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Densities, speeds of sound, refractive indices, viscosities and their related thermodynamic properties for *n*-hexadecane + two aromatic hydrocarbons binary mixtures at temperatures from 298.15 K to 318.15 K

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ABSTRACT

The thermophysical properties (density, speed of sound, viscosity and refractive index) for the binary mixtures of *n*-hexadecane with *n*-propylbenzene and *sec*-butylbenzene, were measured at temperatures in the range of (298.15–318.15) K and pressure of 0.1 MPa. The obtained experimental results were used to calculate the excess and deviation quantities, namely the excess molar volumes, the excess speed of sound, the excess isentropic compressibilities, excess molar isentropic compressibility, the deviation in viscosities, the deviation in refractive indices, and the excess molar refractions. The correlation of these excess properties was made by help of the Redlich-Kister type polynomial expression.

The experimental viscosity values were compared with those calculated by using several different equations: Grunberg–Nissan, Katti Chaudry, Hind, Dolezalek, and three-body McAllister interaction model.

Some theoretical (n,ρ) mixing rules (Lorentz-Lorenz, Gladstone-Dale, Arago-Biot, Edwards and Eykman) usually used in predicting the refractive indexes were assessed.

The experimental and calculated results are discussed from the point of view of the molecular interactions between components of mixtures and their structural effects.

1. Introduction

The thermophysical and thermodynamic properties are very important for obtaining the fundamental data of various molecular liquids mixtures from different classes of compounds and for understanding the behaviour of interactions occurred between the components of these mixtures. These data are useful in chemical and petrochemical engineering designs with diverse applications: for phase separation processes and waste materials recycling, for surface facilities production operations and pipeline systems, etc., as well as in solutions theory and molecular thermodynamics for confirmation and development of theoretical and empirical models of pure fluids and mixtures [1].

The thermophysical properties such as the densities, speeds of sound, kinematic and/or dynamic viscosities and the refractive indices, as well as their related magnitudes (the excess/deviation thermodynamic quantities and volumetric/apparent molar quantities) are largely revealed in open literature [2–5].

In recent years the studies of the thermophysical properties and thermodynamic behavior of *n*-alkane with long chain, both pure and in mixture with different organic compounds, have received a considerable interest [6–8].

Our present paper represents a continuation of the research project on studying the thermophysical properties for some binary mixtures of heavy alkanes with alkyl benzenes and follows up the program we have started with *n*-hexadecane + *iso*-propylbenzene and + *tert*-butylbenzene mixtures, whose results were recently published [9].

A review of the open literature has shown that the experimental measurements of physico-chemical properties for *n*-hexadecane + alkylbenzenes mixtures are rather scarce [10–13] and, for the presented systems, there are no experimental data available [14,15].

In this paper we report the experimental data of densities, speeds of sound, viscosities and refractive indices, for new selected

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binary mixtures of *n*-hexadecane with *n*-propylbenzene and *sec*-butylbenzene, in the temperature range (298.15–318.15) K and pressure of 0.1 MPa.

At the same time, our experimental data could lead to the enlargement of thermodynamic database required to engineering design in industries of fuels derived from petroleum and from alternative sources, because the mixtures of *n*-hexadecane + alkylbenzenes represent fuel surrogate mixtures often studied for reducing the complexity of the combustion modeling of different types of fuels. Fuel surrogates are mixtures of one or more simple fuels that are designed to simulate the physical properties or combustion properties of a more complex fuel.

A short survey of literature related to these industrial applications for the mixtures of n-hexadecane with aromatic hydrocarbons are presented in papers [11–13].

2. Experimental

2.1. Chemicals

In this study the commercial products of first grade purity from Sigma-Aldrich (*n*-Propylbenzene 98%) and Aldrich (*n*-Hexadecane 99%, *sec*-Butylbenzene 99%) were used.

In Table 1 the providers and the purity levels of the chemicals are shown. Before using, the liquids were dried and stored on 4A molecular sieves and no further purification was applied.

The purity of substances was further checked by comparing measured properties (densities, speeds of sound, refractive indices, and viscosities) of pure liquids with the literature data [6,10–13,16–59] at different temperatures, results being shown in Table 2. After a chromatographic analysis (received from Aldrich) of the pure chemicals, the purity of substances was better than that stated, as 0.995 mass fraction, for *n*-hexadecane, 0.998 mass fraction, for *n*-propylbenzene, and 0.995 mass fraction, for *sec*-butylbenzene, respectively.

Furthermore, a graphical comparison between our values and those selected from literature, on the studied properties for the pure compounds, has been made and shown in Figs. S1-S10 in the Supplementary Material. The absolute deviations for the studied properties, at different temperatures (red filled circles points) were obtained by using the Excel function "AVEDEV", between our experimental data and our calculated data from fitting equations of the type: $y = ax + b$. For dynamic viscosity of pure *n*-propylbenzene, the fitting equation was of the type: $y = ax^2 + bx + c$. The fitting equations were presented in the legend of each comparison figure. All the other points of deviations were obtained by using the same "AVEDEV" function, between our experimental data and the literature data (the references specified in each figure).

Between the two kinds of data in this Table 2 and Figs. S1–S10, a fairly good agreement is observed.

2.2. Apparatus and procedure

The density and speed of sound, both for pure components and for binary mixtures were measured at the same time by means of a digital vibrating-tube densitometer and speed of sound analyzer (Anton Paar DSA 5000 M) with an accuracy in densities and speed of sound better than ±0.05 $kg\cdot m^{-3}$ and ± 0.01 $m\cdot s^{-1}$, the temperature being maintained constant by an included Peltier element within ± 0.001 K.

The refractive index was measured by means of a digital automatic refractometer (Anton Paar RXA 170) with accuracy of ± 0.01 K for temperature and of ± 0.000001 for refractive index. The measurements were performed at sodium D-line, λ_D = 589.3 nm.

At the start of each series of measurements, the DSA cell and the automatic refractometer were cleaned and calibrated by measuring the density, sound velocity and the refractive index, of dried air and degased distilled and deionized ultra-pure water (SH Calibration Service GmbH), at different temperatures and atmospheric pressure. The obtained experimental values for water densities: 0.998195×10^{-3} $kg\cdot m^{-3}$ (T = 293.15 K), 0.997056×10^{-3} $kg\cdot m^{-3}$ (T = 298.15 K), and 0.995669×10^{-3} $kg\cdot m^{-3}$ (T = 303.15 K) were in good agreement with those from standard calibration set of apparatus: 0.99820×10^{-3} $kg\cdot m^{-3}$ (T = 293.15 K), 0.99704×10^{-3} $kg\cdot m^{-3}$ (T = 298.15 K), and 0.99565×10^{-3} $kg\cdot m^{-3}$ (T = 303.15 K).

For the measurements of dynamic viscosities of pure liquids and their mixtures we used an Anton-Paar AMVn automated viscometer, which works on the rolling-ball principle. A built-in Peltier thermostat controls the temperature within ± 0.01 K. The measurements of viscosities from (0.3 to 10) mPa·s, were made by means of a calibrated capillary of 1.6 mm diameter, with a ball having density of 7.67 $g\cdot cm^{-3}$, and an angle of inclination of 70°.

The accuracy in the dynamic viscosity measurements was of ± 0.001 mPa·s, and its reproducibility was of less than 0.005 mPa·s.

Practically, our experimental measurements for density, speed of sound, viscosity and refractive index were affected by the folowing uncertainties: the combined expanded uncertainties U_c (level of confidence = 0.95, k = 2): $U_c(\rho)$ = 0.4 $kg\cdot m^{-3}$; $U_c(u)$ = 0.8 $m\cdot s^{-1}$, for *n*-hexadecane and *sec*-butylbenzene, and $U_c(\rho)$ = 0.2 $kg\cdot m^{-3}$; $U_c(u)$ = 0.6 $m\cdot s^{-1}$, for *n*-propylbenzene; $U_c(\eta)$ = 0.06 mPa·s; $U_c(\nu)$ = 0.08 $mm^2\cdot s^{-1}$, for *n*-hexadecane, and $U_c(\eta)$ = 0.02 mPa·s; $U_c(\nu)$ = 0.02 $mm^2\cdot s^{-1}$, for *n*-propylbenzene and *sec*-butylbenzene; $U_c(n_D)$ = 0.0003, respectively.

Each binary mixture was prepared by mixing the suitable volumes of liquids in airtight glass bottles and weighed with an GH-252 (A&D Japan) electronic balance in the limits of ± $0.1\cdot10^{-6}$ kg. By means of an ultrasonic bath (VWR TM International model USC 300TH) the samples were degassed for 30 min to prevent the formation of gas bubbles in the densimeter capillary at higher temperatures. The experimental uncertainty in mole fractions was estimated to be less than 0.005.

3. Results and discussion

3.1. Excess volume

The excess molar volumes, V^E, for the each mixture were calculated using the experimental densities data of the pure liquids and their mixtures by means of relation:

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \quad (1)$$

Table 1
Materials description.

Chemical name	Source	Stated Purity	Mass fraction purity	Purity analysis method	Purification method
n-hexadecane	Aldrich	0.99	0.995	Chromatography	None
n-propylbenzene	Sigma-Aldrich	0.98	0.998	Chromatography	None
sec-butylbenzene	Aldrich	0.99	0.995	Chromatography	None