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Thermophysical properties of phosphonium-based ionic liquids

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ABSTRACT

Experimental data for density, viscosity, refractive index and surface tension of four phosphonium-based ionic liquids were measured in the temperature range between (288.15 and 353.15) K and at atmospheric pressure. The ionic liquids considered include tri(isobutyl) methylphosphonium tosylate, $[P_{i(444)\ 1}][Tos]$, tri(butyl) methylphosphonium methylsulfate, $[P_{4441}][CH_3SO_4]$, tri(butyl) ethylphosphonium diethylphosphate, $[P_{4442}][(C_2H_5O)_2PO_2]$, and tetraoctylphosphonium bromide, $[P_{8888}][Br]$. Additionally, derivative properties, such as the isobaric thermal expansion coefficient, the surface thermodynamic properties and the critical temperatures for the investigated ionic liquids were also estimated and are presented and discussed. Group contribution methods were evaluated and fitted to the density, viscosity and refractive index experimental data.

1. Introduction

In recent years, ionic liquids (ILs) appeared as effective replacement solvents for many volatile organic compounds (VOCs), and thus contributed to the promotion and enlargement of more sustainable chemistry and technological processes. ILs are composed of large organic cations and organic or inorganic anions that cannot easily form an ordered crystal and thus remain liquid at or near room temperature. The academic and industrial interest, on these molten salts, results from their outstanding properties, such as negligible volatility, non-flammability, wide liquid electrochemical window, large liquidus temperature range, thermal stability, and the ability to dissolve a wide range of organic, inorganic and polymeric compounds [1–8], but mostly derived from the possibility of synthesizing an IL with a set of target properties suitable for a specific process or application. This ability to tune the ILs properties, through the combination or functionalization of cations and anions, lead to the designation of '*designer solvents*'. Moreover, these outstanding characteristics make ILs suitable candidates for a large number of applications, viz. as extractants, lubricants, thermal fluids, ionogels, plasticizers, catalysts, capacitors, sensors, among others [2,9–13].

For the accurate design, optimization, and operation of (industrial) processes and an efficient investigation of the ILs potential as designer solvents, the knowledge of their thermophysical properties, namely viscosity, density, and interfacial tension, is important. Furthermore, reliable thermophysical data is required for the application of models employed in the development of efficient industrial processes and equipment design. Due to the large number of ILs that can be synthesized, the measurement of the thermophysical properties for all of them stands impractical, even unviable. Therefore, the selection and investigation of systematic series of compounds, representative of the different families, can provide insights on the ILs structure-property relationships and thus, allow the development of adequate correlations, equations of state or other models for these properties.

Phosphonium-based ILs, thermally more stable (in basic and nucleophilic conditions due to the absence of acidic protons in their moieties) and less expensive than their equivalent imidazolium ILs [14–16], are widely reported in the literature covering a large set of properties [17–24]. Fraser and MacFarlane [19] stated that phosphonium ILs clearly offer, in some cases, several advantages over other types of ILs, including, in specific cases and applications, higher thermal stability, lower viscosity, and higher stability in strongly basic or strongly reducing conditions. Frackowiak et al. [22] demonstrated that phosphonium ILs are potential compounds for application as super capacitors due to their enhanced electrochemical window. Tsunashima and Sugiya [23] studied the applicability of phosphonium ILs as battery electrolytes; their studies revealed that through chemical tuning, the low-viscosity phosphonium ILs display excellent electrochemical and thermal stabilities. Furthermore, their extreme low

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melting temperatures are of great importance in separation processes. These characteristics offer better scope and have proved to be valuable for many specific applications, like in the purification of biomolecules in aqueous two-phase systems [25,26], in the separation of ethanol–water mixtures as entrainers able to break the system azeotrope [27,28], in the extraction of metals [29,30] and in CO_2 capture and gas separation processes [31–33].

Despite the numerous advantages reported for phosphonium ILs, their applications will remain limited without further characterization of their thermophysical properties. Thus, the collection of novel experimental density, viscosity, refractive index and surface tension data measured in this work, as well as other retrieved from literature, allows to infer on specific structural effects of ILs, such the impact of the cation's alkyl chain length, ramification and symmetry and on the anion type. Additionally, derivative properties, such as the isobaric thermal expansion coefficient, the surface thermodynamic properties and critical temperature were also determined. Group contribution methods [34,35] for the density, viscosity and refractive index were also applied and evaluated.

2. Materials and methods

2.1. Materials

Four ILs were studied in this work, namely tri(isobutyl) methylphosphonium tosylate $[P_{i(444)\ 1}][Tos]$, tri(butyl) methylphosphonium methylsulfate $[P_{4441}][CH_3SO_4]$, tri(butyl) ethylphosphonium diethylphosphate $[P_{4442}][(C_2H_5O)_2PO_2]$ and tetraoctylphosphonium bromide $[P_{8888}][Br]$. The ILs chemical structures and corresponding designations are presented in Table 1. All the ILs were kindly offered by CYTEC Industries Inc. with mass fraction purities higher than 98%.

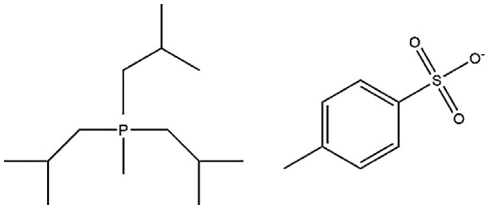
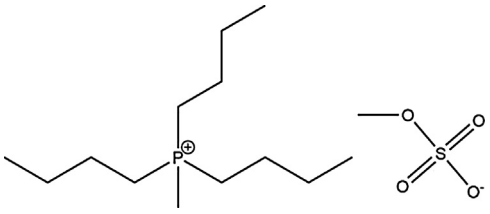
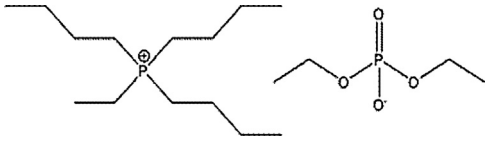
The water content plays an important role in the IL properties, especially on the surface tension and viscosity [36,37], and significant deviations can be found due to small amounts of water. Therefore, in order to remove traces of water and volatile compounds, individual samples of each IL were dried at moderate temperature (≈323 K), vacuum ($\approx 10^{-1}$ Pa) and under continuous stirring, for a minimum period of 48 h prior to the measurements. The purity of each IL was checked by ^1H and ^{13}C NMR to assure that no degradation occurred during the purification procedure and measurements. The final IL water content, after the drying step and immediately before the measurements, was determined with a Metrohm 831 Karl Fischer coulometer (using the Hydranal-Coulomat AG from Riedel-de Haën as analyte) and is reported in Table 1.

2.2. Experimental

2.2.1. Density and viscosity

Density (ρ) and dynamic viscosity (η) measurements were carried out using an automated SVM3000 Anton Paar rotational Stabinger viscometer–densimeter in the (283.15–353.15) K temperature range and at atmospheric pressure (≈0.1 MPa). The

Table 1
Ionic structure, compound description, CAS number, molecular weight, water content and mass fraction purity of the studied ILs.

IL	Ionic structure
Tri(isobutyl) methylphosphonium tosylate $[P_{i(444)\ 1}][Tos]$ (CAS: 374683-35-9; M = 388.5 g mol^{-1}; H_2O wt% = 0.0842%; wt% = 98%)	
Tri(butyl) methylphosphonium methylsulfate $[P_{4441}][CH_3SO_4]$ (CAS: 69056-62-8; M = 328.5 g mol^{-1}; H_2O wt% = 0.0783%; wt% = 98%)	
Tri(butyl) ethylphosphonium diethylphosphate $[P_{4442}][(C_2H_5O)_2PO_2]$ (CAS: 20445-94-7; M = 384.5 g mol^{-1}; H_2O wt% = 0.0741%; wt% = 98%)	
Tetraoctylphosphonium bromide $[P_{8888}][Br]$ (CAS: 23906-97-0; M = 563.8 g mol^{-1}; H_2O wt% = 0.0105%; wt% = 98%)