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High pressure speed of sound and density of (decalin + *n*-decane), (decalin + *n*-hexadecane) and (*n*-decane + *n*-hexadecane) systems and thermodynamic modeling with PHCT equation of state

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ABSTRACT

Decalin, *n*-decane and *n*-hexadecane are chemicals asymmetrical in shape, length and chemical nature that can be found in diesel and kerosene fractions. To evaluate the influence of these differences on the physical properties of mixtures involving these components, speed of sound for *n*-decane, *n*-hexadecane and decalin, as well as for binary mixtures composed of these hydrocarbons, were determined at pressures (0.1, 5, 10, 15, 20 and 25) MPa and temperatures (313.15, 323.15 and 333.15) K at different compositions. Additional density data at atmospheric pressure for the same systems were measured experimentally at temperatures of (313.15, 323.15 and 333.15) K. From these results and thermodynamic definitions, density at high pressures and excess molar volume were calculated. The experimental data were correlated with the Perturbed-Hard-Chain Theory (PHCT) equation of state. The PHCT model correlated well experimental densities for pure components and mixtures but did not correlate so well the speed of sound dependency with temperature and pressure. The model calculated well excess molar volumes, with correct signs, magnitudes, and the qualitative effect of pressure and temperature on this property.

1. Introduction

To predict the behavior of hydrocarbons streams, the petroleum industry uses different thermodynamic models, based on equations of state and mixing rules. Development and modifications of these models depends on the reliability and diversity of the experimental data. Generally, models are selected by comparing experimental and calculated phase equilibria and density data over wide ranges of temperature, pressure and composition. However, the usual model parameterization may lead to poor prediction of other properties. Speed of sound, which can also be considered as a thermodynamic quantity, due to its close linkage to certain volumetric and isentropic properties of fluids, can be used as supplementary information in comparative tests of models. It can also be used as a discriminating quantity during comparative tests of different models [1–3].

The accurate measurement of ultrasonic velocity plays an important role in the characterization of the effect of pressure on thermodynamic properties of liquids if it coincides perfectly with the speed of sound in the low frequency limit [3]. For the systems studied in this investigation, this condition is satisfied because the hydrocarbons present in the mixtures do not present dispersive effects in the frequency domain concerned by the experiments [4,5].

In a previous work [6], our group measured density and speed of sound data in binary systems of (tetralin + *n*-decane) and (tetralin + *n*-hexadecane). Tetralin is an aromatic molecule with two fused rings. As a continuation to this study, in the present work tetralin was replaced by a mixture of *cis*- and *trans*-decalin, at a fixed composition, hereafter called only decalin. This is a reference naphthenic compound with two fused rings used as a surrogate to naphthenic compound in diesel and kerosene fractions [7]. In this context, studies of speed of sound and density at high pressures of binary mixtures of decalin with *n*-decane or *n*-hexadecane can be used to simulate the properties of kerosene and diesel fractions.

Letcher and Lucas [8] measured the excess molar volume of (decalin + *n*-hexadecane) at temperature of 308.15 K and atmospheric pressure. Oswal and Maisuria [9] experimentally determined speed of sound and excess volumes of mixtures

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containing (cycloalkane + alkane) at temperature of 303.15 K and atmospheric pressure. The results were correlated with Prigogine–Flory–Patterson (PFP) model [10,11]. Bamgbade et al. [12] measured excess volumes of (propane + *n*-decane) and (propane + *n*-icosane) at high-temperatures and high-pressures. The reported data were correlated with Perturbed-Chain SAFT [13] and Peng–Robinson [14] equations of state, with better results obtained with Perturbed-Chain SAFT. High pressure density and speed of sound data of mixtures of alkanes and cycloalkanes are scarce, and no speed of sound data at high pressure for (decalin + *n*-decane) and (decalin + *n*-hexadecane) mixtures are available in the open literature. Also, few equations of state have been tested.

In this work, speed of sound, *c*, for *n*-decane, *n*-hexadecane and decalin, as well as for binary mixtures involving these hydrocarbons, were determined at pressures, *P*, of (0.1, 5, 10, 15, 20 and 25) MPa and temperatures, *T*, of (313.15, 323.15 and 333.15) K at different compositions. Density (ρ) measurements for the systems at atmospheric pressure were performed at the same temperatures. From these data and based on thermodynamic definitions, the following properties were calculated: density at high pressures and excess molar volume, V^E, in the same temperature interval and pressure range of the speed of sound measurements. Density and speed of sound data were used to estimate the parameters of the studied substances to be used along with Perturbed-Hard-Chain Theory (PHCT) equation of state [15,16].

2. Experimental section

The suppliers and mass fraction purities of the chemicals used in the study are shown in table 1.

2.1. Speed of sound and density determination

The speed of sound measurements were carried out in a modified version of the high-pressure equilibrium apparatus described in Rocha et al. [17]. The main modification was made in the pressure cell. The pressure cell, fabricated in stainless steel (304), was based on an apparatus previously proposed by Oag et al. [18] and described in Nascimento et al. [6]. Speed of sound data were measured using the time of flight technique with ultrasonic pulses being generated in a frequency of 4 MHz in intervals of 2 ms. As reported by Nascimento et al. [6], water was used to calibrate the apparatus. The free path between the ultrasonic transducers was measured at $T = 298.15$ K and the time delay in the metal walls was calculated as a function of temperature and pressure to reproduce the data for water. Calibration error was within experimental uncertainty, and so was the deviation of speed of sound of hydrocarbons from literature values obtained with this calibration [6]. This uncertainty is due to the simultaneous fluctuations in controlled temperature, controlled pressure, and to those implicit in the measurement of time of flight. No effect of fluctuation in composition was analyzed.

TABLE 1
Suppliers and purity of chemicals used in the study.

Chemical	Supplier	Purity (mass fraction)[a]	Purification
Decalin isomer mixture	Vetec Química Fina	>0.99 (0.4106 *cis* and 0.5869 *trans*)	No further purification
n-Decane	Vetec Química Fina	>0.99	
n-Hexadecane	Vetec Química Fina	>0.99	

[a] Informed by supplier.

The mixtures were prepared by weighing a desired mass of each pure hydrocarbon using an analytical balance (Mettler Toledo AR2140) with a precision of 10^{-7} kg. The estimated standard uncertainty in the mole fractions, without taking into account the samples impurity, was $1 \cdot 10^{-4}$. Taking into account the effect of impurity, the relative standard uncertainty is 1%, since the dominating component of uncertainty is this term.

The estimated standard uncertainty in speed of sound measurements, without taking into account the samples impurity, was $0.5\ \text{m} \cdot \text{s}^{-1}$ and the expanded uncertainty in speed of sound, with a 0.95 level of confidence (coverage factor equal to 2) was $1.0\ \text{m} \cdot \text{s}^{-1}$.

Density at atmospheric pressure was obtained using an automatic digital densimeter (Anton Paar DMA 4500) calibrated with air and bi-distilled water and presenting an estimated standard uncertainty, without taking into account the samples impurity, of $2 \cdot 10^{-2}\ \text{kg} \cdot \text{m}^{-3}$. For density measurement at atmospheric pressure the standard uncertainty in temperature is 0.01 K and is 1 hPa for pressure.

For speed of sound measurement at atmospheric pressure, the standard uncertainty in the temperature is 0.1 K and is 1 hPa for pressure. For density and speed of sound measurements at high pressures, the standard uncertainty in temperature is 0.1 K and is 0.005 MPa for pressure. The expanded uncertainty with 0.95 level of confidence in ρ at high pressures is $0.1\ \text{kg} \cdot \text{m}^{-3}$ without taking into account the samples impurity, and in V^E is $4 \cdot 10^{-8}\ \text{m}^3 \cdot \text{mol}^{-1}$.

Taking into account the samples impurity, considering the procedure reported in [19] in which the impurities are supposed to present properties that are 10% away from those of the almost pure component, with a 1% impurity level, impurity impairs uncertainty of 0.1% of the property. This is the dominating component of uncertainty, and doing so the standard uncertainties for density and speed of sound turn into $0.8\ \text{kg} \cdot \text{m}^{-3}$ and $1.2\ \text{m} \cdot \text{s}^{-1}$.

3. Calculations

3.1. Density at high pressures

The methodology to calculate density at high pressures from speed of sound data was detailed by Nascimento et al. [6]. The values of liquid molar heat capacities of pure hydrocarbons at atmospheric pressure, required for the calculation of density at high pressures were taken from literature [20]. The reported average deviation in liquid molar heat capacity is of 0.4% for *cis*-decalin and of 0.2% for *trans*-decalin, *n*-decane and *n*-hexadecane. For hydrocarbons mixtures the ideal solution hypothesis was applied. According to Daridon et al. [21], the molar heat capacity represents just a small percentage of density, therefore this consideration does not influence significantly the final value of density. Our calculations agree to the observation of Daridon et al. [21], in which 0.4% of variation in heat capacity impacts calculated density below the calculated uncertainty.

3.2. Perturbed-Hard-Chain Theory

The PHCT developed by Beret, Donohue and Prausnitz [15,16] is a theory based on approximations to describe molecular behavior and can be used to predict accurately thermodynamic properties. PHCT takes into account the effect of molecular motions from rotational, vibrational and translational degrees of freedom into the partition function of the system and reduces correctly to the ideal gas equation at low densities. The model uses only three molecular parameters for each pure fluid (v°, $\varepsilon q/k$ and C). The mixing rule was derived from statistical mechanics and has only one binary interaction parameter [16,22,23].