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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 $T = (293.15 \text{ to } 343.15) \text{ K}$ for the three phosphonium-based ionic liquids: tributyl methyl phosphonium methylsulfate ($\text{P}_{4441} \text{ C}_1\text{SO}_4$), tributyl ethyl phosphonium diethylphosphate ($\text{P}_{4442} (\text{C}_2)_2\text{PO}_4$) and tributyl octyl phosphonium chloride ($\text{P}_{4448} \text{ Cl}$). 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.

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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 $(1 \text{ to } 1.6) \text{ g} \cdot \text{cm}^{-3}$. 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 $T = (293.15 \text{ to } 343.15) \text{ K}$ 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.

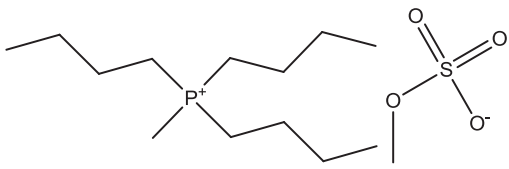
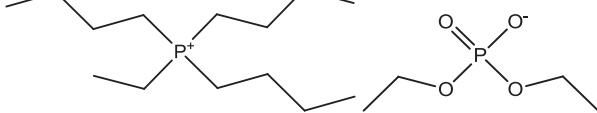
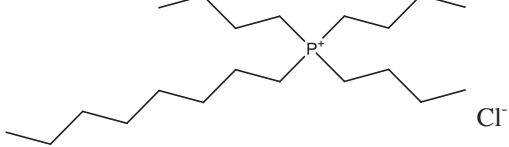
2.2.1. Densities and speed of sound

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 $\pm 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ for the density and $\pm 0.3 \text{ m} \cdot \text{s}^{-1}$ 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	

2.2.3. Dynamic viscosities

Experimental dynamic viscosities were carried out with an automated AMV 200 Anton Paar microviscometer. This apparatus is based on the rolling ball principle where a gold-covered steel ball rolls down the inside of inclined, sample-filled glass capillary. The apparatus is equipped with an automatic timer (± 0.01 s) so the time taken for the ball to roll a fixed distance between two magnetic sensor allows one to evaluate the viscosity of the fluid mixture. The time measuring range is from (12 to 250) s., the accuracy and the precision in this one are ± 0.01 s. and ± 0.1 s., respectively. The capillary was placed in a block, thermostated with a PolyScience controller bath model 9010 with a temperature stability of $\pm 10^{-2}$ K. Apparatus calibration was made daily using three fluids of known viscosity supplied by the company. The maximum deviation between experimental and calculated measurements is 3%.

3. Results and discussion

The experimental density, ρ , speed of sound, u , isentropic compressibility, κ_s , refractive index, n_D , and dynamic viscosity, η , of pure P_{444n} X, being $n = 1, 2$ or 8 , and $X = C_1SO_4, (C_2)_2PO_4$ or Cl , respectively, have been determined from $T = (293.15$ to $343.15)$ K and the experimental values are listed in table 2. An exhaustive review of the literature data allows concluding that there are no data about the physical properties of the selected ionic liquids except for $P_{4442} (C_2)_2PO_4$. The comparison reveals a good agreement, especially at high temperatures, and a maximum deviation lower of 0.15% at low temperatures as it can be visualized in figure 1.

The experimental physical properties as a function of the temperature are graphically plotted in figures 2 to 5. In general, it becomes clear that all the data follow an expected behavior along the temperature range, with a systematic decrease in the values of the considered physical properties when the temperature is increased.

Although imidazolium ILs are generally denser than water, the densities for phosphonium-based families reach values similar to or even less than those recorded for pure water [31]. Besides, the density data behaved as expected, following the rule of thumb that the density of comparable ionic liquids decreases with the increased molecular volume. On the other hand, different authors have suggested that the viscosity followed inverse trends to the density when changing the structure both in the anion and in the cation [38]. Thus, this behavior can be noticed for the diethylphosphate-based IL, since it leads to the lowest values of dynamic viscosity. The same pattern is followed for the refractive indices and speed of sound. It is remarkable that the change of trend for the speed of sound values at elevated temperatures for the methylsulfate and chloride-based ILs, further demonstrating the impact of the anion in the physical properties.

3.1. Correlation of the physical properties of the phosphonium-based ILs

The experimental values of all the physical properties, except viscosities, were fitted as a function of the temperature to a polynomial of the form:

$$Q = \sum_{i=0}^m A_i T^i, \quad (1)$$

where Q is the physical property (ρ , u , κ_s , and n_D), T is the absolute temperature, A_i are the fitting parameter and m is the degree of the polynomial expansion. The degree of the polynomial expression was optimized applying the F-test. The A_i parameters calculated using equation (1) are listed in table 3, together with their

TABLE 2

Density, ρ , speed of sound, u , refractive index, n_D , isentropic compressibility, κ_s and dynamic viscosity, η , of ($P_{444n}(n=1, 2$ and $8)$ X ($X = C_1SO_4, (C_2)_2PO_4$ and Cl) as a function of temperature.

T/K	$\rho/(g \cdot cm^{-3})$	$u/(m \cdot s^{-1})$	$\kappa_s/(TPa^{-1})$	n_D	$\eta/(mPa \cdot s)$
<i>P₄₄₄₈ Cl</i>					
293.15	0.92722	1627.9	407.0	1.49551	7837.51
298.15	0.92439	1595.8	424.8	1.49392	4669.60
303.15	0.92157	1565.4	442.8	1.49231	2905.82
308.15	0.91874	1537.8	460.3	1.49071	1867.91
313.15	0.91591	1512.6	477.2	1.48911	1237.23
318.15	0.91307	1490.0	493.3	1.48749	842.01
323.15	0.91023	1469.5	508.7	1.48587	587.39
328.15	0.90738	1451.0	523.5	1.48427	419.21
333.15	0.90452	1433.7	537.9	1.48265	305.53
338.15	0.90169	1416.9	552.4	1.48104	226.99
343.15	0.89886	1401.0	566.8	1.47941	171.66
<i>P₄₄₄₂ (C₂)₂PO₄</i>					
293.15	1.01212	1439.9	476.6	1.46897	438.69
298.15	1.00876	1422.3	490.0	1.46732	306.41
303.15	1.00542	1405.5	503.5	1.46567	219.45
308.15	1.00207	1389.4	516.9	1.46402	160.8
313.15	0.99871	1373.8	530.5	1.46234	120.32
318.15	0.99535	1358.5	544.4	1.46069	91.76
323.15	0.99200	1343.5	558.5	1.45904	71.22
328.15	0.98865	1328.8	572.8	1.45738	56.17
333.15	0.98531	1314.3	587.5	1.45573	44.99
338.15	0.98201	1299.8	602.7	1.45409	36.47
343.15	0.97871	1285.6	618.2	1.45240	29.96
<i>P₄₄₄₁ C₁SO₄</i>					
293.15	1.06163	1564.0	385.1	1.47489	719.09
298.15	1.05855	1546.2	395.1	1.47344	508.51
303.15	1.05547	1529.8	404.8	1.47199	367.68
308.15	1.05241	1514.4	414.3	1.47054	271.32
313.15	1.04938	1499.9	423.6	1.46907	203.97
318.15	1.04635	1485.8	432.9	1.46762	155.97
323.15	1.04331	1472.2	442.2	1.46616	121.14
328.15	1.04027	1458.9	451.6	1.46474	95.46
333.15	1.03724	1445.9	461.1	1.46328	76.24
338.15	1.03421	1433.2	470.8	1.46188	61.66
343.15	1.03118	1420.3	480.7	1.46048	50.46

Standard uncertainties u are $u(T) = 0.01$ K, $u(\rho) = 0.00001$ g \cdot cm $^{-3}$, $u(u) = 0.3$ m \cdot s $^{-1}$, $u(n_D) = 0.00004$, $u(\eta) = 0.03$ mPa \cdot s.

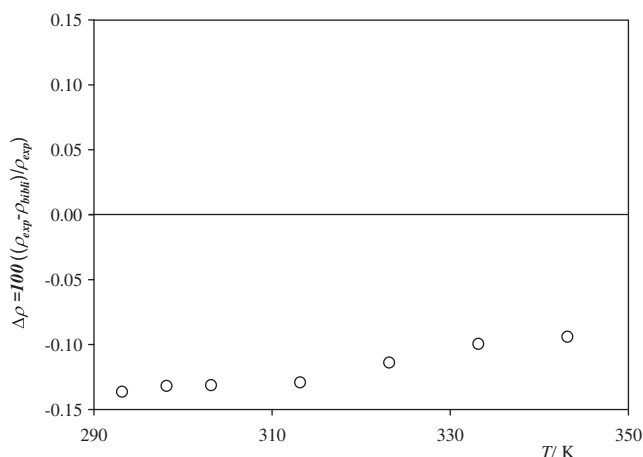


FIGURE 1. Plot of percentage deviations, $\Delta\rho$, against T for (\circ), $P_{4442} (C_2)_2PO_4$ compared to experimental data from Ficke et al. [31].

corresponding standard deviations determined using the following equation:

$$S.D. = \left(\sum_i^{n_{DAT}} (z_{exp} - z_{adjust})^2 / n_{DAT} \right)^{1/2}, \quad (2)$$

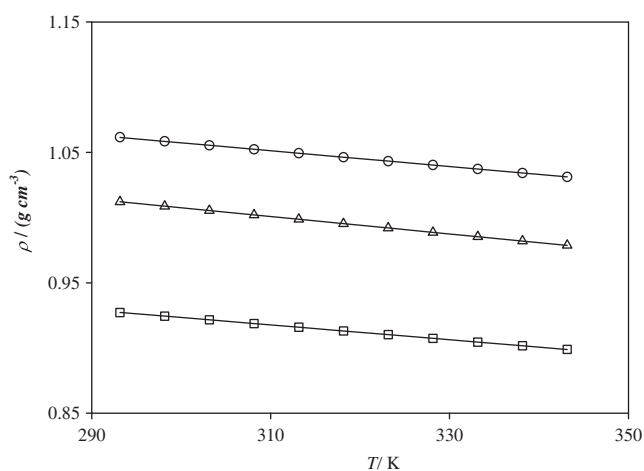


FIGURE 2. Plot of densities, ρ , against T and fitted curves for: (○), $P_{4441} C_1SO_4$, (△), $P_{4442} (C_2)_2PO_4$, (□) $P_{4448} Cl$.

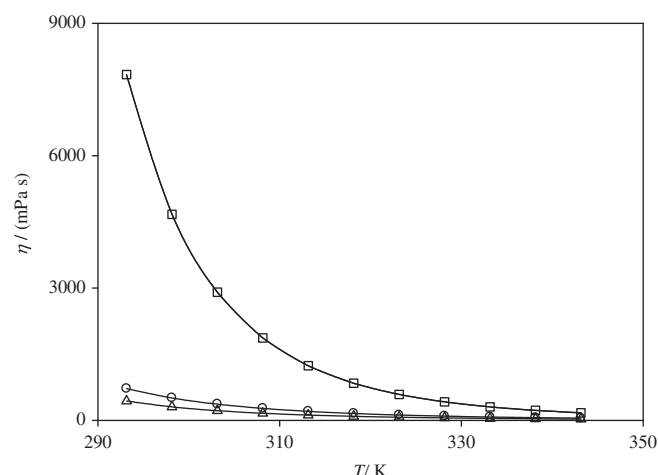


FIGURE 5. Plot of dynamic viscosities η , against T for: (○), $P_{4441} C_1SO_4$, (△), $P_{4442} (C_2)_2PO_4$, (□) $P_{4448} Cl$.

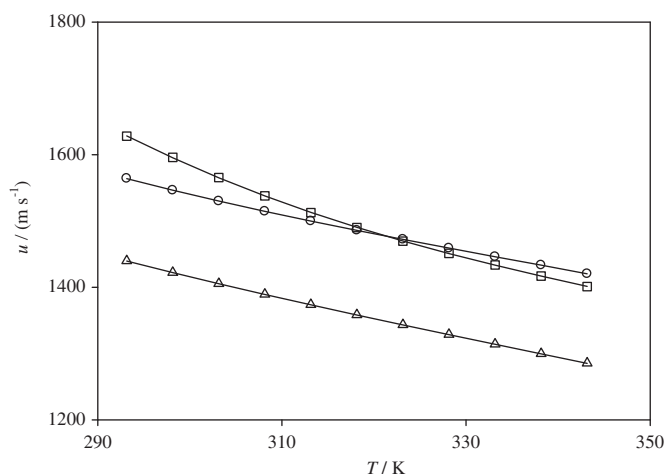


FIGURE 3. Plot of speed of sound, u , against T and fitted curves for: (○), $P_{4441} C_1SO_4$, (△), $P_{4442} (C_2)_2PO_4$, (□) $P_{4448} Cl$.

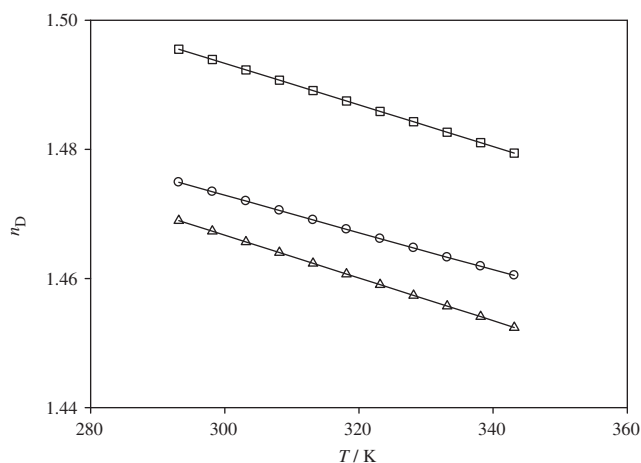


FIGURE 4. Plot of refractive index, n_D , against T and fitted curves for: (○), $P_{4441} C_1SO_4$, (△), $P_{4442} (C_2)_2PO_4$, (□) $P_{4448} Cl$.

where the property values and the number of experimental and adjustable data are represented by z and n_{DAT} , respectively. The

TABLE 3

Fitting parameters and standard deviations to correlate the physical properties of ($P_{444n}(n=1,2 \text{ and } 8) X$ ($X = C_1SO_4$, $(C_2)_2PO_4$ and Cl)) as a function of temperature.

Physical properties	A_0	A_1	A_2	A_3	SD
<i>P₄₄₄₈ Cl</i>					
$\rho/(g \cdot cm^{-3})$	1.09430	−0.00057			0.00004
n_D	1.59149	−0.00033			0.00008
$u/(m \cdot s^{-1})$	18559	−139.9	0.3870	−0.0004	0.349
$\kappa_s/(TPa^{-1})$	−3662	29.61	−0.0729	0.0001	0.322
<i>P₄₄₄₂ (C₂)₂PO₄</i>					
$\rho/(g \cdot cm^{-3})$	1.20849	−0.00067			0.00003
n_D	1.56644	−0.00330			0.00002
$u/(m \cdot s^{-1})$	6482	−40.12	0.1099	−0.0001	0.322
$\kappa_s/(TPa^{-1})$	−2233	22.15	−0.0657	0.0001	0.099
<i>P₄₄₄₁ C₁SO₄</i>					
$\rho/(g \cdot cm^{-3})$	1.23899	−0.00061			0.00006
n_D	1.56048	−0.00029			0.00005
$u/(m \cdot s^{-1})$	9410	−65.97	0.1885	−0.0002	0.088
$\kappa_s/(TPa^{-1})$	−2960	28.61	−0.0850	0.0001	0.682

analysis of the standard deviation data collected in table 3 allows one to conclude a suitable description of the experimental data in all cases.

Furthermore, different linear empirical equations [30] such as Lorentz–Lorenz, Dale–Gladstone, Eykman and modified Eykman considering an additional parameter d , Oster, Arago–Biot, and Newton were used to describe the behavior between the experimental refractive index and density. In these equations, k is an empirical constant that depends on the liquid and the wavelength at which the refractive index determination is carried out.

The values of the standard deviations and the parameters k and d are listed in table 4. Following a thorough analysis of the deviation results it becomes patent that Eykman and modified Eykman equations are those supporting a better correlation. Nonetheless, the introduction of an additional parameter (d) does not entail a significant improvement on the quality of the fittings. Additionally, the relationship between refractive index and density is more satisfactorily described for $P_{4442} (C_2)_2PO_4$ by all the selected equations.

The next step was to correlate the experimental values of dynamic viscosities of the selected ILs, in terms of fluidity (η^{-1}), at several temperatures by means of the following linear equation:

$$(1/\eta)^\phi = a + bT, \quad (3)$$

TABLE 4

Fitting parameters and standard deviations to correlate the physical properties of ($P_{444n}(n=1, 2 \text{ and } 8)$ X ($X = C_1SO_4$, $(C_2)_2PO_4$ and Cl) as a function of temperature.

	k	d	SD
$P_{4448} Cl$			
Lorentz–Lorenz	0.3153		0.00027
Dale–Gladstone	0.5339		0.00030
Oster	3.2565		0.00417
Arago–Biot	1.6290		0.00953
Newton	0.8164		0.01113
Eykman	0.7036		0.00002
Eykman modified	0.0114	114.86	0.00003
$P_{4442} (C_2)_2PO_4$			
Lorentz–Lorenz	0.2755		0.00023
Dale–Gladstone	0.4628		0.00034
Oster	2.8117		0.00422
Arago–Biot	1.4674		0.01028
Newton	0.7761		0.01123
Eykman	0.6121		0.00004
Eykman modified	0.0108	103.97	0.00003
$P_{4441} C_1SO_4$			
Lorentz–Lorenz	0.2655		0.00022
Dale–Gladstone	0.4469		0.00027
Oster	2.7178		0.00357
Arago–Biot	1.4025		0.00893
Newton	0.7863		0.00982
Eykman	0.5905		0.00003
Eykman modified	0.0109	100.00	0.00003

where T is the absolute temperature and a , b and ϕ are adjustable parameters, that are shown in table 5, together with the standard deviations. In a first approach, two considerations have been taken into account. Primarily, the exponent was considered as a variable and was optimized for the selected phosphonium-based ILs. The second approach consisted in fixing this parameter at 0.3, a typical value used with other ILs in the literature [39].

Other equations usually employed for the correlation of dynamic viscosity data with temperature are the Arrhenius-like law [32] and its empirical extensions, the Vogel–Fulcher–Tamman (VFT) equations [31–32]:

$$\eta = \eta_{\infty} \exp[-E_a/RT], \quad (4)$$

$$\eta = A \exp \left[\frac{k}{(T - T_0)} \right], \quad (5)$$

$$\eta = A\sqrt{T} \exp \left[\frac{k}{(T - T_0)} \right], \quad (6)$$

TABLE 5

Fitting parameters and standard deviations to correlate the dynamic viscosities of ($P_{444n}(n=1, 2 \text{ and } 8)$ X ($X = C_1SO_4$, $(C_2)_2PO_4$ and Cl) as a function of temperature.

Equation	a/η_{∞}	b/E_a	ϕ/A	k	T_0	D	SD
$P_{4448} Cl$							
η^{ϕ}	−0.9154/(mPa · s)	0.0035/(mPa · s · K)	0.24				0.002
$\eta^{0.3}$	−0.7951/(mPa · s)	0.0029/(mPa · s · K)					0.003
Arrhenius	3.2E−08/(mPa · s)	−63.66/(kJ · mol ^{−1})					0.061
VFT			0.013/(mPa · s)	1658/K	168.8/K	9.82	0.001
VFT-m			0.00049/(mPa · s)	1733/K	167.0/K		0.001
$P_{4442} (C_2)_2PO_4$							
η^{ϕ}	−1.0097/(mPa · s)	0.0042/(mPa · s · K)	0.25				0.000
$\eta^{0.3}$	−1.0115/(mPa · s)	0.0040/(mPa · s · K)					0.001
Arrhenius	4.3E−06/(mPa · s)	−44.76/(kJ · mol ^{−1})					0.042
VFT			0.034/(mPa · s)	1192/K	167.1/K	7.14	0.001
VFT-m			0.0013/(mPa · s)	1281/K	163.9/K		0.001
$P_{4441} C_1SO_4$							
η^{ϕ}	−0.8713/(mPa · s)	0.0037/(mPa · s · K)	0.24				0.000
$\eta^{0.3}$	−0.8608/(mPa · s)	0.0034/(mPa · s · K)					0.001
Arrhenius	8.5E−06/(mPa · s)	−44.34/(kJ · mol ^{−1})					0.034
VFT			0.035/(mPa · s)	1363/K	155.8/K	8.75	0.005
VFT-m			0.001/(mPa · s)	1529/K	149.2/K		0.001

VFT from equation (5) and VFT-m from equation (6).

where R is the universal gas constant, and the characteristic parameters are η_{∞} (viscosity at infinite temperature), E_a (activation energy), A , k and T_0 are the adjustable parameters, which values are also shown in table 5, together with the corresponding standard deviations. In a visual inspection of the results, it is clear that the VFT models allow describing in a more precise way the drastic decrease in the viscosity when the temperature is increased. Generally speaking, the dynamic viscosity of the selected phosphonium-based ILs exhibit a non-Arrhenius type dependence with temperature. The explanation behind this can be based on the statements reported by Seddon et al. [40], regarding the symmetry and size of the cations.

Bearing in mind the data obtained from the model presented in equation (5), another interesting classification of the ILs can be performed based on the Angell strength parameter, $D = k/T_0$, proposed by Xu et al. [41]. From the data of T_0 and D listed in table 5, it is possible to conclude that the studied phosphonium-based ILs can be classified as “fragile” liquids.

3.2. Prediction of the density of the phosphonium-based ILs

A plethora of analytical expressions to predict the density have been tested by many authors, although their validity for ILs is now an issue in the limelight. Due to this, another important issue to be addressed is to check the validity of different known correlations and models: Riedel, Narsimham, Bradford–Thodos, Yen–Woods, Rackett, Spencer–Danner, Gunn–Yamada, Hankinson–Thomson (COSTALD model), VSY, VSD, MH, and Linear Generalized Model or LGM to predict the density of the ILs under study. However, this type of generalized predictive models was not specifically developed for ILs and they have not been tested for appropriateness and accuracy with these special fluids yet. This handicap can be attributed to the lack of some common basic data such as critical properties, normal boiling temperatures and acentric factors. In this work, the critical properties, V_c , T_c , P_c , the normal boiling temperatures, T_b , and the acentric factors, w , of the selected phosphonium-based ILs have been determined using an extended group contribution method [42–44] and they are listed in table 6.

The analysis of the reliability of each of the proposed models was performed in terms of standard deviations. The fitting to the predictive equations considered in this work gave rise to varying results and three of them can be claimed as suitable ones due to the low deviations for all the ILs at all temperatures.

On the one hand, from the data listed in table 7, it becomes clear that the VSY, MH and LGM equations are able to predict the density of the phosphonium-based ILs in a more accurate manner.

TABLE 6

Critical Properties of ($P_{444n(n=1, 2 \text{ and } 8)}$ X (X = C_1SO_4 , $(C_2)_2PO_4$ and Cl).

Ionic liquid	$V_c/(\text{cm}^3 \cdot \text{mol}^{-1})$	T_c/K	P_c/MPa	T_b/K	w
$P_{4441} C_1SO_4$	998.40	991.14	2.169	725.38	0.5609
$P_{4442} (C_2)_2PO_4$	1317.81	913.46	1.216	740.72	1.0028
$P_{4448} \text{Cl}$	1316.84	904.14	1.167	731.59	0.9474

TABLE 7

Standard deviations to predict the density of ($P_{444n(n=1, 2 \text{ and } 8)}$ X (X = C_1SO_4 , $(C_2)_2PO_4$ and Cl) at different temperatures.

	SD		
	$P_{4448} \text{Cl}$	$P_{4442} (C_2)_2PO_4$	$P_{4441} C_1SO_4$
Riedel	0.1052	0.1350	0.0639
Narsimham	0.0245	0.0154	0.0325
Bradford–Thodos	0.0232	0.0201	0.0384
Yen–Woods	0.1603	0.1390	0.0291
Rackett	0.1709	0.1607	0.0112
Spencer–Danner	0.1454	0.1631	0.0549
Gunn–Yamada	0.1662	0.2850	0.1886
Hankinson–Thomson	0.0859	0.1258	0.0517
VSY	0.0748	0.0936	0.0122
VSD	0.2624	0.2817	0.2380
MH	0.0125	0.0104	0.0084
LGM	0.0164	0.0141	0.0342

Additionally, it is possible to conclude that the selected ILs containing shorter alkyl chains in the cation present the lowest values of standard deviations. The reason for the low standard deviation values obtained after applying the LGM equation is supported by the linear behavior followed by density against temperature for all the ILs. Besides, it is remarkable that the model of Mchaweh–Alsaygh–Nasrifar–Moshfeghian (MH) is able to predict the density in a more satisfactory way for all the studied ILs. The reason can be that this model presents a complex temperature functionality based on the use of the Soave–Redlich–Kwong (PSRK) equation of state.

On the other hand, Bradford–Thodos and Narsimham equations for $P_{4448} \text{Cl}$ and $P_{4442} (C_2)_2PO_4$ led to standard deviations with the same order of magnitude than those obtained for the models based on the corresponding state principle methods. In the case of the density obtained by means of the Rackett equation for the methylsulfate-based IL, a very low standard deviation was observed in relation to the values derived from the recent models based on the corresponding state principle.

4. Conclusions

Three hydrophilic phosphonium-based ILs ($P_{4448} \text{Cl}$, $P_{4442} (C_2)_2PO_4$ and $P_{4441} C_1SO_4$) were characterized at several temperatures by determining the density, speed of sound, isentropic compressibility, refractive index and dynamic viscosity. The experimental values were correlated by means of polynomial and exponential equations. The Eykman empirical equation turned out to be the best model to relate the densities and refractive indices for the three ILs. The VFT analytical expressions led to lower values of standard deviations than those provided when the Arrhenius-like law was used for all the phosphonium-based ILs. In relation to density prediction, a clear predominance of the models based on the corresponding state principles was concluded, with a remarkable role of the MH and LGM equations. These results point to the suitability of calculating the critical properties, normal boiling temperatures and acentric factors of the ILs under study by using the group contribution methods.

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