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Study of thermodynamic and transport properties of phosphonium-based ionic liquids

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ABSTRACT

In this work, the experimental values of density, speed of sound, refractive index and dynamic viscosity have been obtained from $T = (293.15$ to $343.15)$ K for the three phosphonium-based ionic liquids: tributyl methyl phoshponium methylsulfate (P_{4441} C_1SO_4), tributyl ethyl phosphonium diethylphosphate (P_{4442} $(C_2)_2PO_4$) and tributyl octyl phosphonium chloride (P_{4448} Cl). The isentropic compressibility has been calculated by means of the Laplace equation from the experimental speed of sound results for the three ionic liquids at different temperatures. Density, speed of sound, refractive index and isentropic compressibility have been correlated by polynomial equations. The Lorentz–Lorenz, Dale–Gladstone, Eykman, Oster, Arago–Biot, Newton and modified Eykman equations were the empirical models used to correlate satisfactorily the relationship between the densities and refractive indices of the ionic liquids selected. The temperature dependence of the experimental dynamic viscosities for the ionic liquids selected can be described by an Arrhenius-like law and by VFT equations. The Riedel, Narsimham, Bradford–Thodos, Yen–Woods, Rackett, Spencer–Danner, Gunn–Yamada, Hankinson–Thomson (COSTALD model), VSY, VSD, MH and LGM equations were employed to predict the densities of the pure ionic liquids.

1. Introduction

In recent years, ionic liquids (IL) have gained rising attention as possible replacement solvents for volatile organic compounds, thus contributing to the development of more sustainable chemistry and technological processes. The great academic and industrial interest triggered by these molten salts lies in their utmost characteristics such as their negligible volatility, thermal stability, non-flammability, and high ability to dissolve a wide range of organic, inorganic and polymeric compounds [1–4]. Due to these characteristics, the neoteric solvents have found promising applications in a plethora of industrial sectors to be used in batteries [5], capacitors [6], sensors [7], catalysis [8], synthesis [9], biotechnology [10], separations [11], and fuel cells [12] playing roles such as extractants, lubricants, thermal fluids, ionogels, plasticizers, to name just a few.

All these features have contributed to popularize them with the label of green solvents, since they minimize the risk of atmospheric pollution and reduce health concerns associated with the use of volatile conventional organic solvents. However, the ILs environmental sustainability is nowadays an issue in the limelight [13,14].

The introduction of structural functionalities on the cationic or anionic part has made it possible to design new ILs with targeted properties, with at least one million simple combinations that can be easily prepared in the laboratory, although up to 2008 only about 300 were commercialized [15]. More recently, ILs appear to be the subject of fundamental publications aimed at improving the understanding of these solvents, to help to develop predictive models, such as the group contribution methods for determining their physical properties [16–21]. An analysis of the published data indicates that in general terms, ILs are denser than either organic solvents or water, with typical density values ranging from (1 to 1.6) $g \cdot cm^{-3}$. In relation to the viscosity, a crucial parameter decisively influencing stirring, mixing and pumping operations, is relatively higher than that of the conventional solvents (by one to three orders of magnitude). Then, the design of less viscous ILs is still a challenge for many applications [22]. On the other hand, a relatively minor number of studies have been focused on the determination of refractive indices and speed of sound.

In this work, alkylphosphonium-based ionic liquids have been selected since they have several advantages that could make them an obvious choice for industrial purposes. Thus, contrarily to imidazolium ILs, they are usually less dense than water which eases their separation from aqueous streams by decanting. Furthermore, they are more stable in basic and nucleophilic conditions than imidazolium and pyridinium ILs due to the absence of acidic protons in their moieties [23]. Another recent finding highlight is focused on their ability to present extreme low melting temperature, which is of great importance for separation purposes [24]. In this sense,

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the most recent remarkable applications of these molten salts are based on their capacity as extractant of biobutanol [25], rare earths metals and noble metals [26].

This work is a continuation of the thermodynamic study of ILs [27–30] in which several physical properties (density, speed of sound, refractive index and dynamic viscosity) of three phosphonium-based ILs combined with methylsulfate, ethylphosphate and chloride anions, have been determined from $T = (293.15$ to $343.15)$ K with the final purpose to widen the ILs physical properties data bank. These ILs were selected among the different possibilities due to the lower toxicity conferred by the short alkyl chain length and the hydrophilic character of the anions. In this case, no data corresponding to these interesting solvents are available in the literature although they can be proposed in different extraction processes, except the experimental density of tributyl ethyl phosphonium diethylphosphate at several temperatures that has been previously determined [31].

Several polynomial equations were used to describe the temperature dependency of the experimental density, refractive index, speed of sound, isentropic compressibility. In addition, different known empirical equations such as those from Lorentz–Lorenz, Dale–Gladstone, Eykman, Oster, Arago–Biot, Newton, and modified Eykman, were used to correlate the relationship between the densities and refractive indices of the selected ILs [30]. The temperature dependence of dynamic viscosity was analyzed in terms of standard deviation by means of the application of an Arrhenius-like law and by VFT-type equations [32–33].

The possibility of tailoring task-specific ILs requires the development of efficient prediction methods avoiding the experimental determination of their physical properties. A diversity of analytical expressions able to correlate and predict the density of liquids is based on the use of adjustable parameters for each fluid and on the concepts of corresponding state principle. One of the challenges of these specific equations is to serve as viable tools in the description of the thermodynamic behavior of ILs. Thus, the absence of basic data such as critical properties, normal boiling temperature and acentric factor hinders a proper use of these models.

In this work, the density was predicted by means of the Riedel [34], Narsimham [35] and Bradford–Thodos [36] expressions. Moreover, different equations based on the corresponding state principle were used, such as Yen–Woods, Rackett, Spencer–Danner (modified Rackett's equation), Gunn–Yamada, Hankinson–Thomson (COSTALD model), VSY and VSD by Valderrama–Abu-Shark, MH by Mchaweh–Alsaygh–Nasrifar–Moshfeghian, and Linear Generalized Model (LGM) by Valderrama–Zarricueta [37]. In these cases, critical properties, normal boiling temperature and acentric factor have been determined using group contribution methods.

2. Experimental

2.1. Materials

The alkylphosphonium-based ILs used in this work: tributyl methyl phosphonium methylsulfate (P_{4441} C_1SO_4), tributyl ethyl phosphonium diethylphosphate (P_{4442} $(C_2)_2PO_4$) and tributyl octyl phosphonium chloride (P_{4448} Cl) were kindly donated by Cytec Industries, Inc. The materials were used as received without further purification but their purity was checked by NMR spectra. The mass fraction purities, molecular structures and respective designations are shown in table 1.

2.2. Apparatus and procedure

Samples containing the pure ILs were taken from glass vials with screw caps to ensure a secure seal and to prevent humidity, with a syringe through a silicone septum and immediately put into the corresponding apparatus.

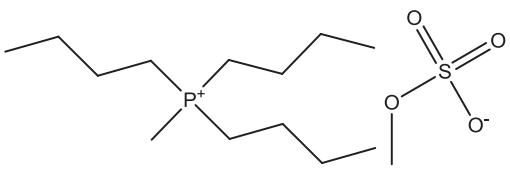
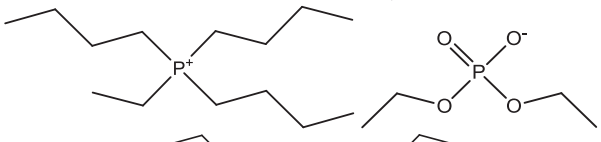
2.2.1. Densities and speed of sound

Densities and speeds of sound of the selected ILs were measured using an Anton Paar DMA-5000 digital vibrating-tube densimeter with a precision of $\pm 10^{-5}$ g · cm^{-3} for the density and ± 0.3 m · s^{-1} for the speed of sound, respectively. The densimeter was previously calibrated by measuring the density of Millipore quality water and ambient air according to the manual instructions. This calibration procedure was tested by measuring the density and speed of sound of known pure solvents.

2.2.2. Refractive indices

Automatic refractometer ABBEMAT-WR Dr. Kernchen was used to determine the refractive indices. The uncertainty in the measurement is $\pm 4 \cdot 10^{-5}$ The apparatus was calibrated by measuring the refractive index of Millipore quality water and tetrachloroethylene (supplied by the company) before each series of measurements according to manual instructions. The calibration was checked with pure liquids with known refractive index.

TABLE 1
Purities and structure of the selected Ils supplied by Cytec.

Ionic liquid	Mass fraction purity	Structure
Tributyl methyl phosphonium Methylsulfate	0.97	
Tributyl ethyl phosphonium Diethylphosphate	0.97	
Tributyl octyl phosphonium Chloride	0.94