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Influence of Molecular Structure on Densities and Viscosities of Several Ionic Liquids

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S *Supporting Information*

ABSTRACT: One of the potential applications of the ionic liquids (ILs) is their use as lubricants or lubricant additives. The choice of the cation and the anion of the ILs, as well as the side chain design, determine their fundamental properties, which permits us to create tailor-made lubricants and lubricant additives among other functional fluids. In this work we have studied 10 ILs for which we report densities and viscosities from 283.15 K (and for some ILs at lower temperatures) up to 373.15 K. The viscosities of the ILs fall in the range of the applications of hydraulic fluid or lubricants. Four of these ILs were composed by the anion tris(pentafluoroethyl)trifluorophosphate $[(C_2F_5)_3PF_3]^-$ and one of the following cations: 1-butyl-2,3-dimethylimidazolium $[C_4C_1C_1min]^+$, 1-butyl-1-methylpyrrolidinium $[C_4C_1Pyrr]^+$, 1-(2-methoxyethyl)-1-methyl-pyrrolidinium $[C_1OC_2C_1Pyrr]^+$, and trihexyl(tetradecyl)-phosphonium $[P_{6,6,6,14}]^+$. Furthermore, three of the ILs contain the anion bis(trifloromethylsulfonyl)imide $[NTf_2]^-$ and one of the following cations $[C_4C_1C_1mim]^+$, $[C_4C_1Pyrr]^+$, or $[C_1OC_2C_1Pyrr]^+$. Two other ILs contain the 1-ethyl-3-methylimidazolium cation $[C_2C_1mim]^+$ and an alkyl sulfate anion (ethylsulfate $[C_2SO_4]^-$ or *n*-hexylsulfate $[C_6SO_4]^-$). The last one is composed by $[C_4C_1Pyrr]^+$ and trifluoromethanesulfonate $[CF_3SO_3]^-$. The experimental values were used to determine the glass-transition temperature and fragility of these ILs and to analyze the capability of two group contribution methods recently proposed by Gardas and Coutinho for the density and viscosity prediction of ILs.

1. INTRODUCTION

Interest in ionic liquids (ILs) has been spectacularly increased because they are a remarkable class of solvents, catalysts, additives, and lubricants, among with many other uses. Therefore, they are involved in different application fields, such as electrochemistry, extraction technology, organic synthesis, development of new materials, and tribology. The potential use of ILs as lubricants was proposed for the first time in 2001.[1] Subsequently, several studies[2−7] have shown good potential properties of ILs to be used as base lubricants or lubricant additives. Their significant physicochemical characteristics include their negligible volatility, nonflammability, high thermal stability and high thermal conductivity, low melting point, low temperature fluidity, and broad liquid range. In addition, the high polarity of the ILs makes them able to form very strong effective adsorption films and ready tribochemical reactions, which contributes to their prominent antiwear capability.[5] Their properties, such as density and viscosity, can be adjusted by selecting different lengths of the nonpolar alkyl chain of the cations or different types of anions.[3,5]

Most of the tribological studies have been focused on ILs containing the anions $[BF_4]^-$ and $[PF_6]^-$, which are also the two most common anions in articles concerning other applications. However, hydrophilic ILs containing $[BF_4]^-$ or $[PF_6]^-$ have been reported[8] to produce corrosive hydrogen fluoride in the presence of water that could be inevitable in engine operation during storage under air. Thus, the formation of hydrogen fluoride by the introduction of water in the system can damage tribological systems.[9] Furthermore, hydrophilic ILs tend to form bonds to the substrate on which they are deposited.[2,6]

For these reasons, several authors have proposed hydrophobic ILs based on the anions tris(pentafluoroethyl)trifluorophosphate $[(C_2F_5)_3PF_3]^-$, also named FAP, and bis(trifloromethylsulfonyl)-imide $[NTf_2]^-$ due to their higher hydrophobicity[2,10] combined with their excellent hydrolytic stability. Furthermore, according to the studies of Minami et al.[8] for ILs with the same cations, those with $[(C_2F_5)_3PF_3]^-$ or $[NTf_2]^-$ anions have generally better antiwear properties than those composed by $[BF_4]^-$ or $[PF_6]^-$ anions. The former ILs have lower viscosities than the later ILs.[3] It is necessary to take this trend into account to combine these anions with the cations for getting ILs with the appropriate viscosity for the different lubricant applications. Apart from the seven ILs based on $[(C_2F_5)_3PF_3]^-$ and $[NTf_2]^-$ anions, in this work we will study three ILs based in alkyl sulfate anion (ethylsulfate, $[C_2SO_4]^-$, or *n*-hexylsulfate, $[C_6SO_4]^-$) or trifluoromethanesulfonate, $[CF_3SO_3]^-$. The two first anions can be considered as hydrophilic moieties, whereas the $[CF_3SO_3]^-$ as an hydrophobic one because of the presence of fluorine atoms.[11] There are few studies with ILs lubricants composed by this kind of anions, and most of them are based in 1,3-imidazolium cations.[2] Nainaparampil et al.[12] have found better friction and wear reduction with two ILs with the $[C_2SO_4]^-$ anion than those with $[NTf_2]^-$ for the sliding microelectromechanical systems (MEMS) contacts.

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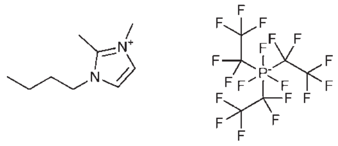
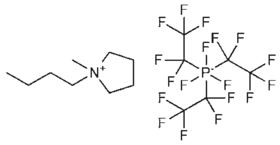
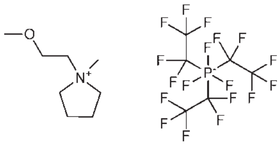
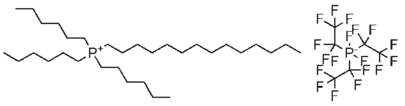
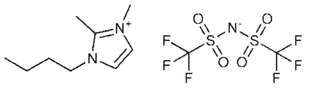
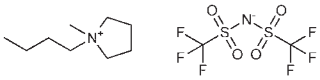
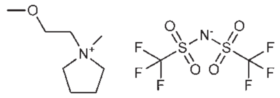
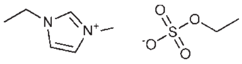
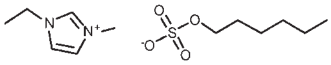
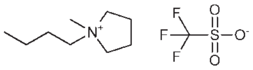
Table 1. Ionic Liquids Studied in This Paper

Chemical Formula CAS Number	Chemical structures	Name
$[C_4C_1C_1Im][(C_2F_5)_3PF_3]$		1-butyl-2,3-dimethylimidazolium tris(pentafluoroethyl)trifluorophosphate
$[C_4C_1Pyrr][(C_2F_5)_3PF_3]$ 851856-47-8		1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate
$[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$ 1195983-48-2		1-(2-Methoxyethyl)-1-methyl- pyrrolidinium tris(pentafluoroethyl)triflorophosphate
$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ 883860-35-3		Trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate
$[C_4C_1C_1Im]\ [NTf_2]$ 350493-08-2		1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide
$[C_4C_1Pyrr][NTf_2]$ 223437-11-4		1-butyl-1-methylpyrrolidinium bis(trifloromethylsulfonyl)imide
$[C_1OC_2C_1Pyrr][NTf_2]$ 757240-24-7		1-(2-Methoxyethyl)-1-methyl- pyrrolidinium bis(trifluoromethylsulfonyl)imide
$[C_2C_1Im][C_2SO_4]$ 342573-75-5		1-ethyl-3-methylimidazolium ethylsulfate
$[C_2C_1Im][C_6SO_4]$ 942916-86-1		1-ethyl-3-methylimidazolium hexylsulfate
$[C_4C_1Pyrr][CF_3SO_3]$ 367522-96-1		1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate

Concerning the cation, most of the tribological studies were performed with 1,3-alkyl methylimidazolium-based ILs $[C_nC_1Im]^+$, and a few others investigated ammonium-, pyridinium-, and phosphonium-based ILs.[2,3] Fox et al.[13] have found that the 1,2,3-trialkylimidazolium ILs exhibit slightly higher thermal stabilities than the corresponding 1,3-dialkylimidazolium compounds. In this article we have chosen ILs with the following cations: 1-butyl-2,3-dimethylimidazolium $[C_4C_1C_1Im]^+$, 1-butyl-1-methylpyrrolidinium $[C_4C_1Pyrr]^+$, 1-(2-methoxyethyl)-1-methyl-pyrrolidinium $[C_1OC_2C_1Pyrr]^+$, and trihexyl(tetradecyl)-phosphonium $[P_{6,6,6,14}]^+$. The 10 ILs studied in this article are presented in Table 1. We present new experimental viscosity and density measured with a rotational Couette viscometer Anton Paar Stabinger which includes a vibrating tube densimeter, in a broad range of temperature at atmospheric pressure. The viscosity

Table 2. Water Content (w_{H_2O}) in ppm of the ILs

IL	w_{H_2O}/ppm
$[C_4C_1C_1Im][(C_2F_5)_3PF_3]$	35
$[C_4C_1Pyrr][(C_2F_5)_3PF_3]$	24
$[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$	34
$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$	16
$[C_4C_1C_1Im][NTf_2]$	24
$[C_4C_1Pyrr][NTf_2]$	66
$[C_1OC_2C_1Pyrr][NTf_2]$	28
$[C_2C_1Im][C_2SO_4]$	304
$[C_2C_1Im][C_6SO_4]$	68
$[C_4C_1Pyrr][CF_3SO_3]$	72

Table 3. Experimental Density, ρ ($kg\cdot m^{-3}$), of the ILs Studied at Different Temperatures and Atmospheric Pressure

T / K	ρ / $kg\cdot m^{-3}$	T / K	ρ / $kg\cdot m^{-3}$	T / K	ρ / $kg\cdot m^{-3}$	T / K	ρ / $kg\cdot m^{-3}$	T / K	ρ / $kg\cdot m^{-3}$
$[C_4C_1C_1Im][(C_2F_5)_3PF_3]$									
263.15	1639.8	288.15	1609.7	313.15	1582.0	338.15	1554.9	358.15	1532.8
268.15	1633.8	293.15	1604.0	318.15	1576.6	343.15	1549.5	363.15	1527.2
273.15	1627.9	298.15	1598.4	323.15	1571.2	348.15	1544.1	368.15	1521.9
278.15	1622.0	303.15	1592.9	328.15	1565.8	353.15	1538.5	373.15	1516.8
283.15	1615.5	308.15	1587.4	333.15	1560.4				
$[C_4C_1Pyrr][(C_2F_5)_3PF_3]$									
283.15	1599.8	303.15	1577.9	323.15	1556.9	343.15	1536.3	363.15	1515.3
288.15	1594.2	308.15	1572.6	328.15	1551.7	348.15	1531.1	368.15	1510.4
293.15	1588.6	313.15	1567.4	333.15	1546.6	353.15	1525.7	373.15	1505.5
298.15	1583.2	318.15	1562.1	338.15	1541.5	358.15	1520.4		
$[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$									
258.15	1678.1	283.15	1647.9	308.15	1620.0	333.15	1592.5	358.15	1565.5
263.15	1672.2	288.15	1642.2	313.15	1614.4	338.15	1587.1	363.15	1559.8
268.15	1666.1	293.15	1636.6	318.15	1608.9	343.15	1581.6	368.15	1554.3
273.15	1659.8	298.15	1631.0	323.15	1603.4	348.15	1576.2	373.15	1549.1
278.15	1653.8	303.15	1625.5	328.15	1598.0	353.15	1570.9		
$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$									
268.15	1207.4	293.15	1186.0	318.15	1165.3	338.15	1149.3	358.15	1132.7
273.15	1203.2	298.15	1181.7	323.15	1161.3	343.15	1145.3	363.15	1128.7
278.15	1198.9	303.15	1177.6	328.15	1157.3	348.15	1141.2	368.15	1124.9
283.15	1194.6	308.15	1173.5	333.15	1153.3	353.15	1137.0	373.15	1121.1
288.15	1190.3	313.15	1169.4						
$[C_4C_1C_1Im][NTf_2]$									
273.15	1443.3	298.15	1419.4	318.15	1401.0	338.15	1382.8	358.15	1364.4
278.15	1438.4	303.15	1414.8	323.15	1396.4	343.15	1378.4	363.15	1359.8
283.15	1433.5	308.15	1410.1	328.15	1391.8	348.15	1373.9	368.15	1355.5
288.15	1428.7	313.15	1405.5	333.15	1387.3	353.15	1369.3	373.15	1351.3
293.15	1424.0								
$[C_4C_1Pyrr][NTf_2]$									
278.15	1412.9	298.15	1394.9	318.15	1377.4	338.15	1360.0	358.15	1342.5
283.15	1408.3	303.15	1390.5	323.15	1373.0	343.15	1355.7	363.15	1338.3
288.15	1403.8	308.15	1386.1	328.15	1368.7	348.15	1351.4	368.15	1334.3
293.15	1399.3	313.15	1381.8	333.15	1364.3	353.15	1346.9	373.15	1330.3
$[C_1OC_2C_1Pyrr][NTf_2]$									
258.15	1494.1	283.15	1468.8	308.15	1445.2	333.15	1422.0	358.15	1398.6
263.15	1488.7	288.15	1464.0	313.15	1440.5	338.15	1417.4	363.15	1394.2
268.15	1483.6	293.15	1459.3	318.15	1435.9	343.15	1412.9	368.15	1389.9
273.15	1478.5	298.15	1454.7	323.15	1431.2	348.15	1408.2	373.15	1385.7
278.15	1473.7	303.15	1450.0	328.15	1426.6	353.15	1403.3		
$[C_2C_1Im][C_2SO_4]$									
253.15	1270.6	278.15	1252.0	303.15	1234.4	328.15	1217.4	353.15	1200.4
258.15	1266.9	283.15	1248.3	308.15	1231.0	333.15	1214.0	358.15	1197.2
263.15	1263.3	288.15	1244.8	313.15	1227.6	338.15	1210.6	363.15	1194.1
268.15	1259.5	293.15	1241.3	318.15	1224.2	343.15	1207.2	368.15	1191.1
273.15	1255.7	298.15	1237.8	323.15	1220.8	348.15	1203.8	373.15	1188.2
$[C_2C_1Im][C_6SO_4]$									
268.15	1151.4	293.15	1133.8	318.15	1117.2	338.15	1104.4	358.15	1091.2
273.15	1147.9	298.15	1130.4	323.15	1114.0	343.15	1101.2	363.15	1088.1

Table 3. Continued

T K	ρ kg·m^{-3}	T K	ρ kg·m^{-3}	T K	ρ kg·m^{-3}	T K	ρ kg·m^{-3}	T K	ρ kg·m^{-3}
278.15	1144.4	303.15	1127.0	328.15	1110.8	348.15	1097.9	368.15	1085.1
283.15	1140.9	308.15	1123.7	333.15	1107.6	353.15	1094.5	373.15	1082.3
288.15	1137.4	313.15	1120.5						
				$[C_4C_1Pyrr][CF_3SO_3]$					
283.15	1263.6	303.15	1248.7	323.15	1234.4	343.15	1220.3	363.15	1205.9
288.15	1259.9	308.15	1245.1	328.15	1230.8	348.15	1216.8	368.15	1202.5
293.15	1256.1	313.15	1241.5	333.15	1227.3	353.15	1213.3	373.15	1199.2
298.15	1252.4	318.15	1238.0	338.15	1223.8	358.15	1209.7		

index was also determined using the ASTM D2270-04 standard. Up to our knowledge, for six of these ILs no previous measurements were published on density or viscosity as a function of temperature.

2. EXPERIMENTAL SECTION

2.1. Materials. All of the samples of the ILs summarized in Table 1 were kindly provided by Merck KGaA with a purity higher than 98 %. Before measuring the properties, all samples were treated by vacuum evaporation to remove the residual volatile impurities at room temperature, at least during 30 h. The water content of each liquid, summarized in Table 2, was determined by the Karl Fischer method using a Mettler Toledo DL32 coulometric titrator.

2.2. Measurement Technique. The density, viscosity, and viscosity index at atmospheric pressure were measured with an Anton Paar Stabinger SVM3000. This apparatus allows measuring density and dynamic and kinematic viscosity from (233.15 to 373.15) K, in a viscosity range from 0.2 mPa·s to 20 Pa·s. The SVM 3000 Stabinger viscometer has a cylindrical geometry, and it is based on a modified Couette principle with a rapidly rotating outer tube and an inner measuring bob that rotates more slowly. The SVM 3000 apparatus also has a density measuring cell that employs the well-known oscillating U-tube principle. Both density and viscosity cells are filled in one cycle, and the measurements are carried out simultaneously. Experimental uncertainties of 1 % and 0.05 % have been estimated for dynamic viscosity and density, respectively. We have verified the viscosity uncertainty with one reference fluid from Cannon Instrument Comp., N35, finding that the average absolute deviation (AAD %) is lower than 1 %. Moreover, the uncertainty was also verified using diisodecylphthalate (DIDP) which has been proposed as a reference fluid for viscosity measurements. Caetano et al.[14] have reported the viscosity reference values for DIDP at atmospheric pressure together with the corresponding density data. Our data for DIDP agree with the values reported by Caetano et al. obtaining an AAD of 0.15 % and standard deviation, σ, of 0.17 mPa·s for viscosity and AAD = 0.004 % and $\sigma = 0.13$ kg·m^{-3} for density. These values confirm the high-quality operation mode of our experimental device.

3. RESULTS AND DISCUSSION

3.1. Density. The densities of the different samples measured in the temperature range from (253.15 to 373.15) K and atmospheric pressure are presented in Table 3 and plotted in Figure 1. Density values were correlated with temperature using the same equation that Nieto de Castro et al.[15] have used for their ILs:

$$\ln(\rho/\mathrm{kg \cdot m^{-3}}) = A + B\cdot(T/\mathrm{K}) + C\cdot(T/\mathrm{K})^2 + D\cdot(T/\mathrm{K})^3 \qquad (1)$$

The parameter values obtained for eq 1 for the different ILs are given in Table 4. For all of the ILs the standard deviation of the correlation obtained with eq 1 was lower than 0.34 kg·m^{-3} in agreement with the reproducibility of the apparatus. As it can be seen in Figure 1 the denser liquids are three ILs with the $[(C_2F_5)_3PF_3]^-$ anion, the densest IL being $[C_1OC_2C_1Pyrr]$-$[(C_2F_5)_3PF_3]$. On the other hand, the lightest of the studied ILs is $[C_2C_1Im][C_6SO_4]$. The density of ILs with the same cation ($[C_4C_1Pyrr]^+$) decreases with the type of anion following the trend $[(C_2F_5)_3PF_3]^- > [NTf_2]^- > [CF_3SO_3]^-$. This trend is determined by the molecular mass, as it was found previously for ILs composed by imidazolium cations.[16,17] For the ILs with the same anion the trend of the density is: $[C_1OC_2C_1Pyrr]^+ > [C_4C_1C_1Im]^+ > [C_4C_1Pyrr]^+ > [P_{6,6,6,14}]^+$. This trend is not given by the molecular mass of the cation which follows the trend ($[P_{6,6,6,14}]^+ > [C_4C_1C_1Im]^+ > [C_1OC_2C_1Pyrr]^+ > [C_4C_1Pyrr]^+$) but mainly by its molecular volume ($[C_1OC_2C_1Pyrr]^+ < [C_4C_1Pyrr]^+ < [C_4C_1C_1Im]^+ < [P_{6,6,6,14}]^+$). This is in agreement with the results previously found by Fröba et al.[16] for two ILs based on $[NTf_2]^-$ anion. These authors found that the IL with the largest cation (trioctylmethylammonium) exhibits lower densities than that with the smaller one ($[C_2C_1Im]^+$). In addition, the density of ILs with $[C_nC_1Im]^+$ cations decreases with the alkyl chain length[18] due to the increase of dispersive interactions.[19,20] Similarly, for the ILs with the $[C_2C_1Im]^+$ cation the density decreases with the alkyl chain of the $[C_nSO_4]^-$ anion. Density decreasing with the alkyl chain size also occurs with nonassociated-polar-molecular compounds, as halogenoalkanes, esters, ketones, and so forth.[19,20] Therefore, in polar molecular liquids, as for ILs, increasing dispersive interactions between the aliphatic carbon chains, by means of increasing chain length, leads to lower density packing.

In the Supporting Information (Table S1) we present the comparison among our density values and those of the literature[15,16,21−58] for some of the studied ILs. For $[C_2C_1Im]$-$[C_2SO_4]$ and $[C_4C_1Pyrr][NTf_2]$ the relative deviations between the experimental values of this work (Table 3) and those published in literature[15,16,21−52] are plotted in Figures 2a and 3a, respectively. Almost all of the authors claim to have dried their samples before the measurements, but the water content is not always reported. In certain cases the differences among the

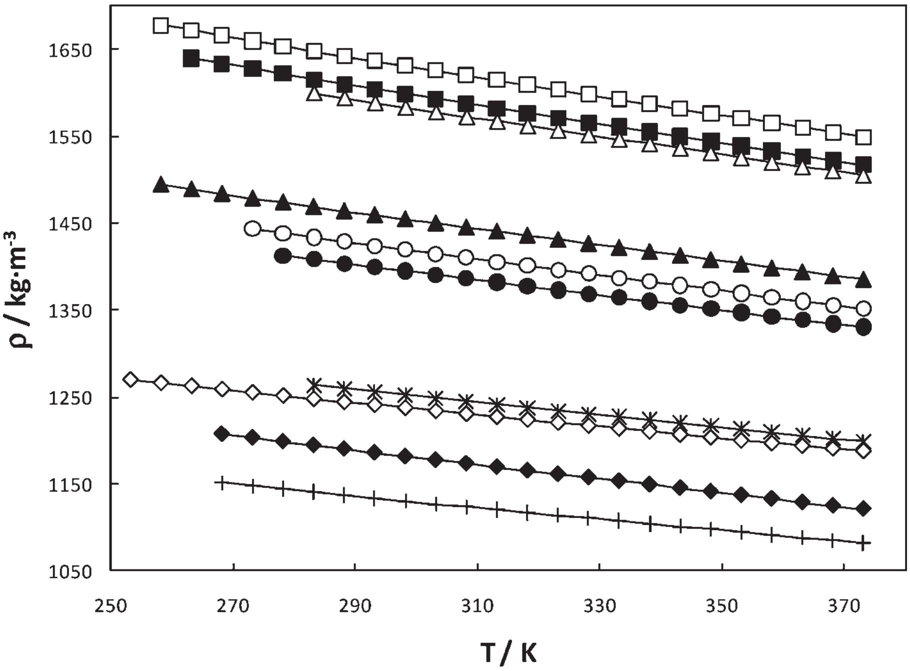


Figure 1. Experimental density as a function of temperature. □, $[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$; ■, $[C_4C_1C_1Im][(C_2F_5)_3PF_3]$; △, $[C_4C_1Pyrr][(C_2F_5)_3PF_3]$; ▲, $[C_1OC_2C_1Pyrr][NTf_2]$; ○, $[C_4C_1C_1Im][NTf_2]$; ●, $[C_4C_1Pyrr][NTf_2]$; ∗, $[C_4C_1Pyrr][CF_3SO_3]$; ◇, $[C_2C_1Im][C_2SO_4]$; ◆, $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$; +, $[C_2C_1Im][C_6SO_4]$.

Table 4. Correlation Coefficients of Equation 1 and Absolute Average Deviation (AAD) between Experimental Values of Density and Those Obtained through Equation 1

		$10^4 \cdot B$	$10^7 \cdot C$	$10^{10} \cdot D$	AAD	σ
IL	A	K^{-1}	K^{-2}	K^{-3}	%	$kg \cdot m^{-3}$
$[C_4C_1C_1Im][(C_2F_5)_3PF_3]$	7.8313	−30.0481	71.7682	−74.154	0.0106	0.22
$[C_4C_1Pyrr][(C_2F_5)_3PF_3]$	7.6793	−16.9187	30.9837	−31.306	0.0074	0.16
$[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$	7.7769	−23.2508	50.8394	−52.336	0.0064	0.13
$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$	7.3997	−17.8285	33.6245	−34.795	0.0094	0.15
$[C_4C_1C_1Im][NTf_2]$	7.6286	−22.8586	50.4084	−51.760	0.0088	0.18
$[C_4C_1Pyrr][NTf_2]$	7.4036	−3.88610	−7.64530	7.8545	0.0068	0.13
$[C_1OC_2C_1Pyrr][NTf_2]$	7.5638	−14.6201	25.0032	−25.553	0.0101	0.20
$[C_2C_1Im][C_2SO_4]$	7.3220	−8.0792	5.44350	−3.1623	0.0109	0.17
$[C_2C_1Im][C_6SO_4]$	7.4925	−31.9454	78.5600	−78.510	0.0178	0.34
$[C_4C_1Pyrr][CF_3SO_3]$	7.4454	−18.5934	38.9077	−39.287	0.0045	0.09

literature density and viscosity data can be attributed to the presence of water.

In Figure 2a and in the Supporting Information we can see that our data of $[C_2C_1Im][C_2SO_4]$ are in good agreement with most of the 24 literature values; thus, most of the density relative deviations are between 0.02 % and 0.25 %. The higher deviations in density values present AADs of 0.26 %,[21] 0.28 %,[22] 0.29 %,[23] 0.33 %,[24] 0.36 %,[25] 0.40 %,[26] and 0.65 %.[27] In Figure 3a it can be observed for $[C_4C_1Pyrr][NTf_2]$ an excellent agreement with the values reported by Jacquemin et al.[28] and Pereiro et al.[29] finding AADs of 0.04 % and 0.03 %, respectively. For this IL the relative deviations range from −1.10 % to 0.49 %. The highest deviation has been obtained with the data of Kato et al.[30] at 348.15 K.

For the other ILs the literature density values are scarce. For $[C_4C_1Pyrr][(C_2F_5)_3PF_3]$ we have only found three published data sets,[31,32,55] measured with vibrating tube densimeters. The AAD% with these data are 0.02 %,[55] 0.04 %,[31] and 0.21 %.[32]

For the other ILs the literature density values are scarce, as can be seen in the Supporting Information (Table S1). The highest deviation (0.34 %) was found for $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ with the value of Yao et al.[55] at 293.15 K. This big difference can be explained because their sample had higher water content. For this IL there are no more data.

From density measurements we can determine the isobaric thermal expansion coefficient (α_P). This property shows the fractional change in density when temperature increases at constant pressure. It is defined by the following expression:

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

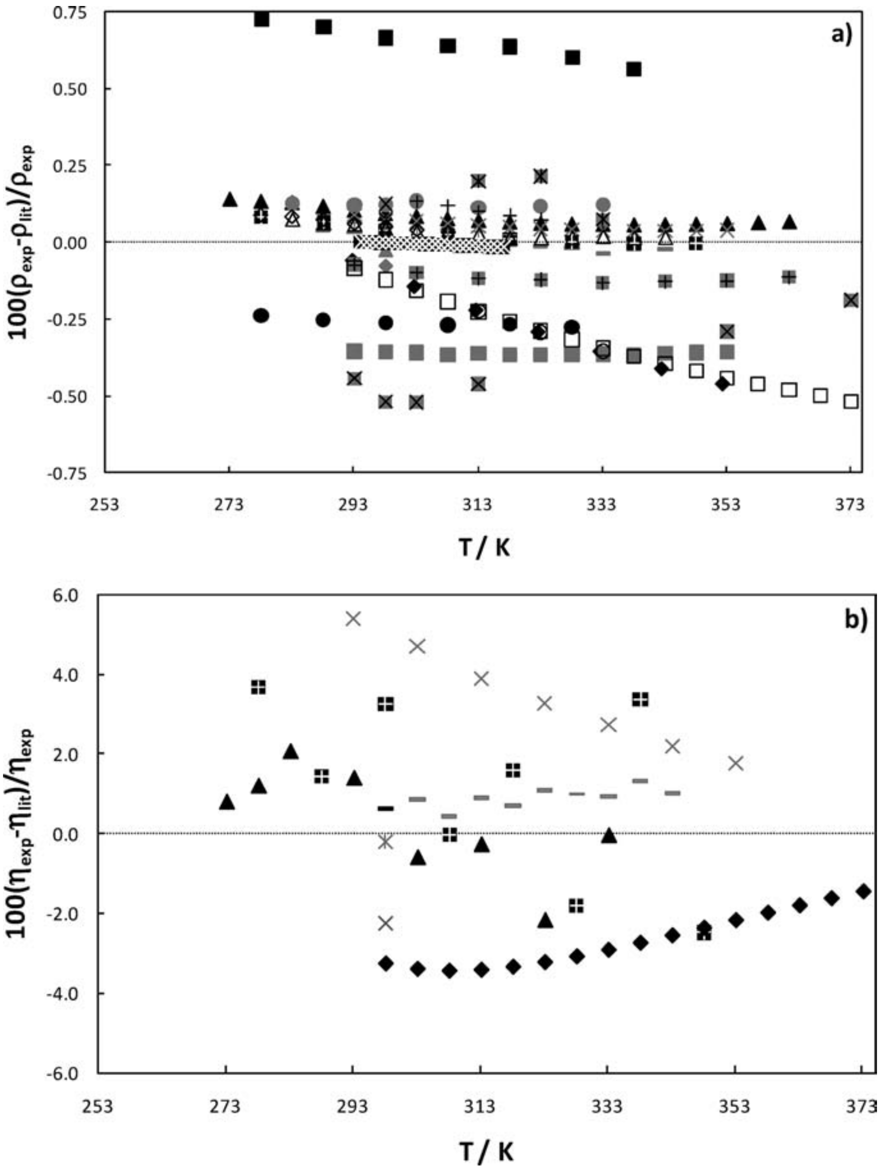


Figure 2. Percentage deviation between our data and literature for $[C_2C_1Im][C_2SO_4]$: (a) density, (b) viscosity. ●, Wandschneider et al.;[21] gray ●, Hofman et al.;[41] ○, Palgunadi et al.;[23] ■, Yang et al.;[27] gray ■, Krummen et al.,[25] □, Jacquemin et al.;[24] ▲, Fröba et al.;[16] gray ▲, Alonso et al.;[42] △, Matkowska et al.;[43] ◆, Jacquemin et al.,[22] gray ◆, Arce et al.;[44] ◇, Lehmann et al.;[45] +, Wong et al.;[46] gray +, García-Miaja et al.;[47] + with gray background, Jacquemin et al.;[31] + with black background, Rodríguez and Brennecke;[48] ×, Kim et al.;[49] gray ×, Fernández et al.;[36] × with gray background, Tomé et al.;[26] × with black background, Nieto de Castro et al.;[15] ∗, Domanska and Laskowska;[38] gray ∗, McHale et al.;[32] ∗ with gray background, Blanchard et al.;[50] —, González et al.;[35] gray —, Gómez et al.[34]

Equation 1 with parameters of Table 4 has been used to calculate this derivative property. The α_P values are gathered in the Supporting Information (Table S2). In Figure 4 the behavior of α_P with the temperature at atmospheric pressure is shown. Equation 1 permits us to reproduce positive and negative slopes $\alpha_P(T)$, as well as non-monotonic $\alpha_P(T)$ curves, as has been found previously in the literature for ILs.[15,41,59] All of the α_P values for our ILs range from $(5.34 \text{ to } 7.97)\cdot 10^{-4}\ K^{-1}$, the lowest values being those of $[C_2C_1Im][C_2SO_4]$ and the highest ones those of $[C_4C_1C_1Im][(C_2F_5)_3PF_3]$ and $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$. Matkowska et al.[43] have remarked that the isobaric expansivities for ILs usually vary between $(4 \text{ to } 7)\cdot 10^{-4}\ K^{-1}$ and are significantly lower than those of typical organic liquids.

For $[C_2C_1Im][C_2SO_4]$ the isobaric thermal expansion coefficient decreases with temperature, varying from $5.90\cdot 10^{-4}\ K^{-1}$ to $5.36\cdot 10^{-4}\ K^{-1}$. For $[C_4C_1Pyrr][NTf_2]$ it can be seen in Figure 4b that α_P presents a slight maximum around 323 K, but we can consider that α_P is constant in this temperature range for this IL since the α_P varies only a 0.7 % between its maximum and minimum values. For the other eight ILs we have observed the same α_P behavior: $\alpha_P(T)$ curves present a local minimum. These behaviors could be explained taking into account the work by Troncoso et al.[60,61] These authors try to clarify the controversial literature results regarding the temperature dependence of α_P for ILs. They state that $(\partial\alpha_P/\partial T)_P$ is negative far below the critical temperature. ILs are special in that they verify this condition at atmospheric pressure and ambient temperature, because their critical temperatures are higher than those of the molecular fluids.

3.2. Viscosity. The dynamic viscosities, η, experimentally determined in the present work for the 10 ILs are given in Table 5.

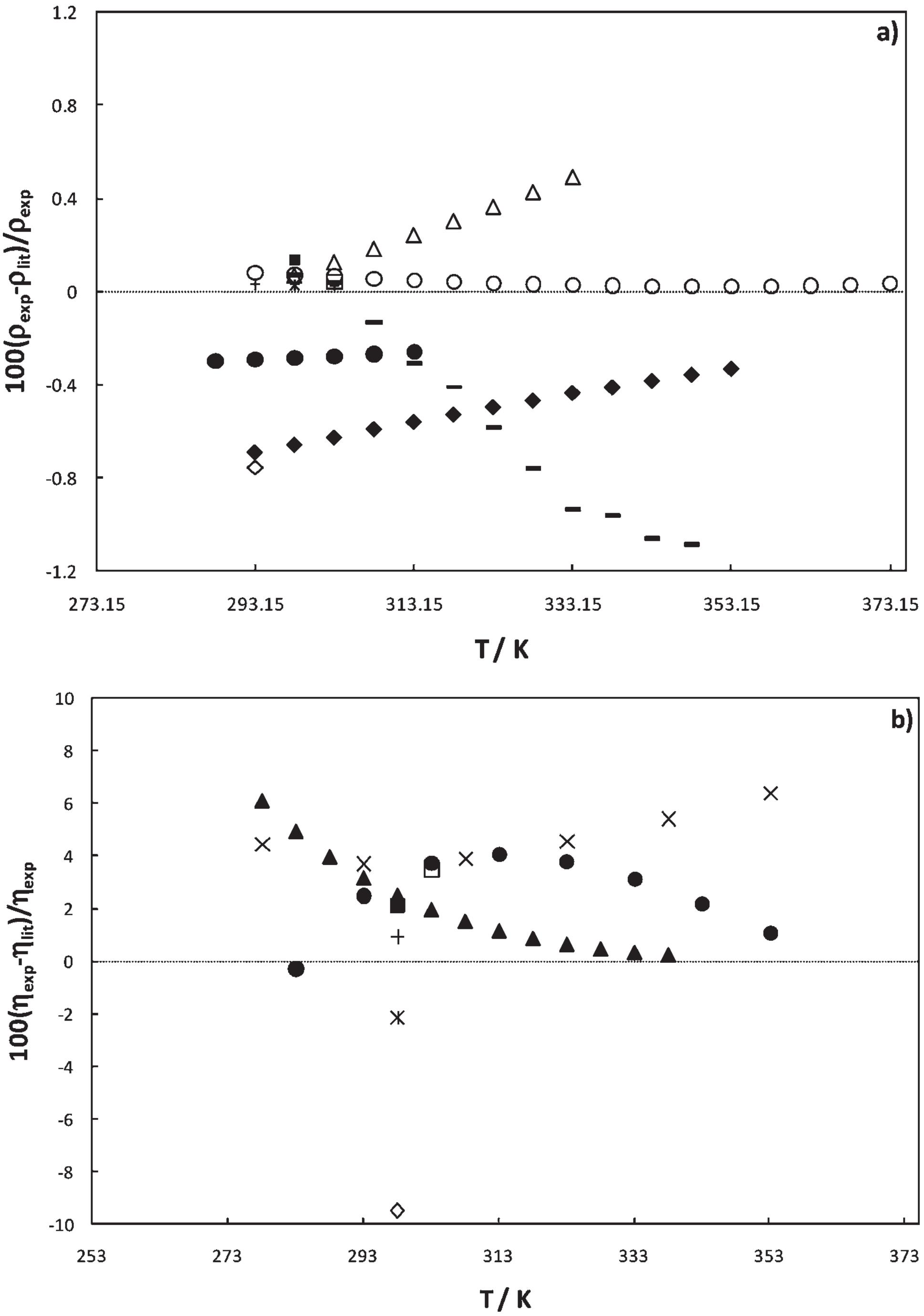


Figure 3. Percentage deviation between our data and literature for $[C_4C_1Pyrr][NTf_2]$: (a) density, (b) viscosity. ●, Tokuda et al.;[39] ○, Jacquemin et al.;[28] ■, Zhou et al.;[33] □, Tokuda et al.;[40] ▲, Jin et al.;[67] △, Anthony et al.;[51] ◆, Gardas et al.;[52] ◇, MacFarlane et al.;[37] +, Pereiro et al.;[29] ×, Funston et al.;[68] *, McHale et al.;[32] —, Kato et al.[30]

The viscosity of ILs strongly depends on the molecular structure and interactions between ions: electrostatic, van der Waals, and hydrogen bonds. The viscosity data have been plotted against temperature in Figure 5. We can observe that the viscosity of ILs with the same cation ($[C_4C_1Pyrr]^+$) decreases with the type of anion following the trend $[(C_2F_5)_3PF_3]^-$ > $[CF_3SO_3]^-$ > $[NTf_2]^-$. The same sequence was found by Pensado et al.[3] for the cation 1-alkyl-3-methylimidazolium. The lowest viscosity values for the ILs with $[NTf_2]^-$ can be explained for the high flexibility of this anion. However, the viscosity of the IL for each type of anion varies differently depending on the type of cation. Thus, for the anion $[(C_2F_5)_3PF_3]^-$ the trend of the viscosity is $[P_{6,6,6,14}]^+$ > $[C_4C_1Pyrr]^+$ > $[C_4C_1C_1Im]^+$ > $[C_1OC_2C_1Pyrr]^+$, while for the anion $[NTf_2]^-$ the trend is $[C_4C_1C_1Im]^+$ > $[C_4C_1Pyrr]^+$ > $[C_1OC_2C_1Pyrr]^+$.

Experimental data were correlated using different equations that had been previously analyzed by Mauro et al.[62] to compare their ability to provide reliable descriptions of the viscosity—temperature behavior for inorganic and organic liquids. The first viscosity model we have applied is the Vogel—Fulcher—Tammann

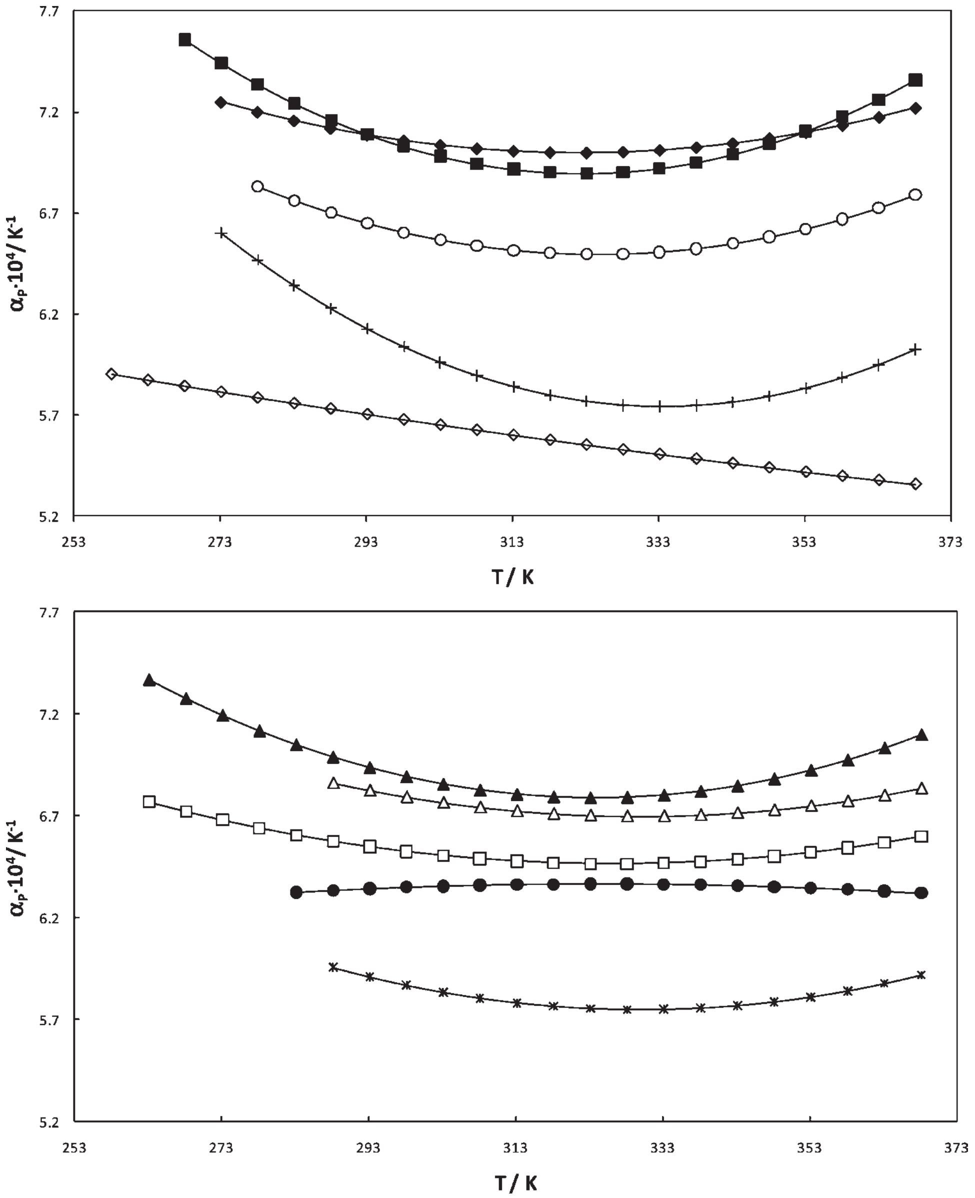


Figure 4. Isobaric thermal expansivity as a function of temperature: □, $[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$; ■, $[C_4C_1C_1Im][(C_2F_5)_3PF_3]$; △, $[C_4C_1Pyrr][(C_2F_5)_3PF_3]$; ▲, $[C_1OC_2C_1Pyrr][NTf_2]$; ○, $[C_4C_1C_1Im][NTf_2]$; ●, $[C_4C_1Pyrr][NTf_2]$ ∗, $[C_4C_1Pyrr][CF_3SO_3]$; ◇, $[C_2C_1Im][C_2SO_4]$; ◆, $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$; +, $[C_2C_1Im][C_6SO_4]$.

(VFT):

$$\log_{10}\eta(T) = \log_{10}\eta_0 + \frac{A}{T-B} \quad (3)$$

Another viscosity model is the Avramov–Milchev (AM):

$$\log_{10}\eta(T) = \log_{10}\eta_0 + \left(\frac{A}{T}\right)^B \quad (4)$$

Mauro et al.[62] have recently proposed to use a equation that had empirically been proposed earlier by Waterton:[63]

$$\log_{10}\eta(T) = \log_{10}\eta_0 + \frac{A}{T}\exp\left(\frac{B}{T}\right) \quad (5)$$

Mauro et al.[62] have indicated that this equation provides an improved description of the viscosity–temperature relationship, for both inorganic and organic liquids, using the same number of parameters as VFT and AM models. In a new article, Smedskjaer et al.[64] named eq 5 the MYEGA equation. In eqs 3 to 5, T is the temperature in K, and η_0, A, and B are correlation parameters.

In addition, we have also used the following empirical equation proposed by Roelands[65] to describe the viscosity–temperature relationship of lubricants oils at atmospheric pressure:

$$\log_{10}\eta = G_0\cdot 10^{-S_0\log_{10}\left(1+\frac{T-273.15}{135}\right)} - 1.2 \quad (6)$$

where G_0 and S_0 are dimensionless parameters.

The logarithms of the viscosity values reported in Table 5, $\log_{10}\eta$, have been correlated using eqs 3 to 6. This procedure leads to lower relative viscosity deviations than those obtained fitting viscosity values. The fitting coefficients obtained are given in Table 6 along with the average absolute deviations, AADs.

Table 5. Experimental Viscosity, η (mPa·s), of the Studied ILs at Different Temperatures and Atmospheric Pressure

T	η	T	η	T	η	T	η	T	η
K	mPa·s	K	mPa·s	K	mPa·s	K	mPa·s	K	mPa·s
$[C_4C_1C_1Im][(C_2F_5)_3PF_3]$									
283.15	436.03	303.15	115.49	323.15	44.859	343.15	22.077	363.15	12.713
288.15	297.78	308.15	88.592	328.15	36.890	348.15	18.996	368.15	11.278
293.15	211.04	313.15	69.381	333.15	30.728	353.15	16.490	373.15	10.066
298.15	154.10	318.15	55.336	338.15	25.906	358.15	14.426		
$[C_4C_1Pyrr][(C_2F_5)_3PF_3]$									
283.15	593.7	303.15	159.61	323.15	61.130	343.15	29.493	363.15	16.63
288.15	409.8	308.15	122.18	328.15	50.033	348.15	25.242	368.15	14.678
293.15	291.5	313.15	95.36	333.15	41.482	353.15	21.795	373.15	13.037
298.15	213.1	318.15	75.75	338.15	34.793	358.15	18.968		
$[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$									
258.15	2282.1	283.15	272.88	308.15	69.800	333.15	27.336	358.15	13.728
263.15	1377.1	288.15	198.10	313.15	56.364	338.15	23.435	363.15	12.215
268.15	865.70	293.15	147.72	318.15	46.178	343.15	20.267	368.15	10.930
273.15	569.17	298.15	112.74	323.15	38.341	348.15	17.672	373.15	9.8320
278.15	387.25	303.15	87.880	328.15	32.198	353.15	15.525		
$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$									
268.15	3067.3	293.15	471.76	318.15	120.76	338.15	52.393	358.15	26.789
273.15	2010.0	298.15	347.06	323.15	96.233	343.15	43.710	363.15	23.116
278.15	1345.2	303.15	260.12	328.15	77.677	348.15	36.803	368.15	20.087
283.15	928.39	308.15	198.30	333.15	63.446	353.15	31.274	373.15	17.567
288.15	654.20	313.15	153.61						
$[C_4C_1C_1Im][NTf_2]$									
273.15	518.55	298.15	102.19	318.15	41.526	338.15	21.026	358.15	12.296
278.15	353.44	303.15	79.465	323.15	34.445	343.15	18.172	363.15	10.942
283.15	249.26	308.15	62.974	328.15	28.913	348.15	15.831	368.15	9.7936
288.15	180.50	313.15	50.755	333.15	24.536	353.15	13.899	373.15	8.8135
293.15	134.22								
$[C_4C_1Pyrr][NTf_2]$									
278.15	230.30	298.15	77.650	318.15	34.780	338.15	18.772	358.15	11.497
283.15	169.60	303.15	62.140	323.15	29.376	343.15	16.440	363.15	10.325
288.15	128.00	308.15	50.520	328.15	25.074	348.15	14.500	368.15	9.3200
293.15	98.740	313.15	41.650	333.15	21.603	353.15	12.872	373.15	8.4540
$[C_1OC_2C_1Pyrr][NTf_2]$									
258.15	620.30	283.15	112.96	308.15	37.150	333.15	17.090	358.15	9.6170
263.15	412.30	288.15	87.140	313.15	31.150	338.15	15.034	363.15	8.7180
268.15	286.40	293.15	68.610	318.15	26.427	343.15	13.324	368.15	7.9400
273.15	204.56	298.15	55.060	323.15	22.657	348.15	11.883	373.15	7.2630
278.15	149.89	303.15	44.900	328.15	19.586	353.15	10.661		
$[C_2C_1Im][C_2SO_4]$									
253.15	3146.4	278.15	321.37	303.15	77.005	328.15	29.400	353.15	14.680
258.15	1789.6	283.15	229.15	308.15	61.708	333.15	25.151	358.15	13.063
263.15	1094.4	288.15	168.31	313.15	50.247	338.15	21.720	363.15	11.694
268.15	700.85	293.15	126.89	318.15	41.506	343.15	18.910	368.15	10.520
273.15	466.03	298.15	97.843	323.15	34.730	348.15	16.604	373.15	9.5178
$[C_2C_1Im][C_6SO_4]$									
268.15	3425.9	293.15	437.53	318.15	107.82	338.15	47.521	358.15	25.043
273.15	2124.1	298.15	316.78	323.15	86.062	343.15	39.912	363.15	21.798
278.15	1362.1	303.15	234.83	328.15	69.707	348.15	33.862	368.15	19.111

Table 5. Continued

T	η	T	η	T	η	T	η	T	η
K	mPa·s	K	mPa·s	K	mPa·s	K	mPa·s	K	mPa·s
283.15	904.77	308.15	177.81	333.15	57.208	353.15	28.997	373.15	16.868
288.15	620.25	313.15	137.23						
$[C_4C_1Pyrr][CF_3SO_3]$									
283.15	414.90	303.15	129.71	323.15	54.480	343.15	27.838	363.15	16.292
288.15	299.40	308.15	102.06	328.15	45.344	348.15	24.085	368.15	14.483
293.15	221.70	313.15	81.620	333.15	38.165	353.15	20.996	373.15	12.947
298.15	167.87	318.15	66.240	338.15	32.445	358.15	18.437		

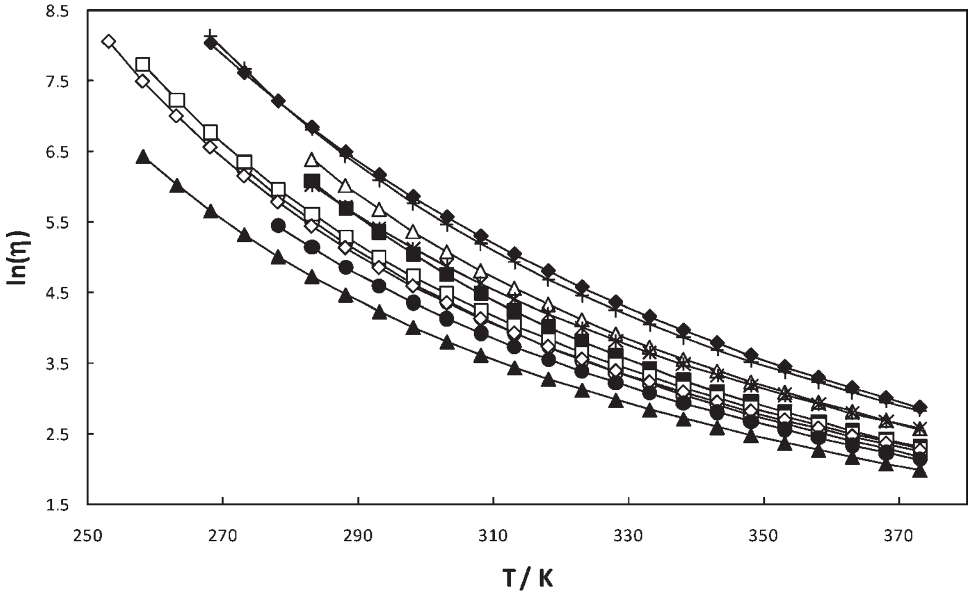


Figure 5. Experimental viscosity as a function of temperature: ◆, $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$; +, $[C_2C_1Im][C_6SO_4]$; △, $[C_4C_1Pyrr][(C_2F_5)_3PF_3]$; ∗, $[C_4C_1Pyrr][CF_3SO_3]$; ■, $[C_4C_1C_1Im][(C_2F_5)_3PF_3]$; □, $[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$; ○, $[C_4C_1C_1Im][NTf_2]$; ◇, $[C_2C_1Im][C_2SO_4]$; ●, $[C_4C_1Pyrr][NTf_2]$; ▲, $[C_1OC_2C_1Pyrr][NTf_2]$.

For eight of the ILs the best description of the viscosity—temperature behavior in terms of AAD is obtained by the VFT equation. For the other two ILs, $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ and $[C_2C_1Im][C_6SO_4]$, which are the most viscous, the AM and MYEGA equations represent the temperature dependence of the viscosity slightly better than the VFT model. For all of the ILs, the highest AADs are obtained with the Roelands equation. This could be due to the fact that (a) its number of parameters is lower than that of the other equations and (b) the shape of this equation is not adequate for broad temperature ranges. This is in agreement with the analysis performed by Seeton[66] about different correlation equations to describe viscosity—temperature behavior. Seeton indicated that the Roelands equation performs only over a narrow temperature range.

In the literature there are viscosity data measured by other authors for some of the ILs studied.[8,16,22,29,32−37,39,40,44,48,55−58,67−71] To compare our data with data from literature we have chosen the equation that provides a lower standard deviation. We summarize the deviations obtained with these literature data in the Supporting Information (Table S3). It is important to keep in mind that the water content may be different for every data set. For $[C_2C_1Im][C_2SO_4]$ and $[C_4C_1Pyrr][NTf_2]$ several experimental η values exist.[16,22,29,32−37,39,40,44,48,67,68] Relative deviations between the experimental values of this work and those published in the literature are plotted in Figures 2b and 3b. In Figure 2b it can be seen that the relative deviations of viscosity for $[C_2C_1Im][C_2SO_4]$ are in a range of ± 4 %, except for the data by Fernández et al.[36] The best agreement with our η values is with the data from McHale et al.,[32] González et al.,[34] and Gómez et al.,[35] finding an AAD % of 0.2 %, 0.6 %, and 0.9 %, respectively.

For $[C_4C_1Pyrr][NTf_2]$ Figure 3b shows that the relative deviations are lower than 6.5 %, except for one experimental value from MacFarlane et al.[37] that presents a relative deviation of 9.5 % at 298.15 K. The best agreement is obtained with the data published by Pereiro et al.[29] at 298.15 K with a relative deviation of 0.9 %.

For the other ILs, viscosity experimental data are scarcer. For $[C_4C_1Pyrr][(C_2F_5)_3PF_3]$ we have only found the data reported by McHale et al.[32] at 298.15 K and by Yao et al.[55] at 293.15 K. The absolute relative deviations with these data are 3.8 % and 0.2 %, respectively. For $[C_4C_1C_1Im][NTf_2]$ there are four literature η values being the lowest deviation 2.7 % from a datum reported by Campbell et al.[57] For $[C_1OC_2C_1Pyrr][NTf_2]$ we have found only two values measured by Shirota et al.[58] and Zhou et al.[33]

Table 6. Parameters of Equations 3 to 6 and Average Absolute Deviations (AAD) for Each Ionic Liquid

	VFT				AM				MYEGA				Roelands		
	η_0	A	B	AAD[a]	η_0	A		AAD[a]	η_0	A	B	AAD[a]			AAD[a]
IL	mPa·s	K	K	%	mPa·s	K	B	%	mPa·s	K	K	%	S_0	G_0	%
$[C_4C_1C_1Im][(C_2F_5)_3PF_3]$	0.1563	343.01	183.59	0.06	1.2432	364.16	3.7030	0.60	0.5637	81.515	652.52	0.41	1.156	4.131	3.25
$[C_4C_1Pyrr][(C_2F_5)_3PF_3]$	0.1388	388.60	176.17	0.05	1.2157	376.85	3.4553	0.45	0.4962	111.66	581.66	0.27	1.124	4.276	2.61
$[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$	0.1551	364.93	170.68	0.24	1.4614	355.54	3.6175	1.16	0.6103	92.264	593.96	0.70	1.099	3.957	5.00
$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$	0.0362	616.87	143.13	0.49	0.5043	437.80	2.7152	0.08	0.1234	300.97	366.26	0.20	1.103	4.506	0.57
$[C_4C_1C_1Im][NTf_2]$	0.1452	358.07	172.41	0.10	1.1112	362.59	3.4584	0.63	0.4806	102.53	570.45	0.39	1.091	3.881	3.11
$[C_4C_1Pyrr][NTf_2]$	0.1644	356.78	164.74	0.06	1.0044	364.60	3.1661	0.43	0.4405	127.11	495.67	0.27	0.943	3.419	1.76
$[C_1OC_2C_1Pyrr][NTf_2]$	0.2025	322.61	165.67	0.16	1.3139	343.35	3.4377	0.85	0.6068	93.630	545.87	0.51	0.991	3.511	4.20
$[C_2C_1Im][C_2SO_4]$	0.1870	343.06	172.03	0.34	1.7237	346.31	3.7577	1.30	0.7554	77.674	624.12	0.72	1.087	3.884	6.35
$[C_2C_1Im][C_6SO_4]$	0.0992	458.27	167.32	0.51	1.2692	386.71	3.3653	0.41	0.4310	140.53	538.30	0.13	1.139	4.509	3.06
$[C_4C_1Pyrr][CF_3SO_3]$	0.1402	407.90	165.64	0.03	1.0718	383.02	3.1426	0.36	0.4210	147.89	494.17	0.22	1.042	4.092	1.86

[a] $\mathrm{AAD} = (100/N)\cdot\Sigma_{i=1}^{N}((|\eta_{\mathrm{cal}_i} - \eta_{\mathrm{exp}_i}|)/\eta_{\mathrm{exp}_i})$.

Table 7. Glass Transition Temperature for the Studied ILs

	T_g/K				
IL	VFT	AM	MYEGA	Roelands	lit.
$[C_4C_1C_1Im][(C_2F_5)_3PF_3]$	205.29	175.56	184.31	179.55	
$[C_4C_1Pyrr][(C_2F_5)_3PF_3]$	200.68	172.39	181.1	179.42	
$[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$	193.76	168.7	176.27	175.58	
$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$	180.65	160.31	167.8	180.45	
$[C_4C_1C_1Im][NTf_2]$	195.01	165.86	174.84	174.60	
$[C_4C_1Pyrr][NTf_2]$	187.34	155.01	165.48	176.08	192.15,[76] 190.15[41,42] 186.15,[75] 184.15[35]
$[C_1OC_2C_1Pyrr][NTf_2]$	186.23	156.54	165.74	167.02	178.15,[77] 182.15[35]
$[C_2C_1Im][C_2SO_4]$	193.85	169.17	176.47	174.44	194.75,[62] 192.25,[74] 187.65,[40] 195[73]
$[C_2C_1Im][C_6SO_4]$	195.95	173.31	180.49	182.06	
$[C_4C_1Pyrr][CF_3SO_3]$	191.37	161.90	171.52	174.19	

finding AADs of 2.5 % and 3.9 %, respectively. For $[C_2C_1Im][C_6SO_4]$ the only literature viscosity value measured by Himmler et al.,[53] using a MCR 100 rheometer, has an absolute relative deviation of 15.3 %. For $[C_4C_1Pyrr][CF_3SO_3]$ the only literature value was reported by Biso et al.[69] with a high relative deviation of 28.7 %. For $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ the value measured by Yao et al.[55] at 293.15 K deviate 24.6 % from our η values, whereas the two kinematic viscosity values reported by Minami et al.[8] deviate only 0.8 % from our data.

3.3. Glass Transition Temperature. The glass transition temperature is often defined as that of the liquid when its shear viscosity is 10^{12} Pa·s.[62,72] Following this definition we have calculated the T_g values from eqs 3 to 6 with the parameters indicated in Table 6. The T_g values obtained are reported in Table 7. As expected, the T_g values vary with the type of equation used for its calculation (VFT, AM, MYEGA, or Roelands model). For every IL, we have obtained the highest T_g values with the VFT equation and the lowest ones with the AM equation.

Several authors had measured T_g's by differential scanning calorimetry for some of the ILs studied in this work.[33,38−40,73−78] For the $[C_4C_1Pyrr][NTf_2]$, the predicted value of T_g from VFT equation, 187.34 K, is in good agreement with those measured by Zhou et al.[33] (184.15 K), Dean et al.[76] (186.15 K), Tokuda et al.[39,40] (190.15 K), and Martinelli et al.[77] (192.15 K). For $[C_1OC_2C_1Pyrr][NTf_2]$ the two T_g values measured by Zhou et al.[33] (182.15 K) and by Yuyama et al.[78] (178.15 K), deviate 2.2 % and 4.3 %, from that obtained using VFT (Tables 6 and 7), respectively. For $[C_2C_1Im][C_2SO_4]$, the glass-transition temperature was measured by Fernández et al.,[73] Ribeiro,[74] Shamim and McKenna,[75] and Domanska and Laskowska[38] obtaining values of 194.75 K, 195.00 K, 192.25 K, and 187.65 K, respectively. These values have absolute relative deviations of 0.5 %, 0.6 %, 0.8 %, and 3.2 % from the value obtained from VFT equation, respectively. Thus, for these ILs, VFT equation can be used to estimate the glass transition temperature with a good accuracy. For the three ILs, AM, MYEGA, and Roelands correlations lead to higher deviations.

3.4. Fragility. The fragility concept can be utilized to categorize liquids for their viscosity−temperature dependence. The fragility index m is defined as the limiting slope in a plot of $\log(\eta)$ versus T_g/T at the glass transition temperature T_g, that is,

$$m = \left.\frac{d(\log_{10}\eta)}{d(T_g/T)}\right|_{T=T_g} \qquad (7)$$

which is a measure for the viscosity−temperature dependence at the glass transition temperature. The larger the value of m, the

Table 8. Fragility Values Obtained through the VFT Equation and Viscosity Index of the ILs Studied in This Work

IL	m	VI
$[C_4C_1C_1Im][(C_2F_5)_3PF_3]$	150	107
$[C_4C_1Pyrr][(C_2F_5)_3PF_3]$	130	119
$[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$	133	137
$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$	79	128
$[C_4C_1C_1Im][NTf_2]$	137	150
$[C_4C_1Pyrr][NTf_2]$	131	176
$[C_1OC_2C_1Pyrr][NTf_2]$	142	191
$[C_2C_1Im][C_2SO_4]$	140	174
$[C_2C_1Im][C_6SO_4]$	110	136
$[C_4C_1Pyrr][CF_3SO_3]$	118	156

higher the fragility, and the stronger the viscosity changes for a temperature increment at T_g. We have estimated the fragility parameter by using the VFT model due to the fact that this equation gives the most reliable T_g values of the ILs for which there are available experimental values. Thus, using eqs 3 and 7 we obtain the following expression:

$$m = A\frac{T_g}{(T_g - B)^2} \tag{8}$$

In Table 8 we report the m values calculated from eq 8 by using the T_g values of Table 7 and the A and B parameters of Table 6. The fragility values range from 79 for $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ to 150 for $[C_4C_1C_1Im][(C_2F_5)_3PF_3]$, this last one being the most weak and fragile IL studied in the present work. Thus, Schreiner et al.[79] have concluded that the fragility should range from 16 (from strong liquids, i.e., Arrhenius behavior) to below 200 because this value corresponds to a solid. Strong inorganic glasses and orientational glasses (which are also very strong glasses) have fragilities between 15 and 35, while organic polymeric systems are often very fragile, with fragility values[80] often higher than 100. Schreiner et al.[79] have also determined fragility values for 15 fluoroborate-based ILs finding values ranging from 119 to 196 and concluding that the ILs could be classified as extremely weak and fragile liquids. The same conclusion is obtained from Table 8 for the studied ILs in this work except for $[P_{6,6,6,14}][(C_2F_5)_3PF_3]$ for which $m = 79$. Besides, Ribeiro[74] has determined the fragility index values for nine imidazolium-based ILs finding values ranging from 70 to 104. The high fragility seems to be connected to the observed extensive supercooling tendency and low glass transition temperatures for ILs.[79]

For the 10 compounds studied, there are only literature fragility values for $[C_2C_1Im][C_2SO_4]$ for which Ribeiro[74] has reported a m value of 97 determined from low frequency Raman spectra and Shamim and McKenna[75] obtained $m = 80$ from rheological measurements at low temperatures. These m values are quite lower than that determined in this article ($m = 140$). We should point out that fragility values obtained from different properties and with different equations can strongly differ, that is, for other $[C_nC_1Im]$ ILs the m values of Ribeiro[74] are up to 46 lower than those of Schreiner et al.,[79] which use the same procedure as in this work.

3.5. Viscosity Index. The viscosity index values calculated following the ASTM D2270-04 standard using kinematic viscosity at (313.15 and 373.15) K are given in Table 8. With regard to the behavior of the viscosity with temperature, it is considered that a good lubricant is that whose viscosity varies as little as possible with temperature. Thus, the effectiveness of lubrication and energy losses do not vary with external factors concerning the temperature. The viscosity index of the commonly used lubricants ranges from 20 to 240. Lubricants with a high viscosity index show small changes in viscosity with temperature. Table 8 shows that VI strongly changes with the ILs structure, ranging from 107 to 191. Among the ILs studied in this work, those with the best viscosity index are the ILs with the $[NTf_2]^-$ anion, whereas the $[(C_2F_5)_3PF_3]^-$ ILs present the lowest VI values. This result agrees with the previous conclusions reported by Pensado et al.[3] Taking into account their results along with ours, we can conclude that the ILs that present higher VIs are those with $[NTf_2]^-$ anion and $[C_1OC_2C_1Pyrr]^+$, $[C_2C_1Im]^+$, and $[C_4C_1Pyrr]^+$ cations. Furthermore, the longer alkyl chains of imidazolium cations and of alkylsulfate anions the lower the VI, whereas for the ammonium and phosphonium cations VI increases with the length of alkyl chains.[3]

4. GROUP CONTRIBUTION METHODS FOR THE DENSITY AND VISCOSITY ESTIMATION OF ILS

We have used density values to analyze the prediction goodness of the method proposed by Gardas and Coutinho.[81] These authors have proposed an extension of the group contribution method, proposed previously by Ye and Shreeve,[82] to estimate the density in a wide range of temperatures [(273.15 to 393.15) K] and pressures [(0.10 to 100) MPa]. Densities are predicted using the following equation:

$$\rho = \frac{M}{NV_0(a + bT + cP)} \tag{9}$$

where ρ is the density in $kg\cdot m^{-3}$, M is the molar mass in $kg\cdot mol^{-1}$, N is the Avogadro constant, and V_0 is the molecular volume of the salt, in $m^3\cdot$molecule unit^{-1}, which is assumed as the linear sum of the volumes of the cation and the anion. Gardas and Coutinho[81] consider that the values of the coefficients a, b, and c do not depend on the IL, being 0.8005 ± 0.0002, $6.652\cdot 10^{-4} \pm 0.007\cdot 10^{-4}$ K^{-1}, and $-5.919\cdot 10^{-4} \pm 0.024\cdot 10^{-4}$ MPa^{-1}, respectively. These values were determined by Gardas and Coutinho[81] from a correlation of the experimental densities in wide ranges of pressure and temperature. The values of the ion volumes, V_0, of the ILs studied in this work were obtained for $[C_2C_1Im]^+$, $[P_{6,6,6,14}]^+$, $[C_4C_1C_1Im]^+$, and $[NTf_2]^-$ from Gardas et al.,[81] for $[CF_3SO_3]^-$ from Gardas and Coutinho,[83] and for $[C_2SO_4]^-$ from Tomé et al.[26] In the case of $[C_1OC_2C_1Pyrr]^+$ and $[(C_2F_5)_3PF_3]^-$ ions, the volumes were calculated by Shreeve,[84] while for the $[C_4C_1Pyrr]^+$ and $[C_6SO_4]^-$ were calculated in this work using the group contribution method proposed by Ye and Shreeve.[82] All of these values are summarized in Table 9.

With this method we obtain AADs between experimental and predicted densities ranging between 0.1 % and 1.3 %. We have not found a clear dependence among the AAD and the IL structure. The results show that this group contribution method is an appropriate method to predict the density of these ILs.

For the determination of viscosity it was used the group contribution approach proposed by Gardas and Coutinho[83] based on the method of Orrick-Erbar.[85] This procedure[83] uses a group contribution to estimate the parameters A and B of the following equation for each IL:

$$\ln\frac{\eta}{\rho M} = A + \frac{B}{T} \tag{10}$$

Table 9. Molecular Volume of the Ions Studied[a]

	M	cation	anion	AAD
IL	$g \cdot mol^{-1}$	$A^3 \cdot molecule^{-1}$	$A^3 \cdot molecule^{-1}$	%
$[C_4C_1C_1Im][(C_2F_5)_3PF_3]$	597.79	266[b]	360[84]	0.1
$[C_4C_1Pyrr][(C_2F_5)_3PF_3]$	587.27	253[81]	360[84]	0.7
$[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$	589.24	235[84]	360[84]	1.0
$[P_{6,6,6,14}][(C_2F_5)_3PF_3]$	922.88	947[81]	360[84]	0.5
$[C_4C_1C_1Im][NTf_2]$	433.39	266[b]	248[81]	1.3
$[C_4C_1Pyrr][NTf_2]$	422.41	253[81]	248[81]	0.4
$[C_1OC_2C_1Pyrr][NTf_2]$	424.38	235[84]	248[81]	0.4
$[C_2C_1Im][C_2SO_4]$	236.29	182[81]	134[26]	0.3
$[C_2C_1Im][C_6SO_4]$	292.40	182[81]	256[b]	0.3
$[C_4C_1Pyrr][CF_3SO_3]$	291.33	253[81]	129[83]	1.0

[a] AAD is the absolute average deviation between our experimental data and those calculated following the method proposed by Gardas and Coutinho.[81] [b] Value calculated following the group contribution method of Ye and Shreeve.[82]

Table 10. Parameters A and B Used to Estimate the IL Viscosity[a]

	M		B	AAD
IL	$g \cdot mol^{-1}$	A	K	%
$[C_4C_1Pyrr][NTf_2]$	422.41	−13.85	3494.5	8.3
$[C_2C_1Im][C_2SO_4]$	236.29	−13.13	3594.8	7.2
$[C_2C_1Im][C_6SO_4]$	292.40	−15.65	4596.4	32.8
$[C_4C_1Pyrr][CF_3SO_3]$	291.33	−14.18	3890.1	30.6

[a] AAD is the absolute average deviation between our experimental data and those calculated following the method proposed by Gardas and Coutinho.[83]

where η and ρ are the viscosity in $mPa \cdot s$ and the density in $g \cdot cm^{-3}$, respectively, M is the molecular weight in $kg \cdot mol^{-1}$, and T is the absolute temperature. Gardas and Coutinho[83] have obtained values of parameters A and B corresponding to 29 ILs composed by 13 different cations and 8 different anions from the adjustment of nearly 500 experimental values of viscosity in a temperature range from (293.15 to 393.15) K. By comparison of A and B values of ILs having similar cations and anions, Gardas and Coutinho[83] estimated the values of A and B for each of the different cations and anions. Subsequently splitting the cation and the anion in groups, these authors determined the parameter values for several groups. With these parameter values, the deviations obtained by these authors for 29 ILs range from 0.04 % for $[C_4C_1Im][BF_4]$ to 23 % for $[C_3C_1Im][BF_4]$. In their study there are two ILs ($[C_2C_1Im][C_2SO_4]$ and $[C_4C_1Pyrr][NTf_2]$) of the 10 fluids studied in the present work. Moreover, there is also experimental information about the $[CF_3SO_3]^-$ anion combined with two imidazolium cations, whereas the anion $[C_6SO_4]^-$ was not present in any IL of the database. From the values of parameters A and B for different groups taken from Gardas and Coutinho,[83] it is only possible to obtain the parameters of eq 10 for these four ILs: $[C_2C_1Im][C_2SO_4]$, $[C_2C_1Im][C_6SO_4]$, $[C_4C_1Pyrr][NTf_2]$, and $[C_4C_1Pyrr][CF_3SO_3]$. The parameter values and the AADs obtained between predicted and experimental values for these four ILs are summarized in Table 10. The average absolute deviation ranges from 7.2 % for $[C_2C_1Im][C_2SO_4]$ to 32.8 % for $[C_2C_1Im][C_6SO_4]$. As expected, the ILs which present the highest deviations are those which were not included in the database. We should point out that it is necessary to have a more extensive database to determine the parameters A and B with better precision to improve the predictions.

5. CONCLUSIONS AND FUTURE WORK

In this work we have studied several thermophysical properties of 10 ILs: density, isobaric thermal expansion coefficient, viscosity, glass-transition temperature, fragility, and the viscosity index. We have found that, for the ILs with the same cation, those containing the $[(C_2F_5)_3PF_3]^-$ anion are the densest and also the most viscous. Besides, we have calculated the α_P values obtaining different behaviors with temperature. Moreover, we have correlated the viscosity data as a function of temperature by means of Vogel−Fulcher−Tammann, Avramov-Milchev, MYEGA, and Roelands correlations. In general, we have found that the first equation represents the viscosity temperature dependence of the studied ILs slightly better. Besides, we have used the Vogel−Fulcher−Tammann equation to estimate the glass-transition temperature of the ILs obtaining a good agreement with experimental values determined by calorimetric methods. The obtained fragility values range from 79 to 150 with $[C_4C_1C_1Im][(C_2F_5)_3PF_3]$ as the most weak and fragile. In addition, we have used the Gardas and Coutinho group contribution methods to predict the density for our liquids and viscosity of four of them with maximum AADs of 1.3 % and 32.8 %, respectively.

To evaluate the reliability of these ILs in the elastohydrodynamic regime, their viscosity-pressure behavior is also needed.[3,86,87] For this reason we plan in a near future to extent the present study with high-pressure viscosities. Besides, the knowledge of rheological behavior at high shear strains is also needed to develop ILs as lubricants.[87,88] Unfortunately there are very few published studies on this matter.[89] Accordingly, new works in this area are encouraged.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Comparisons between our density values and literature data (Table S1), the isobaric thermal expansivity of the ILs studied in this work (Table S2), and comparisons between our viscosity values and literature results

(Table S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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