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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.

Keywords

Phosphonium; ionic liquids; density; viscosity; refractive index; surface tension

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,

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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 et al.[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 et al.[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 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 CO₂ 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}][CH₃SO₄], tri(butyl)ethylphosphonium diethylphosphate [P_{4442}][(C₂H₅O)₂PO₂] 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 ¹³C 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 Section

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 to 353.15) K temperature range and at atmospheric pressure (≈ 0.1 MPa). The density absolute uncertainty is $\pm 5 \times 10^{-4}$ g·cm⁻³, the dynamic viscosity relative uncertainty $\pm 1\%$ and the temperature relative uncertainty is ± 0.02 K. Further details about the equipment and methodologies can be found elsewhere.[38]

2.2.2. Refractive Index—Measurements of refractive indices (n_D) were performed in the 589.3 nm wave length using an automated Abbemat 500 Anton Paar refractometer. Refractive index measurements were carried out in the (283.15 to 353.15) K temperature range and at atmospheric pressure. The Abbemat 500 Anton Paar refractometer uses reflected light to measure the refractive index, where the sample on the top of the measuring prism is irradiated from different angles by a light-emitting diode (LED). The maximum deviation in temperature is ± 0.05 K, and the maximum uncertainty in the refractive index measurements is $\pm 2 \cdot 10^{-5} n_D$. The capability of the equipment to determine accurate refractive indices of ILs has been previously verified.[39–42]

2.2.3. Surface Tension—The surface tensions of each IL were determined through the analysis of the shape of a pendant drop using a Data physics contact angle system, OCA-20 (Data Physics Instruments GmbH, Germany). Pendant drops were created using a Hamilton DS 500/GT syringe connected to a Teflon coated needle placed inside an aluminium air chamber capable of maintaining the temperature within ± 0.1 K. The temperature was attained by circulating water in the double jacketed aluminium cell by means of a Julabo

F-25 water bath. The temperature inside the aluminium chamber was measured with a Pt100 which is at a distance of approximately 2 cm of the drop. The surface tension measurements were performed in the (293 to 344) K temperature range and at atmospheric pressure. After reaching a specific temperature, the drop was formed and the measurements were carried out after a minimum period of 30 min to guarantee the thermal equilibrium. Silica gel was kept inside the air chamber to maintain a dry atmosphere. For the surface tension determination, at each temperature and for each IL, at least three drops were formed and analyzed. For each drop, an average of 100 images was additionally captured. The analysis of the drop shape was achieved with the software module SCA 20. The IL density data required to the surface tension determination were those determined in this work. The equipment was previously validated through the measurement of the surface tension of ultra-pure water, decane and dodecane, as well as with a large number of ILs.[43]

3. Results and discussions

3.1.Density

The density measurements were carried out at atmospheric pressure and in the (283.15 to 353.15) K temperature range for $[P_{i(444)1}][Tos]$, $[P_{4441}][CH_3SO_4]$ and $[P_{4442}][(C_2H_5O)_2PO_2]$ and from (318.15 to 353.15) K for $[P_{8888}][Br]$. The respective values of densities are reported in Table 2 and depicted in Figure 1. As commonly observed the phosphonium-based ILs density is generally lower than that of the imidazolium-based ones. [39,44–46] At a given temperature, the density of the studied ILs follows the order: $[P_{i(444)1}][Tos] > [P_{4441}][CH_3SO_4] > [P_{4442}][(C_2H_5O)_2PO_2] > [P_{8888}][Br]$. Furthermore, both $[P_{8888}][Br]$ and $[P_{444(16)}][Br]$, [24] with the same number of methylene units at the cation (same molecular weight), present similar densities.

As depicted in Figure 2, the density decreases, for a common anion, with the cation alkyl chain length increase due to the lower density of the methylene groups. The anion, by other hand, imposes a greater effect on the IL density. With the increase of the anion molecular weight, and consequently the overall size and charge dispersion, there is an increase in the density, as depicted in Figure 2.

Molar volumes, V_m , were calculated and are reported in Table 2 and depicted in Figure 3, as function of temperature. For the studied ILs, the molar volumes present a small temperature dependency and increase in the order: $[P_{8888}][Br] > [P_{4442}][(C_2H_5O)_2PO_2] > [P_{i(444)1}][Tos] > [P_{4441}][CH_3SO_4]$.

The relative deviations between the density data measured in this work and those available in the literature [14,18,20,47–51] are displayed in Figure 1. Experimental data for the studied ILs are in good agreement with the available literature values, with absolute average relative deviations ranging from (0.02 to 1.19)%. The absolute average relative deviations towards $[P_{i(444)1}][Tos]$ reported by Bradaric et al.[14], AlTuwaime et al.[18], Anthony et al. [50] and Doma ska et al.[51] are 0.32%, 0.47% 0.31% and 0.57% respectively. The absolute average relative deviations towards the $[P_{4441}][CH_3SO_4]$ reported by Deive et al. [20] is 0.83%. Absolute relative deviations of 0.22%, 1.19% and 0.34% for $[P_{4442}][(C_2H_5O)_2PO_2]$ were found against the data of Deive et al.[20], Kilaru et al.[48] and Ficke

et al.[47], respectively. The data from Kilaru et al.[48] present the higher deviations found, that seem to be related with the high amount of water present in the authors' sample (1080 ppm). Absolute relative deviations towards $[P_{888}][Br]$ was found to be 0.02% when compared to the data reported by Vaughan et al.[49].

Gardas and Coutinho [34] extended the Ye and Shreeve [63] approach to the estimation of IL densities for a wide range of temperatures, (288.15 to 353.15) K, pressures, (0.10 to 100) MPa, and ILs families according to the equation

$$\rho = \frac{M}{NV(a + bT + cp)} \quad (1)$$

where ρ is the density in $\text{kg}\cdot\text{m}^{-3}$, M the molecular weight in $\text{kg}\cdot\text{mol}^{-1}$, N the Avogadro constant, V the molecular volume in $\text{\AA}^3$, T the temperature in K and p the pressure in MPa. The universal coefficients a , b and c are 0.8005 ± 0.0002 , $6.652 \cdot 10^{-4} \pm 0.007 \cdot 10^{-4} \text{ K}^{-1}$ and $-5.919 \cdot 10^{-4} \pm 0.024 \cdot 10^{-4} \text{ MPa}^{-1}$, respectively, at a 95% confidence level.

The experimental density data were additionally used to extend the parameter table on the group contribution method previously proposed by Gardas and Coutinho [34]. Volumes for the $[P_{i(444)1}]^+$ and $[P_{1111}]^+$ cations and $[(C_2H_5O)_2PO_2]^-$ and $[CH_3SO_4]^-$ anions were estimated based on density values taken from literature [20,47,48,52–60,62,64] and those reported in this work. With density data, for the anions investigated here, mainly available for the well characterized imidazolium family, the group contribution anionic volumes were determined using 240 experimental data points from six compounds. Despite the deviations found among different authors, a percentage absolute average deviations of 0.92% and 0.62% were obtained against data for $[CH_3SO_4]^-$ and $[C_2H_5PO_3]^-$ anion-based ILs, respectively. Once the anions volume determined, that of the $[P_{1111}]^+$ cation was fitted against our experimental data and those of Deive et al.[20], Ficke et al.[47] and Kilaru et al. [48] with percentage absolute average deviation of 0.40%. The volumetric parameters for the anions $[Tos]^-$ and $[Br]^-$ were taken from previous works.[24,46] Both the estimated and literature values of cationic and anionic volumes are reported in Table 3. The proposed volumes provide a good description of the experimental density data, as shown in Figure 1, with an absolute relative average deviation of 0.16%, 0.20%, 0.046% and 0.52% for $[P_{i(444)1}][Tos]$, $[P_{4441}][CH_3SO_4]$, $[P_{4442}][(C_2H_5O)_2PO_2]$ and $[P_{888}][Br]$, respectively.

Thermal Expansion Coefficient—The isobaric thermal expansion coefficients, α_p , of the studied ILs, which reflect the ILs volumetric changes with temperature, were calculated from the fitting of the experimental data with the following equation,

$$\alpha_p = \frac{-1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p = - \left(\frac{\partial \ln \rho}{\partial T} \right)_p \quad (2)$$

where ρ is the density in $\text{kg}\cdot\text{m}^{-3}$, T the temperature in K, and p a fixed pressure.

The calculated thermal expansion coefficients for the pure liquids are listed Table 4 where it can be seen that the change in the ILs volume is small as the temperature increases which confirms the weak expansion ability of IL fluids.[65] The values obtained vary between 5.7

and $6.7 \times 10^{-4} \text{ K}^{-1}$ and are of the same order of magnitude, $(5 \text{ to } 7) \times 10^{-4} \text{ K}^{-1}$, of those reported for other ILs families, like ammonium-, sulfonium-, imidazolium-, pyridinium- and pyrrolidinium-based ILs.[39,41,42,65–69] The results also indicate that the alkyl side chain length presents a lower impact on the thermal expansion coefficient than that observed for the anion replacement.[39,46,65,69]

3.2. Viscosity

Viscosity is an important property for the design of industrial processes involving heat and/or mass transfer, dissolution or absorption of compounds in fluids; thereby, it stands as a key property on the selection of ILs suitable for a particular application. The experimental viscosity data for the studied ILs is reported in Table 2 and depicted in Figure 4.

For the studied compounds, few viscosity data is available [18,20,70,71] in the literature. As depicted in Figure 5, viscosity data for $[\text{P}_{i(444)1}][\text{Tos}]$ shows average relative deviations of -17.52% and 51.31% against Green et al.[71] and AlTuwaim et al.[18] data, respectively. Nonetheless, very high deviations of 166.6% , were obtained for $[\text{P}_{4441}][\text{CH}_3\text{SO}_4]$ when comparing the data from Deive et al.[20]. Experimental data for $[\text{P}_{4442}][(\text{C}_2\text{H}_5\text{O})_2\text{PO}_2]$, on the other hand, present average relative deviation of 3.44% , 9.49% and -49.51% when compared to the data reported by Deive et al.[20], Ferguson et al.[70] and Green et al.[71], respectively. To the best of our knowledge no viscosity data are available for $[\text{P}_{888}][\text{Br}]$. When compared with experimental density data, larger differences are detected within viscosity values obtained by different authors. It is well known that viscosity is highly “sensitive” to the presence of impurities, namely to the adsorption of moisture during the experimental manipulation. Therefore, a purification step and a correct sample manipulation are of vital importance to achieve accurate viscosity data. While Green et al.[71] and AlTuwaim et al.[18] reported a purification procedure using vacuum for several days, Ferguson et al.[70] degassed the IL in a desiccator for 3 hours under low vacuum and Deive et al.[20] used the IL as received without further purification. Furthermore, most of the authors evaluated the ILs’ viscosity as a secondary measurement for calculations and, therefore, no special attention was given to its determination. In addition, while AlTuwaim et al.[18] and Deive et al.[20] report viscosity measurements using Anton Paar apparatuses, other authors do not mention the equipment and technique adopted. Thus, large discrepancies, in the viscosity values, are expected and observed among the different authors.

As commonly observed, viscosity markedly decreases with the temperature increase. The viscosity increases in the following order: $[\text{P}_{i(444)1}][\text{Tos}] \gg [\text{P}_{4441}][\text{CH}_3\text{SO}_4] > [\text{P}_{888}][\text{Br}] > [\text{P}_{4442}][(\text{C}_2\text{H}_5\text{O})_2\text{PO}_2]$. Similar to that observed previously for imidazolium- and pyridinium-based ILs [41] the π - π interactions due to the presence of an aromatic ring, now at the $([\text{P}_{i(444)1}][\text{Tos}])$ anion, leads to higher resistance to shear stress, to a more rigid IL structure and therefore to a bulkier distribution and higher viscosities.

The description of viscosities for the ILs studied was carried out using the group contribution method, based on the Vogel-Fulcher-Tammann (VFT) correlation,

$$\ln \eta = A_\eta + B \frac{\eta}{T - T_{0\eta}} \quad (3)$$

where η is the dynamic viscosity in mPa·s, T is the temperature in K, and A_η , B_η and $T_{0\eta}$ are adjustable parameters estimated by fitting the equation to the experimental data. The fitted parameters are presented in Table 5. The fitting results are depicted in Figure 4 and present average absolute relative deviations of 0.16% for $[P_{i(444)1}][Tos]$, 0.11% for $[P_{4441}][CH_3SO_4]$, 0.39% for $[P_{4442}][(C_2H_5O)_2PO_2]$ and 0.93% for $[P_{8888}][Br]$.

3.3. Refractive index

The refractive index specifies the dielectric response of a fluid to an electrical field induced by electromagnetic waves and is thus, an optical property of materials. The experimental refractive indices of the investigated ILs are shown in Figure 6 and reported in Table 2. The refractive indices were scanned upward and downward on temperature, with no hysteresis effects observed, and within the temperature range from (283.15 to 353.15) K. The refractive index decreases with the temperature increase. Furthermore, the refractive indices for the phosphonium-based ILs increase in the following sequence: $[P_{i(444)1}][Tos] > [P_{8888}][Br] > [P_{4441}][CH_3SO_4] > [P_{4442}][(C_2H_5O)_2PO_2]$.

The relative deviations between the data measured in this work and those reported in literature [18,20] are depicted in Figure 6. Experimental data for $[P_{i(444)1}][Tos]$, $[P_{4441}][CH_3SO_4]$ and $[P_{4442}][(C_2H_5O)_2PO_2]$ are in good agreement with available literature values, with absolute relative average deviations ranging from (0.1 to 0.13)%. The absolute relative average deviations towards $[P_{i(444)1}][Tos]$ reported by Altuwaim et al. [18] is 0.13%. Experimental data for $[P_{4441}][CH_3SO_4]$ and $[P_{4442}][(C_2H_5O)_2PO_2]$ present absolute average relative deviations of 0.12% and 0.1% when compared to the values reported by Deive et al. [20], respectively. To the best of our knowledge refractive indices for $[P_{8888}][Br]$ are here reported for the first time.

The refractive indices for the ILs studied were also fitted with the group contribution method proposed by Gardas and Coutinho [35], which results are depicted in Figure 6, and that follow a linear function of the form,

$$n_D = A_{n_D} - B_{n_D} T \quad (4)$$

$$A_{n_D} = \sum_{i=1}^k n_i a_{i,n_D} \quad (5)$$

$$B_{n_D} = \sum_{i=1}^k n_i b_{i,n_D} \quad (6)$$

where n_i is the number of groups of type i and k is the total number of different groups in the molecule. The estimated parameters a_{i,n_D} and b_{i,n_D} for the cations of the studied ILs are given in Table 6 along with the anionic volume previously reported. [35,46,72] The average absolute relative deviation between the experimental and the fitting data are 0.021% for

[P_{i(444)1}][Tos] and [P₄₄₄₁][CH₃SO₄], 0.0079% for [P₄₄₄₂][(C₂H₅O)₂PO₂] and 0.0094% for [P₈₈₈₈][Br].

The derived molar refractions, R_m , free volumes, f_m , and polarizabilities were additionally determined as follows [73–75]:

$$\frac{\alpha_0}{4\pi\epsilon_0} = \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \frac{3M}{4\pi\rho N_A} \quad (7)$$

$$R_m = \frac{N_A \alpha_0}{3\epsilon_0} = \frac{n_D^2 - 1}{n_D^2 + 2} V_m \quad (8)$$

$$f_m = V_m - R_m \quad (9)$$

where n_i is the electronic polarizability, ϵ_0 the vacuum permittivity, R_m the compound's density, M the molecular weight and N_A the Avogadro number. The obtained values for these properties are reported in Table 4.

Recently, on the premise that refractive indices are an indication of the dielectric response to an electrical field, induced by electromagnetic waves, and that refractive indices can be derived as the first order approximation response to electronic polarization within an instantaneous time scale, Seki et al.[76] evaluated the refractive indices of 17 ILs, as a function of temperature, against theoretical polarizabilities obtained through *ab initio* calculations. The authors proposed a correlation between the refractive index and the polarizability normalized in terms of the molecular volume. Following the work of Seki et al.[76] the correlation was previously verified against ammonium-, sulfonium-, phosphonium-, piperidinium- and pyridinium-based ILs experimental data and shown to provide an easy and accurate way to predict the refractive index or polarizabilities of ILs. [41,42,77] Here the phosphonium-based ILs were tested against the correlation and, once again, it was shown that it is able to describe, within the uncertainty of the correlation, this IL family refractive indices and/or polarizability, as depicted in Figure 7.

3.4. Surface tension

Experimental surface tension data measured for all the studied ILs are presented in Table 7 and depicted in Figure 8 as a function of temperature.

Using dynamic contact angle measurements, AlTuwaïm et al.[18] reported surface tension data for [P_{i(444)1}][Tos] that presents average relative deviations of –14.4% to the data measured here. An average relative deviation of –8.90% was obtained for [P₄₄₄₂][(C₂H₅O)₂PO₂], using the Du Noüy ring method, reported by Kilaru et al.[48]. The deviations obtained seem to be associated to small traces of water, the technique employed and/or the sample purity.

From Figure 8, it can be seen that the surface tension of the studied ILs decreases linearly with temperature and follows the order: [P_{i(444)1}][Tos] > [P₄₄₄₁][CH₃SO₄] > [P₄₄₄₂]

$[(\text{C}_2\text{H}_5\text{O})_2\text{PO}_2] > [\text{P}_{888}][\text{Br}]$. It can be observed that both the cation and anion significantly contribute to the surface tension of the IL at the air-liquid interface.[78,79] It is well established that the surface tension is related with the part of the molecule that is present at the interface and pointing towards the air phase. The moiety with the lower surface energy tends to accumulate at the interface. Typically these are alkyl chains oriented towards the gas phase. Santos et al.[80] showed that halide anion-based ILs may present a top layer formed entirely by the cation with the alkyl chains pointing towards the gas phase while the second layer is formed only by the halide. When the cation and anion have similar sizes and both present alkyl chains, as is the case for some of the compounds here studied, the cations and anions may occupy the same plane at the gas-liquid interface,[80] with the alkyl chains projecting towards the vapour phase and the anions and cation's polar head groups forming a second layer. This structural behaviour allows one to picture the surface arrangement of the studied ILs and understand the surface tension values under the light of the intermolecular interactions strength playing an important role on the compactness and strength of the interface layer composed by the anion and cation's head groups.

Surface Thermodynamic Properties—It is possible to derive the surface thermodynamic properties, viz. surface entropy and surface enthalpy, through the temperature dependence of the surface tension. The basic thermodynamic relationship applied to the surface of a homogeneous liquid is

$$H^\gamma = G^\gamma + TS^\gamma \quad (10)$$

where H^γ is surface enthalpy, G^γ is the Gibbs energy, T is the temperature (in K), and S^γ is the surface entropy. The surface entropy per unit area can be calculated according to the following equation [81,82],

$$S^\gamma = - \left(\frac{\partial \gamma}{\partial T} \right) \quad (11)$$

while the surface enthalpy according to [81,82],

$$H^\gamma = T - \left(\frac{\partial \gamma}{\partial T} \right) \quad (12)$$

where γ stands for the surface tension and T for the temperature.

The values of the thermodynamic functions for all the ILs studied and the respective expanded uncertainties, derived from the slope of the curve $\gamma = f(T)$ in combination with the law of propagation of uncertainties, are presented in Table 4.[83]

In agreement with the results previously reported for other ILs families, viz. imidazolium-, pyridinium-, pyrrolidinium- and piperidinium-based cations, [40,41,43,78,79,84], the investigated phosphonium ILs present lower surface enthalpies and entropies when compared with molecular organic compounds. These values reflect a high surface organization, as well as an inherent highly structured liquid phase in ionic liquids. These values of low surface entropies are an indication of a high surface organization as well as a

highly structured liquid phase. Moreover, the results of similar surface entropy and surface enthalpy observed, for the different IL families, are an effect of similar dependency of the surface tension with the temperature.

Estimated critical temperatures—The critical temperature of fluids is one of the most relevant and significant thermophysical property frequently used in corresponding state correlations concerning equilibrium and transport properties.[85] However, owing to the intrinsic nature of ILs coupled with negligible vapor pressures and relatively low decomposition temperatures, the direct determination of the critical temperatures of ILs is not feasible. Rebelo et al.[1] proposed the use of the Eötvös [86] and Guggenheim [87] equations to estimate the hypothetical critical temperature of ILs, as described below,

$$\gamma \left(\frac{M}{\rho} \right)^{2/3} = K_{Eot} (T_c - T) \quad (13)$$

$$\gamma = K_{Gug} \left(1 - \frac{T}{T_c} \right)^{11/9} \quad (14)$$

where T_c is the critical temperature, M the molecular weight, ρ the density, and K_{Eot} and K_{Gug} are fitted parameters. T_c , K_{Eot} and K_{Gug} were determined by fitting Equations 13 and 14 to the experimental data. Both equations are based on the fact that the surface tension becomes null at the critical point and although an overestimation of the critical temperature is expected, since at the critical point the pressure becomes the critical pressure, these equations provide reasonable estimations.[85,88] The critical temperature values estimated from the surface tension data are summarized in Table 4. In agreement with the results obtained for other phosphonium-based ILs studied in a previous work [72] the compounds here reported also present significantly lower critical temperatures than imidazolium-, pyridinium-, piperidinium- or pyrrolidinium-based ILs.[41,43,84]

Conclusions

Experimental data on density, viscosity, refractive index, and surface tension for four phosphonium-based ionic liquids were measured in the temperature range between (283.15 and 353.15) K and at atmospheric pressure. 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 discussed.

In general, for a common anion the density decreases with the increase of the aliphatic moieties. The anion, nonetheless, imposes a greater effect on the IL density, with the anion molecular weight increase, and consequently the overall size and charge dispersion increase, leading to an increase on density. Moreover, the alkyl side chain increase presents a smaller impact on the thermal expansion coefficient than that observed for the anion replacement.

Similar to that observed previously for imidazolium- and pyridinium-based ILs, the π - π interactions due to the presence of an aromatic ring ([P_{i(444)}][Tos]) leads to higher

resistance to shear stress, to a more rigid IL structure and therefore to a bulkier distribution and higher viscosities.

The investigated ILs present low surface enthalpy and entropies when compared with molecular organic compounds. These values reflect a high surface organization, as well as an inherent highly structured liquid phase. Furthermore, the low surface entropies are an indication of a high surface organization as well as a highly structured liquid phase.

The group contribution methods proposed by Gardas and Coutinho for density, viscosity and refractive index were evaluated and fitted to the experimental data, allowing to propose new parameters for the cations and/or anions investigated in this work.

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Figure 1.

Density as a function of temperature (left) and relative deviations between the experimental data from this work and those available in the literature [14,18,20,47–51] (right). The solid lines represent the Gardas and Coutinho [34] group contribution method.

Figure 2.

Density as function of ionic liquids' molecular weight, for tosylate- (308 K), methylsulfate- (298 K), 1-butyl-3-methylimidazolium (298 K) and trihexyl(tetradecyl)phosphonium-based ILs (323 K). [20,47,48,52–62] The lines are guides for the eyes.

Figure 3.

Molar volumes as function of temperature for the studied ILs (left) and molar volume and density as function of ILs at 323.15 K (right).

Figure 4. Viscosity data for the studied ILs. The solid lines represent the Vogel-Tammann-Fulcher (VTF) group contribution correlation.[35]

Figure 5. Relative deviations between the experimental viscosity data of this work and those available in the literature.[18,20,70,71]

Figure 6.

Refractive Index as a function of temperature (left) and relative deviations (right) between the experimental data from this work and those available in the literature.[18,20] The solid lines represent the Gardas and Coutinho [35] group contribution method.

Figure 7.

Relationship between the refractive index and polarizability/molar volume for different ILs at 303.15 K. The unfilled triangles and the solid line represent the experimental data and the correlation of Seki et al.[76]. The unfilled squares and diamonds represent the experimental data reported in previous works.[41,42,77] The full symbols correspond to the ILs data determined in this work.

Figure 8.

Surface tension data for the studied ILs as a function of temperature (left) and relative deviations between this work experimental surface tension data [18,48] and that available in the literature (right).

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; $M = 388.5 \text{ g}\cdot\text{mol}^{-1}$; $H_2O \text{ wt } \% = 0.0842\%$; wt % = 98%)
tri(n-butyl)methylphosphonium methylsulfate $[P_{4441}][CH_3SO_4]$ (CAS: 69056-62-8; $M = 328.5 \text{ g}\cdot\text{mol}^{-1}$; $H_2O \text{ wt } \% = 0.0783\%$; wt % = 98%)
tri(n-butyl)ethylphosphonium diethylphosphate $[P_{4442}][(C_2H_5O)_2PO_2]$ (CAS: 20445-94-7; $M = 384.5 \text{ g}\cdot\text{mol}^{-1}$; $H_2O \text{ wt } \% = 0.0741\%$; wt % = 98%)
tetraoctylphosphonium bromide $[P_{8888}][Br]$ (CAS: 23906-97-0; $M = 563.8 \text{ g}\cdot\text{mol}^{-1}$; $H_2O \text{ wt } \% = 0.0105\%$; wt % = 98%)

Table 2

Densities, ρ , molar volumes, V_m , viscosities, η , and refractive index, n_D , of the studied ILs as a function of temperature and at atmospheric pressure.

[P ₄₄₄₁][Tos]					[P ₄₄₄₁][CH ₃ SO ₄]					[P ₄₄₂][(C ₂ H ₅ O) ₂ PO ₂]					[P ₈₈₈][Br]				
T / K	ρ / kg·m ⁻³	$10^6 V_m$ / m ³ ·mol ⁻¹	η / mPa·s	n_D	ρ / kg·m ⁻³	$10^6 V_m$ / m ³ ·mol ⁻¹	η / mPa·s	n_D	ρ / kg·m ⁻³	$10^6 V_m$ / m ³ ·mol ⁻¹	η / mPa·s	n_D	ρ / kg·m ⁻³	$10^6 V_m$ / m ³ ·mol ⁻¹	η / mPa·s	n_D	ρ / kg·m ⁻³	$10^6 V_m$ / m ³ ·mol ⁻¹	n_D
283.15	1082.4	359.0	21829.0	1.52489	1076.5	305.1	6214.1	1.48038	1021.5	376.4	1018.4	1.47176							
288.15	1079.3	360.0	11305.0	1.52338	1073.4	306.0	3840.1	1.47891	1018.0	377.7	669.5	1.46996							
293.15	1076.2	361.0	6231.9	1.52170	1070.3	306.9	2476.4	1.47742	1014.4	379.0	466.4	1.46809							
298.15	1073.2	362.0	3612.4	1.52030	1067.2	307.8	1629.2	1.47632	1010.9	380.3	316.8	1.46618							
303.15	1070.1	363.1	2199.9	1.51828	1064.1	308.7	1109.1	1.47427	1007.5	381.6	226.7	1.46474							
308.15	1067.0	364.1	1397.3	1.51635	1061.0	309.6	774.5	1.47232	1004.1	382.9	166.0	1.46308							
313.15	1064.0	365.2	917.9	1.51433	1057.9	310.5	555.0	1.47072	1000.7	384.2	124.7	1.46110							
318.15	1060.9	366.2	623.7	1.51233	1054.8	311.4	403.6	1.46912	997.6	385.4	94.6	1.45923	945.0	596.6	376.5	1.48262			
323.15	1057.7	367.3	436.2	1.51055	1051.8	312.3	300.0	1.46758	994.3	386.7	73.4	1.45738	942.0	598.5	289.9	1.48092			
328.15	1054.7	368.4	313.1	1.50872	1048.9	313.1	227.0	1.46603	990.9	388.0	57.9	1.45563	938.9	600.4	226.4	1.47916			
333.15	1051.8	369.4	230.1	1.50698	1045.9	314.0	174.7	1.46457	987.6	389.3	46.4	1.45385	935.9	602.4	178.7	1.47699			
338.15	1048.8	370.5	172.7	1.50537	1043.0	314.9	136.3	1.46318	984.3	390.6	37.5	1.45212	932.9	604.3	142.1	1.47523			
343.15	1045.9	371.5	132.1	1.50391	1040.1	315.8	107.9	1.46185	980.9	392.0	30.8	1.45045	929.8	606.3	114.4	1.47354			
348.15	1043.1	372.5	102.8	1.50252	1037.3	316.6	86.4	1.46067	977.6	393.3	25.6	1.44880	926.8	608.3	93.4	1.47195			
353.15	1040.2	373.5	81.3	1.50124	1034.4	317.5	70.0	1.45965	974.3	394.6	21.6	1.447176	923.7	610.3	76.8	1.47035			

Standard temperature uncertainty is $u(T) = \pm 0.02$ K and the combined expanded uncertainties, U_C , are $U_C(\rho) = \pm 0.5$ kg·m⁻³; $U_C(\eta) = 0.1\%$; $U_C(n_D) = 2 \times 10^{-5}$ with an approximately 95% level of confidence.

Table 3

Ionic Volumes, V , determined using the Gardas and Coutinho Group Contribution Model [34] for the studied ILs.

Ionic species	$V / \text{\AA}^3$
Cation	
$[\text{P}_{(444)}\text{I}]^+$	544
$[\text{P}_{1111}]^+$	154
Anion	
$[\text{Tos}]^-$ [46]	248
$[\text{CH}_3\text{SO}_4]^-$	106
$[(\text{C}_2\text{H}_5\text{O})_2\text{PO}_2]^-$	199
$[\text{Br}]^-$ [24]	36
Group	
$-\text{CH}_2$ [34]	28

Table 4

Coefficients of thermal expansion, α_p , refractive indices, n_D , isotropic polarizabilities, derived molar refractions, R_m , and free volumes, f_m , surface entropy, S^s , surface enthalpy, H^s , and estimated critical temperatures using both Eötvös, $T_{c,Eot}$, [86] and Guggenheim, $T_{c,Gug}$, [87] empirical equations for the studied ILs.

	[P _{i(444)1}][Tos]	[P ₄₄₄₁][CH ₃ SO ₄]	[P ₄₄₄₂][(C ₂ H ₅ O) ₂ PO ₂]	[P ₈₈₈₈][Br]
$10^4 \cdot (\alpha_p \pm \sigma) / K^{-1}$	5.706 ± 0.073	5.715 ± 0.073	6.726 ± 0.101	6.508 ± 0.052
$n_D^{[\#]}$	1.51233	1.46912	1.45923	1.48262
Polarizability ^[#] / bohr ³	294.15	232.04	281.98	455.48
$R_m^{[\#]} / cm^3 \cdot mol^{-1}$	109.95	86.74	105.40	170.26
$f_m^{[\#]} / cm^3 \cdot mol^{-1}$	256.28	224.65	279.99	426.31
$10^5 \cdot (S^s \pm \sigma) / J \cdot m^{-2} \cdot K^{-1}$	7.7 ± 0.31	6.4 ± 0.24	7.5 ± 0.27	5.7 ± 0.17
$10^2 \cdot (H^s \pm \sigma) / J \cdot m^{-2}$	6.1 ± 0.10	5.5 ± 0.06	8.5 ± 0.08	4.5 ± 0.05
$T_{c,Eot} / K$	891 ± 27	901 ± 3	792 ± 21	922 ± 22
$T_{c,Gug} / K$	892 ± 23	900 ± 3	796 ± 17	906 ± 17

^[#] at 318.15 K.

Table 5

Vogel-Fulcher-Tammann (VFT) correlation parameters, A_η , B_η and $T_{0\eta}$ for the studied ILs.

IL	A_η	B_η/K	$T_{0\eta}/\text{K}$
[P ₍₄₄₄₎₁][Tos]	-3.15	1238	189
[P ₄₄₄₁][CH ₃ SO ₄]	-3.75	1559	158
[P ₄₄₄₂][(C ₂ H ₅ O) ₂ PO ₂]	-3.37	1199	167
[P ₈₈₈₈][Br]	-1.51	961	189

Table 6

Group contribution parameters, $a_{i,nD}$ and $b_{i,nD}$, determined using the Gardas and Coutinho group contribution method [35] for the refractive index.

Ionic Species	$a_{i,nD}$	$10^4 b_{i,nD} / \text{K}^{-1}$
Cation		
$[\text{P}_{i(444)}\text{I}]^+$	1.4474	3.140
$[\text{P}_{1111}]^+$	1.3972	2.617
Anion		
$[\text{Tos}]^-$ [46]	0.1787	0.4261
$[\text{CH}_3\text{SO}_4]^-$ [35]	0.1314	0.1016
$[(\text{C}_2\text{H}_5\text{O})_2\text{PO}_2]^-$	0.1302	0.4782
$[\text{Br}]^-$ [72]	0.1084	0.5866
Group		
$-\text{CH}_2$ [35]	0.0045	0.04587

Table 7

Surface tension, γ , for the studied ILs as a function of temperature and at atmospheric pressure.

	$[\text{P}_{i(444)1}][\text{Tos}]$	$[\text{P}_{4441}][\text{CH}_3\text{SO}_4]$	$[\text{P}_{4442}][(\text{C}_2\text{H}_5\text{O})_2\text{PO}_2]$	$[\text{P}_{8888}][\text{Br}]$
T/K	$\gamma/\text{mN}\cdot\text{m}^{-1}$	$\gamma/\text{mN}\cdot\text{m}^{-1}$	$\gamma/\text{mN}\cdot\text{m}^{-1}$	$\gamma/\text{mN}\cdot\text{m}^{-1}$
293.2	38.1	35.5	31.4	
298.2	37.3	34.7	30.5	
303.2	36.6	34.1	29.8	
313.1	35.5	33.5	29.2	
318.1				27.4
323.1	35.0	32.9	28.5	27.1
333.1	34.3	32.2	27.5	26.6
343.1	38.1	35.5	31.4	26.0

Standard temperature uncertainty is $u(T) = \pm 0.1$ K and the surface tension expanded uncertainty is $U_C(\gamma) = 0.1 \text{ mN}\cdot\text{m}^{-1}$, with an approximately 95% level of confidence.