calorimetric principle, being the output signal given by the difference of the heat flux received by the flux meters located around the

Table 1
Sample description.

Compound	Source	Formula	Molar mass/g mol^{-1}	Stated purity[a]	CAS number
HFE-7500[b]	3M Company	$C_9H_5F_{15}O$	414.11	>99.5[c]	297730-93-9
Diisopropyl ether	Sigma-Aldrich	$C_6H_{14}O$	102.17	>99.5[d]	108-20-3

[a] Determined by gas chromatography (GC) by the supplier.
[b] HFE-7500 = 2-trifluoromethyl-3-ethoxydodecafluorohexane.
[c] Mass fraction purity/wt%.
[d] Mole fraction purity/mol%.