Temperature Dependence and Structural Influence on the Thermophysical Properties of Eleven Commercial Ionic Liquids

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · FEBRUARY 2012

Impact Factor: 2.59 · DOI: 10.1021/ie2029255

7 AUTHORS, INCLUDING:

Elena Gómez
University of Vigo
54 PUBLICATIONS **1,388** CITATIONS
SEE PROFILE

Noelia Calvar
University of Vigo
78 PUBLICATIONS **1,886** CITATIONS
SEE PROFILE

Emilio J. González
Complutense University of Madrid
67 PUBLICATIONS **962** CITATIONS
SEE PROFILE

Angeles Domínguez
University of Vigo
119 PUBLICATIONS **2,616** CITATIONS
SEE PROFILE

I&EC research
Industrial & Engineering Chemistry Research

Correlation

pubs.acs.org/IECR

Temperature Dependence and Structural Influence on the Thermophysical Properties of Eleven Commercial Ionic Liquids

Raquel G. Seoane,[†] Sandra Corderí,[†] Elena Gómez,*[,†] Noelia Calvar,[‡] Emilio J. González,[‡] Eugenia A. Macedo,[‡] and Ángeles Domínguez[†]

[†]Advanced Separation Processes Group, Department of Chemical Engineering, University of Vigo, Lagoas-Marcosende Campus, 36310 Vigo, Spain

[‡]LSRE-Laboratory of Separation and Reaction Engineering-Associated Laboratory LSRE/LCM, Faculdade de Engenharia, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

ABSTRACT: Density, speed of sound, refractive index, and viscosity of the commercial ionic liquids 1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, [EMpy][NTf_2], 1-propyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, [PMpy][NTf_2], 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, [BMpy][NTf_2], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMim][NTf_2], 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [HMim][NTf_2], 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [BMpyr][NTf_2], 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate, [BMpyr][TFO], 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [BMim][TFO], 1-hexyl-3-methylimidazolium trifluoromethanesulfonate, [HMim][TFO], 1-butyl-3-methylimidazolium dicyanamide, [BMim][$N(CN)_2$], and 1-hexyl-3-methylimidazolium dicyanamide, [HMim][$N(CN)_2$] were measured as a function of temperature at atmospheric pressure. The density, speed of sound, and refractive index data were properly fitted to a linear equation, while viscosity data were fitted to Arrhenius-like law, Vogel−Fulcher−Tamman (VFT), a modified VFT, Litovitz, and fluidity equations. Besides, from the experimental density values, the thermal expansion coefficient, α, was calculated. Moreover, the experimental data were used to analyze the effect of temperature, the role of the alky chain length of the cation, and the influence of the nature of the ions (cation and anion) on the physical properties. Finally, an exhaustive comparison with available literature data of the studied ionic liquids was also carried out.

1. INTRODUCTION

Ionic liquids (ILs) are attracting increasing attention of scientists and engineers because of their unique properties and wide range of applications.[1−11] Their negligible vapor pressure[12] makes them good replacements for volatile organic compounds as solvents in the chemical industry, as shown by the increasing number of published works in recent years.[13] ILs are salts with a low melting point (below 100 °C) and they are obtained from a combination of organic cations and various anions; the large number of possible combinations allows refinement of the most accurate design for specific applications. Of course, the properties of every imaginable IL cannot be obtained by carrying out the appropriate measurements, since this would represent a substantial investment. Because of this, knowledge about the origins of the fundamental properties of ILs is necessary, resulting in a better understanding of structure−property relationships. Reliable and accurate data are the key for the development of certain and economical process design for industrial applications of ILs.

Density is one of the most important properties for a fluid, as it is fundamental to develop equations of state and is required for the design of different equipments. Also, viscosity is a very important transport property, required for the design of processing units and pumping systems, and to study heat and mass transfer processes.[13] On the other hand, the refractive index can be used as a measure of the electronic polarizability of a molecule and can provide useful information when studying the forces between molecules or their behavior in solution.[14] Finally, the speed of sound together with other properties allow the calculation of derived thermophysical properties such as isentropic compressibility.[15,16]

In this work, as a continuation of our ongoing work on ILs,[17−24] a systematic and extensive study on the physical properties of the ILs 1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)-imide, [EMpy][NTf_2], 1-propyl-3-methylpyridinium bis-(trifluoromethylsulfonyl)imide, [PMpy][NTf_2], 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, [BMpy][NTf_2], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMim][NTf_2], 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [HMim][NTf_2], 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [BMpyr][NTf_2], 1-butyl-1-methylpyrrolidinium trifluoromethanelsulfonate, [BMpyr][TFO], 1-butyl-3-methylimidazolium trifluoromethanelsulfonate, [BMim][TFO], 1-hexyl-3-methylimidazolium trifluoromethanelsulfonate, [HMim][TFO], 1-butyl-3-methylimidazolium dicyanamide, [BMim][$N(CN)_2$], and 1-hexyl-3-methylimidazolium dicyanamide, [HMim][$N(CN)_2$], was carried out at different temperatures. Temperature dependence of the viscosity data has been fitted to an Arrhenius-like law and Vogel−Fulcher−Tamman (VFT), modified Vogel−Fulcher−Tamman (mVFT), Litovitz, and fluidity equations, while density, refractive index and speed of sound were fitted to a linear equation.

Received: December 13, 2011
Accepted: January 10, 2012
Published: January 10, 2012

dx.doi.org/10.1021/ie2029255 | *Ind. Eng. Chem. Res.* 2012, 51, 2492−2504

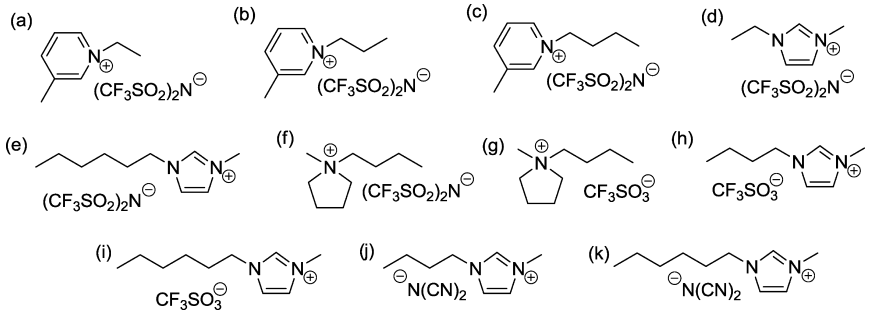

Figure 1. Structures of the ionic liquids studied in this work: (a) [EMpy][NTf_2]; (b) [PMpy][NTf_2]; (c) [BMpy][NTf_2]; (d) [EMim][NTf_2]; (e) [HMim][NTf_2]; (f) [BMpyr][NTf_2]; (g) [BMpyr][TFO]; (h) [BMim][TFO]; (i) [HMim][TFO]; (j) [BMim][$N(CN)_2$]; and (k) [HMim][$N(CN)_2$].

The purpose of choosing different ILs is to study the influence of their structure on the thermophysical properties. Accordingly, with the aim of characterizing the pure components, precise measurements of experimental densities, speeds of sound, refractive indices, and dynamic viscosities of 11 commercial ILs at several temperatures are reported. A comparison between experimental and literature data was also performed when literature was available. To the best of our knowledge, scarce literature data are available for [HMim][$N(CN)_2$] and for the ionic liquids [EMpy][NTf_2], [BMpyr][TFO], [HMim][TFO], and literature was not found.

2. EXPERIMENTAL SECTION

2.1. Chemicals. All the studied ILs were supplied by IoLiTec with mass fraction purity higher than 0.99 for [EMpy][NTf_2], [PMpy][NTf_2], [BMpy][NTf_2], [EMim][NTf_2], [HMim][NTf_2], [BMpyr][NTf_2], [BMpyr][TFO], [BMim][TFO], [HMim][TFO], 0.98 for [BMim][$N(CN)_2$], and 0.97 for [HMim][$N(CN)_2$]. The ionic structures of the studied ILs are presented in Figure 1.

To reduce the water content and volatile compounds to negligible values, since they have influence over the physical properties of the ILs,[25] all of them were dried with stirring at moderate temperature (T = 343 K) and under vacuum (p = 0.2 Pa) for at least 48 h prior to their use. After the drying the ILs were kept in bottles under an inert gas. Table 1 lists the water and halide content supplied by IoLiTec, although the water content values after the drying step were slightly lower but in the same order.

The physical properties of the pure ILs at T = 298.15 K and atmospheric pressure are listed in Table 2 together with recent literature values.[14,26−36] Notice that for [HMim][TFO] these properties are shown at T = 303.15 K since its melting point is around T = 295 K. The possible differences between our values and those reported in literature can be due to the presence of impurities (water and halides) in the pure ILs and/or to the experimental technique employed.

2.2. Apparatus and Procedure. *2.2.1. Density and Speed of Sound.* Density and speed of sound were measured using an Anton Paar DSA-5000 M digital vibrating-tube densimeter with an uncertainty of $\pm 3 \times 10^{-5}$ g·cm^{-3} and ±1 m·s^{-1}, respectively. The apparatus was calibrated by measuring Millipore quality water and air, according to the manual instructions. The calibration was checked with known density and speed of sound of pure liquids. It is important to mention that this equipment automatically corrects the effect of viscosity on density, and also detects the presence of bubbles in the cell.

Table 1. Molar Mass, M, Water Content, w_w, and Halide Content, w_{halide}, of the Studied ILs

		M_{IL} (g·mol^{-1})	w_w (ppm)	w_{halide} (ppm)
1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide	[EMpy][NTf_2]	402.33	80	<100
1-propyl-3-methylpiridinium bis(trifluoromethylsulfonyl)imide	[PMpy][NTf_2]	416.36	90	<100
1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide	[BMpy][NTf_2]	430.39	90	10
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[EMim][NTf_2]	391.31	80	<100
1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[HMim][NTf_2]	447.42	70	<100
1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	[BMpyr][NTf_2]	422.41	60	20
1-butyl-1-methylpyrrolidinium trifluoromethanelsulfonate	[BMpyr][TFO]	291.33	270	<100
1-butyl-3-methylimidazolium trifluoromethanelsulfonate	[BMim][TFO]	288.29	170	50
1-hexyl-3-methylimidazolium trifluoromethanesulfonate	[HMim][TFO]	316.34	520	60
1-butyl-3-methylimidazolium dicyanamide	[BMim][$N(CN)_2$]	205.26	1240	<700
1-hexyl-3-methylimidazolium dicyanamide	[HMim][$N(CN)_2$]	233.31	<1350	n.a.

2.2.2. Refractive Indices. The refractive indices were determined using an automatic refractometer ABBEMAT-WR Dr. Kernchen with an uncertainty in the experimental measurements of $\pm 4 \times 10^{-5}$. The apparatus was calibrated by measuring the refractive index of Millipore quality water and tetrachloroethylene (provided by the supplier) before each series of measurements according to manual instructions. The calibration was checked with the known refractive index of pure liquids.

2.2.3. Dynamic Viscosities. Kinematic viscosities were determined using an automatic viscosimeter Lauda PVS1 with two Ubbelhode microcapillaries of (1.13×10^{-3} and 2.01×10^{-3}) m diameter with an uncertainty in the experimental measurement of ±0.03 and ±0.2 mPa·s, respectively. Gravity fall is the principle of measurement on which this viscosimeter is based. The microcapillaries were maintained in a D20KP LAUDA thermostat with an uncertainty of ±0.01K. The equipment is joined to a control unit PVS1 (Processor Viscosity System) that is a PC-controlled instrument for the precise measurement of the fall time, using standardized glass capillaries. The microcapillaries were calibrated and credited by the company.

The kinematic viscosity was determined from the following relationship:

$$\nu = k(t - y) \quad (1)$$

dx.doi.org/10.1021/ie2029255 | Ind. Eng. Chem. Res. 2012, 51, 2492−2504

Table 2. Experimental and Literature Values of Density, ρ, Speed of Sound, u, Refractive Indiex, n_D, and Dynamic Viscosity, η, of the Studied ILs at T = 298.15 K and Atmospheric Pressure[a]

	ρ (g·cm^{-3})		η (mPa·s)		n_D		u (m·s^{-1})	
	expt	lit.	expt	lit.	expt	lit.	expt	lit.
[EMpy][NTf$_2$]	1.48850	n.a.	38.98	n.a.	1.44376	n.a.	1260	n.a.
[PMpy][NTf$_2$]	1.44794	1.4475[b]	53.8	54.9[b]	1.44485	n.a.	1250	n.a.
[BMpy][NTf$_2$]	1.41476	1.4128[b]	65.3	64.3[b]	1.44595	n.a.	1248	n.a.
[EMim][NTf$_2$]	1.51874	1.51845[c]	32.49	32[d]	1.42307	1.42251[e]	1240	1240 [f]
[HMim][NTf$_2$]	1.37200	1.3721[g]	69.3	70.29[g]	1.43016	1.42954[e]	1227	1226.8[g]
[BMpyr][NTf$_2$]	1.39466	1.39459[h]	75.9	76.9[I]	1.42302	1.42304[h]	1269	1269[h]
[BMpyr][TFO]	1.25271	n.a.	164.3	n.a.	1.43287	n.a.	1461	n.a.
[BMim][TFO]	1.29963	1.2995[e]	89.7	83.644[j]	1.43756	1.43657[e]	1391	1392.1[k]
[HMim][TFO]	1.23255[n]	n.a.	115.5[n]	n.a.	1.43926[n]	n.a.	1358[n]	n.a.
[BMim][N(CN)$_2$]	1.06046	1.0591[l]	30.04	29.3[m]	1.50890	n.a.	1737	n.a.
[HMim][N(CN)$_2$]	1.02847	n.a.	47.9	47.4[m]	1.50419	n.a.	1687	n.a.

[a]n.a. = values not available. [b]Reference 26. [c]Reference 27. [d]Reference 28. [e]Reference 14. [f]Reference 29. [g]Reference 30. [h]Reference 31. [I]Reference 32. [j]Reference 33. [k]Reference 34. [l]Reference 35. [m]Reference 36. [n]Properties measured at T = 303.15 K.

where ν is the kinetic viscosity, k is the Ubbelhode capillary microviscometer constant, t is the flow time, and y is the Hagenbach correction, y and k being provided by the company.

The dynamic viscosity was determined from

$$\eta = \nu\rho \tag{2}$$

where η is the dynamic viscosity, and ρ the density.

3. RESULTS AND DISCUSSION

Experimental data of density, ρ, refractive index, n_D, and speed of sound, u, and viscosity, η, were obtained at atmospheric pressure from T = (293.15 to 343.15) K for [EMpy][NTf$_2$], [PMpy][NTf$_2$], [BMpy][NTf$_2$], [EMim][NTf$_2$], [HMim][NTf$_2$], [BMpyr][NTf$_2$], [BMpyr][TFO], [BMim][TFO], [BMim][N(CN)$_2$], and [HMim][N(CN)$_2$], while for [HMim][TFO] these properties were measured from T = (303.15 to 343.15) K, since its melting point is around T = 295 K; and the obtained values for all the properties of the studied ILs are summarized in Table 3.

A linear equation was used to express the dependence with temperature for density, refractive index, and speed of sound for all the investigated ILs,

$$z = a + bT \tag{3}$$

where z is ρ, n_D, or u, T is the absolute temperature in K, and a and b are the adjustable parameters, given in Table 4. Standard relative deviation, σ, of the experimental density, refractive index, and speed of sound data from their fitting was calculated following eq 4,

$$\sigma = \{\sum_{i}^{n_{dat}} ((z - z_{cal})/z_{cal})^2/n_{dat}\}^{1/2} \tag{4}$$

where z and z_{cal} are the values of experimental and calculated property, respectively, and n_{dat} is the number of experimental points. The σ values are also shown in Table 4. As it can be inferred from the low deviations obtained, linear equations properly fit the experimental data.

The change of the molar volume with temperature can be expressed through the coefficient of thermal expansion, α, also called coefficient of cubical expansion. From density experimental data, ρ, at the temperature range studied, it can be calculated using the following equation:

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_p = -\left(\frac{\partial \ln \rho}{\partial T}\right) \tag{5}$$

Since the variation of ln ρ versus T is linear, α was considered a temperature-independent constant.[37,38] It is observed that, as expected, for all the studied ionic liquids α falls in the range between 5.82 × 10^{-4} and 6.75 × 10^{-4} K^{-1}, being 5.82 × 10^{-4} K^{-1} for [BMpyr][TFO], 5.96 × 10^{-4} K^{-1} for [BMim][N(CN)$_2$], 5.98 × 10^{-4} K^{-1} for [HMim][N(CN)$_2$], 6.14 × 10^{-4} K^{-1} for [BMim][TFO], 6.21 × 10^{-4} K^{-1} for [HMim][TFO], 6.36 × 10^{-4} K^{-1} for [BMpyr][NTf$_2$], 6.51 × 10^{-4} K^{-1} for [EMpy][NTf$_2$], 6.53 × 10^{-4} K^{-1} for [BMpy][NTf$_2$], 6.55 × 10^{-4} K^{-1} for [PMpy][NTf$_2$], 6.66 × 10^{-4} K^{-1} for [EMim][NTf$_2$] and 6.75 × 10^{-4} K^{-1} for [HMim][NTf$_2$]. They are in similar order of magnitude than ILs previously investigated, suggesting a thermal behavior practically independent of the ionic nature and temperature.[31] Nevertheless, these values are considerably lower than those of molecular organic solvents, and higher than those of classical molten salts.

When α values of ILs with the same anion and different alkyl chain length are compared (i.e., [EMim][NTf$_2$]/[HMim][NTf$_2$]), it is possible to observe that ILs containing a smaller alkyl chain present a lower expansion coefficient compared to those having a longer alkyl chain. This suggests that the large cation size of the ILs reduces the electrostatic interactions and thus, facilitates expansion. The α values for the ILs having the same cation with different anions vary in the order: [NTf$_2$]$^-$ > [TFO]$^-$ > [N(CN)$_2$]$^-$. Finally, comparing two ILs with a common anion and different cation, the values of α changes in the order imidazolium > pyridinium > pyrrolidinium for the studied ILs with [NTf$_2$]$^-$ anion, and imidazolium > pyrrolidinium for the studied ILs with [TFO]$^-$ anion. These trends reveal that the size and structure of the ions have an important effect in the interactions of the anion with the cation and in the degree of expansion of the ILs.

The viscosity values, η, were fitted using Arrhenius-like law,[39] Vogel–Fulcher–Tamman (VFT),[40–42] modified Vogel–Fulcher–Tamman (mVFT), Litovitz,[43] and fluidity[44] equations.

Arrenhius-like law is the most commonly used equation to fit the variation of viscosity with temperature:

$$\eta = A\ \exp\left(\frac{-B}{RT}\right) \tag{6}$$

dx.doi.org/10.1021/ie2029255 | Ind. Eng. Chem. Res. 2012, 51, 2492–2504

Table 3. Density, ρ, Refractive Index, n_D, Speed of Sound, u, and Dynamic Viscosity, η, of the Studied ILs at Several Temperatures

T (K)	ρ (g·cm^{-3})	η (mPa·s)	n_D	u (m·s^{-1})
		[EMpy][NTf$_2$]		
293.15	1.49332	48.0	1.44529	1271
298.15	1.48850	38.98	1.44376	1260
303.15	1.48365	32.18	1.44224	1249
308.15	1.47883	26.94	1.44069	1238
313.15	1.47401	22.84	1.43917	1227
318.15	1.46922	19.57	1.43759	1216
323.15	1.46444	16.93	1.43607	1206
328.15	1.45968	14.56	1.43451	1195
333.15	1.45493	12.83	1.43304	1185
338.15	1.45021	11.38	1.43156	1175
343.15	1.44549	10.14	1.43007	1164
		[PMpy][NTf$_2$]		
293.15	1.45270	68.4	1.44639	1261
298.15	1.44794	53.8	1.44485	1250
303.15	1.44320	43.15	1.44324	1239
308.15	1.43847	35.22	1.44169	1228
313.15	1.43376	28.71	1.44015	1217
318.15	1.42907	24.04	1.43862	1206
323.15	1.42439	20.44	1.43709	1195
328.15	1.41974	17.55	1.43555	1185
333.15	1.41510	15.19	1.43403	1175
338.15	1.41047	13.00	1.43259	1164
343.15	1.40586	11.47	1.43110	1154
		[BMpy][NTf$_2$]		
293.15	1.41939	84.2	1.44748	1260
298.15	1.41476	65.3	1.44594	1248
303.15	1.41015	51.2	1.44443	1237
308.15	1.40556	41.41	1.44289	1226
313.15	1.40098	34.01	1.44137	1215
318.15	1.39642	28.31	1.43981	1204
323.15	1.39187	23.87	1.43827	1193
328.15	1.38733	20.33	1.43675	1183
333.15	1.38282	17.49	1.43520	1173
338.15	1.37831	15.19	1.43368	1162
343.15	1.37381	13.31	1.43219	1152
		[EMim][NTf$_2$]		
293.15	1.52380	39.28	1.42451	1251
298.15	1.51874	32.49	1.42307	1240
303.15	1.51368	26.88	1.42157	1229
308.15	1.50866	22.84	1.42012	1218
313.15	1.50364	19.63	1.41865	1208
318.15	1.49864	17.04	1.41721	1197
323.15	1.49366	14.92	1.41574	1187
328.15	1.48870	13.15	1.41430	1176
333.15	1.48377	11.67	1.41286	1166
338.15	1.47882	10.43	1.41143	1156
343.15	1.47391	9.37	1.40998	1146
		[HMim][NTf$_2$]		
293.15	1.37660	88.7	1.43169	1239
298.15	1.37200	69.3	1.43016	1227
303.15	1.36739	55.2	1.42868	1216
308.15	1.36279	44.60	1.42707	1204
313.15	1.35822	36.61	1.42552	1193
318.15	1.35366	30.44	1.42398	1182
323.15	1.34911	25.62	1.42249	1171
328.15	1.34459	21.62	1.42098	1161
333.15	1.34007	18.62	1.41946	1150
338.15	1.33540	16.10	1.41797	1139
343.15	1.33090	14.04	1.41648	1129

T (K)	ρ (g·cm^{-3})	η (mPa·s)	n_D	u (m·s^{-1})
		[BMpyr][NTf$_2$]		
293.15	1.39911	97.1	1.42442	1281
298.15	1.39466	75.9	1.42302	1269
303.15	1.39022	60.6	1.42160	1258
308.15	1.38580	49.2	1.42014	1247
313.15	1.38140	40.16	1.41871	1236
318.15	1.37701	33.47	1.41730	1225
323.15	1.37265	28.26	1.41588	1214
328.15	1.36829	24.11	1.41440	1204
333.15	1.36395	20.75	1.41310	1193
338.15	1.35962	17.77	1.41169	1183
343.15	1.35531	15.59	1.41030	1173
		[BMpyr][TFO]		
293.15	1.25636	217.2	1.43410	1473
298.15	1.25271	164.3	1.43287	1461
303.15	1.24905	126.5	1.4315	1449
308.15	1.24540	99.2	1.43017	1437
313.15	1.24177	78.3	1.42884	1426
318.15	1.23816	63.2	1.42743	1414
323.15	1.23456	51.9	1.42604	1403
328.15	1.23098	43.39	1.42468	1392
333.15	1.22741	35.73	1.42333	1381
338.15	1.22385	30.39	1.42201	1371
343.15	1.22030	26.10	1.42067	1359
		[BMim][TFO]		
293.15	1.30362	115.1	1.43896	1403
298.15	1.29963	89.7	1.43756	1391
303.15	1.29564	70.1	1.43620	1380
308.15	1.29166	56.4	1.43477	1369
313.15	1.28769	46.0	1.43339	1358
318.15	1.28375	38.09	1.43204	1347
323.15	1.27982	31.89	1.43055	1336
328.15	1.27589	26.96	1.42915	1326
333.15	1.27199	23.04	1.42777	1315
338.15	1.26809	19.85	1.42633	1305
343.15	1.26421	17.26	1.42489	1294
		[HMim][TFO]		
303.15	1.23255	115.5	1.43926	1358
308.15	1.22877	90.3	1.43779	1347
313.15	1.22499	70.8	1.43633	1335
318.15	1.22121	57.1	1.43485	1324
323.15	1.21742	46.7	1.43342	1313
328.15	1.21363	38.63	1.43200	1302
333.15	1.20990	32.35	1.43049	1291
338.15	1.20609	27.34	1.42905	1280
343.15	1.20234	23.33	1.42761	1270
		[BMim][N(CN)$_2$]		
293.15	1.06365	36.79	1.51045	1750
298.15	1.06046	30.05	1.50889	1737
303.15	1.05728	24.94	1.50732	1724
308.15	1.05411	20.87	1.50569	1712
313.15	1.05097	17.77	1.50411	1700
318.15	1.04783	15.28	1.50232	1688
323.15	1.04472	13.30	1.50073	1676
328.15	1.04162	11.58	1.49915	1664
333.15	1.03853	10.23	1.49756	1652
338.15	1.03546	9.09	1.49602	1640
343.15	1.03240	8.13	1.49449	1629

dx.doi.org/10.1021/ie2029255 | Ind. Eng. Chem. Res. 2012, 51, 2492−2504

Table 3. continued

T (K)	ρ (g·cm^{-3})	η (mPa·s)	n_D	u (m·s^{-1})	T (K)	ρ (g·cm^{-3})	η (mPa·s)	n_D	u (m·s^{-1})
		[HMim][N(CN)$_2$]					[HMim][N(CN)$_2$]		
293.15	1.03157	60.5	1.50573	1700	323.15	1.01317	18.72	1.49599	1625
298.15	1.02847	47.9	1.50419	1687	328.15	1.01015	16.11	1.49431	1613
303.15	1.02539	38.59	1.50260	1675	333.15	1.00714	13.99	1.49273	1602
308.15	1.02231	31.58	1.50102	1662	338.15	1.00415	12.27	1.49113	1590
313.15	1.01925	26.10	1.49943	1650	343.15	1.00116	10.84	1.48962	1578
318.15	1.01620	21.98	1.49772	1637					

Table 4. Fitting Parameters of eq 3 together with the Correlation Coefficient Squared (R^2) and the Standard Relative Deviations of the Fit (σ) for the Density, Refractive Index, and Speed of Sound of the Studied ILs

		a	b	R^2	σ
[EMpy][NTf$_2$]	ρ (g·cm^{-3})	1.773	-9.57×10^{-4}	0.9999	4.60×10^{-3}
	n_D	1.534	-3.05×10^{-4}	0.9999	1.070×10^{-2}
	u (m·s^{-1})	1895	−2.131	0.9997	4.690×10^{-2}
[PMpy][NTf$_2$]	ρ (g·cm^{-3})	1.727	-9.38×10^{-4}	0.9999	5.16×10^{-3}
	n_D	1.540	3.20×10^{-4}	0.9998	3.84×10^{-3}
	u (m·s^{-1})	1888	−2.143	0.9997	4.670×10^{-2}
[BMpy][NTf$_2$]	ρ (g·cm^{-3})	1.691	-9.27×10^{-4}	0.9999	4×10^{-5}
	n_D	1.541	-3.19×10^{-4}	0.9999	1×10^{-5}
	u (m·s^{-1})	1889	−2.152	0.9996	6.1×10^{-4}
[EMim][NTf$_2$]	ρ (g·cm^{-3})	1.816	-9.98×10^{-4}	0.9999	8.60×10^{-3}
	n_D	1.510	-2.91×10^{-4}	0.9999	4.09×10^{-3}
	u (m·s^{-1})	1865	−2.100	0.9996	4.400×10^{-2}
[HMim][NTf$_2$]	ρ (g·cm^{-3})	1.644	-9.13×10^{-4}	0.9999	8.70×10^{-3}
	n_D	1.521	-3.05×10^{-4}	0.9999	2.70×10^{-3}
	u (m·s^{-1})	1882	−2.196	0.9996	6.010×10^{-2}
[BMpyr][NTf$_2$]	ρ (g·cm^{-3})	1.655	-8.76×10^{-4}	0.9999	4.92×10^{-3}
	n_D	1.507	-2.80×10^{-4}	0.9999	2.07×10^{-3}
	u (m·s^{-1})	1912	−2.158	0.9996	5.700×10^{-2}
[BMpyr][TFO]	ρ (g·cm^{-3})	1.463	7.07×10^{-4}	0.9999	5×10^{-5}
	n_D	1.507	-2.49×10^{-4}	0.9999	3×10^{-5}
	u (m·s^{-1})	2136	−2.267	0.9995	5.4×10^{-4}
[BMim][TFO]	ρ (g·cm^{-3})	1.535	-7.88×10^{-4}	0.9999	7.20×10^{-3}
	n_D	1.521	-2.81×10^{-4}	0.9999	3.60×10^{-3}
	u (m·s^{-1})	2037	−2.167	0.9997	4.220×10^{-2}
[HMim][TFO]	ρ (g·cm^{-3})	1.4616	-7.56×10^{-4}	0.9999	6.40×10^{-3}
	n_D	1.5275	-2.91×10^{-4}	0.9999	4.60×10^{-3}
	u (m·s^{-1})	2027	−2.210	0.9998	3.140×10^{-2}
[BMim][N(CN)$_2$]	ρ (g·cm^{-3})	1.253	-6.44×10^{-4}	0.9999	6.38×10^{-3}
	n_D	1.605	3.23×10^{-4}	0.9998	4.52×10^{-3}
	u (m·s^{-1})	2457	−2.416	0.9998	3.460×10^{-2}
[HMim][N(CN)$_2$]	ρ (g·cm^{-3})	1.209	-6.00×10^{-4}	0.9999	6×10^{-5}
	n_D	1.601	-3.3×10^{-4}	0.9998	8.6×10^{-4}
	u (m·s^{-1})	2413	−2.436	0.9997	4.2×10^{-4}

where the adjustable parameters are A (mPa·s), the viscosity at infinite temperature, B (kJ·mol^{-1}), the activation energy and R = 8.31 J·mol^{-1}·K^{-1}.

According to Seddon et al.,[45] the Arrhenius-like law can generally be applied when the cation presents only a limited symmetry. If this is not the case, and especially in the presence of symmetrical cations with low molar mass, VFT and mVFT equations are recommended.[46,47]

The temperature dependence of the dynamic viscosity values presents convex curved profiles; thus, experimental data were fitted to VFT equation:

$$\eta = A \exp\left(\frac{B}{T - T_0}\right) \tag{7}$$

where A (mPa·s), B (K), and T_0 (K) are adjustable parameters.

Likewise, dynamic viscosity values were fitted to mVFT equation. This equation has been used by other authors with satisfactory outcomes,[17,47] and it can be expressed as

$$\eta = AT^{0.5} \exp\left(\frac{B}{T - T_0}\right) \tag{8}$$

where A (mPa·s), B (K), and T_0 (K) are adjustable parameters.

Litovitz equation[43] can also be used to fit dynamic viscosity values,

$$\eta = A \exp\left(\frac{B}{RT^3}\right) \tag{9}$$

where the adjustable parameters are A (mPa·s), B (kJ·mol^{-1}), and R = 8.31 J·mol^{-1}·K^{-1}.

Latterly it was shown that the temperature dependence of the viscosity can be described by the following simple linear equation. This equation is based in the fact that fluidity ($1/\eta$) is a smooth function of temperature:

$$\left(\frac{1}{\eta}\right)^{\varphi} = A + BT \tag{10}$$

where A (mPa^{-1}·s^{-1}) and B (mPa^{-1}·s^{-1}·K^{-1}) are the adjustable parameters and φ is a characteristic exponent, which usually takes for ILs the value φ = 0.3.[48]

Table 5 lists the parameters for all the proposed fitting equations for viscosity with the correlation coefficient squared (R^2) and the standard relative deviation (σ). In general, the VFT equation provides the best fit for viscosity data, followed by mVFT and Litovitz. The Arrhenius-like law always presents the largest standard relative deviations and consequently the worst fit.

3.1. Effect of Temperature. The temperature dependence of density, refractive index, and speed of sound for the ILs is shown in Figures 2, 3, and 4, respectively. From these figures, it is possible to observe that these properties show a linear decrease with increasing temperature. Regarding to the viscosity, this property presents an exponential decrease as temperature increases, showing that this property is more affected by temperature than the other studied properties, as can be seen in Figure 5.

3.2. Effect of the Alkyl Chain Length of the Cation. The effect of the alkyl chain length was studied comparing the pyridinium-based ILs [EMpy][NTf$_2$]/[PMpy][NTf$_2$]/[BMpy][NTf$_2$], and the imidazolium-based pairs [BMim][N(CN)$_2$]/[HMim][N(CN)$_2$], [EMim][NTf$_2$]/[HMim][NTf$_2$] and [BMim][TFO]/[HMim][TFO]. From the experimental densities

dx.doi.org/10.1021/ie2029255 | Ind. Eng. Chem. Res. 2012, 51, 2492−2504

Table 5. Fitting Parameters of eqs 6−10 together with the Correlation Coefficient Squared (R^2) and the Standard Relative Deviations of the Fit (σ) for the Viscosity of the Studied ILs

		A	B	T_0	R^2	σ
[EMpy][NTf_2]	Arrhenius	1.10×10^{-3}	−25.919			2.2079
	VFT	0.1569	766.60	159.1902		0.3148
	mVFT	0.0050	906.49	149.7230		0.3225
	Litovitz	0.7735	8.64×10^{5}			0.3181
	Fluidity	−0.7770	0.0037		0.9994	2.1638
[PMpy][NTf_2]	Arrhenius	3.3×10^{-4}	−29.703			2.8088
	VFT	0.1056	849.45	161.84		0.5354
	mVFT	0.0064	787.77	170.63		0.5877
	Litovitz	0.5984	9.91×10^{8}			0.6116
	Fluidity	−0.8869	0.0040		0.9995	0.3972
[BMpy][NTf_2]	Arrhenius	2.7×10^{-4}	−30.664			3.4405
	VFT	0.2250	656.42	182.33		0.2210
	mVFT	0.0107	672.08	183.51		0.3670
	Litovitz	0.6282	1.02×10^{9}			0.9784
	Fluidity	−0.8783	0.0039		0.9993	0.8379
[EMim][NTf_2]	Arrhenius	2.14×10^{-3}	−23.812			2.3613
	VFT	0.2896	597.71	171.3971		0.2937
	mVFT	0.0106	688.49	164.9938		0.3021
	Litovitz	0.8813	7.93×10^{5}			0.4938
	Fluidity	−0.7078	0.0036		0.9987	2.9585
[HMim][NTf_2]	Arrhenius	2.8×10^{-4}	−30.719			2.7596
	VFT	0.1186	857.047	163.6287		0.1503
	mVFT	0.0050	907.60	162.4533		0.2062
	Litovitz	0.6654	1.02×10^{6}			0.2575
	Fluidity	−0.8673	0.0039		0.9998	4.2758
[BMpy][NTf_2]	Arrhenius	2.7×10^{-4}	−30.664			3.4405
	VFT	0.2250	656.42	182.33		0.2210
	mVFT	0.0107	672.08	183.51		0.3670
	Litovitz	0.6282	1.02×10^{9}			0.9784
	Fluidity	−0.8783	0.0039		0.9993	0.8379
[BMpyr][TFO]	Arrhenius	1×10^{-4}	−35.422			3.1092
	VFT	0.0997	1006.57	162.24		0.4517
	mVFT	0.0051	996.44	165.73		0.5612
	Litovitz	0.7728	1.18×10^{9}			0.4674
	Fluidity	−0.8436	0.0036		0.9999	0.4752
[BMim][TFO]	Arrhenius	2.5×10^{-4}	−31.6573			3.0596
	VFT	0.1610	810.11	169.9044		0.2535
	mVFT	0.0058	907.48	164.5475		0.2559
	Litovitz	0.7469	1.05×10^{6}			0.4993
	Fluidity	−0.8420	0.0037		0.9998	0.3487
[HMim][TFO]	Arrhenius	1.3×10^{-4}	−34.494			2.19695
	VFT	0.1487	841.93	176.6830		0.2593
	mVFT	0.0059	908.28	173.9289		0.2687
	Litovitz	0.6689	1.19×10^{5}			0.4584
	Fluidity	−0.8826	0.0037		0.9999	0.7227
[BMim][$N(CN)_2$]	Arrhenius	1.17×10^{-3}	−25.127			2.3122
	VFT	0.1769	676.96	166.31		0.1346
	mVFT	0.0088	675.92	170.15		0.3281
	Litovitz	0.6692	8.38×10^{8}			0.2871
	Fluidity	−0.7965	0.0038		0.9991	0.5293
[HMim][$N(CN)_2$]	Arrhenius	4.4×10^{-4}	−28.679			3.0163
	VFT	0.1765	697.53	173.62		0.1812
	mVFT	0.0087	699.66	176.61		0.2233
	Litovitz	0.6231	9.56×10^{8}			0.6675
	Fluidity	−0.8639	0.0040		0.9991	0.5079

and speeds of sound obtained for these ILs, it was observed that as the alkyl chain length increases in imidazolium- and pyridinium-based ILs, the value of both properties decreases, which is in agreement with experimental data obtained by other authors.[14,26,36,49−54] Oliveira et al.[26] found that ILs proved to be essentially directly dependent on the alkyl chain length of the

dx.doi.org/10.1021/ie2029255 | Ind. Eng. Chem. Res. 2012, 51, 2492−2504

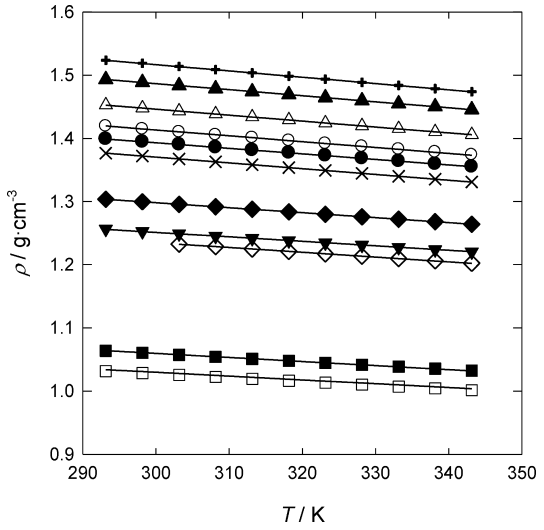

Figure 2. Density, ρ, and fitted curves from eq 3 (—) of the studied ionic liquids as a function of temperature: ▲, [EMpy][NTf_2]; △, [PMpy][NTf_2]; ○, [BMpy][NTf_2]; +, [EMim][NTf_2]; ×, [HMim][NTf_2]; ●, [BMpyr][NTf_2]; ▼, [BMpyr][TFO]; ♦, [BMim][TFO]; ◊, [HMim][TFO]; ■, [BMim][$N(CN)_2$]; □, [HMim][$N(CN)_2$].

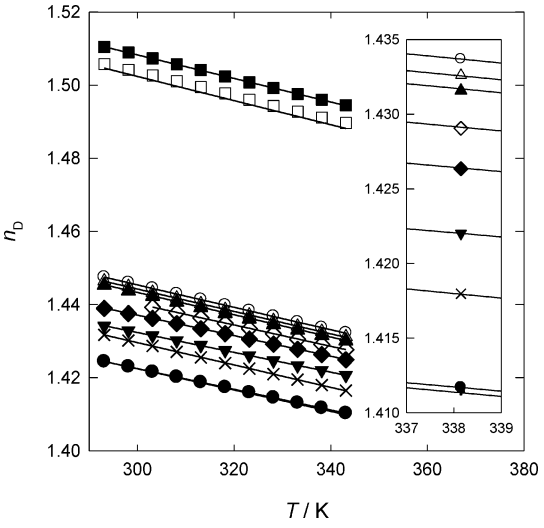

Figure 3. Refractive index, n_D, and fitted curves from eq 3 (—) of the studied ionic liquids as a function of temperature: ▲, [EMpy][NTf_2]; △, [PMpy][NTf_2]; ○, [BMpy][NTf_2]; +, [EMim][NTf_2]; ×, [HMim][NTf_2]; ●, [BMpyr][NTf_2]; ▼, [BMpyr][TFO]; ♦, [BMim][TFO]; ◊, [HMim][TFO]; ■, [BMim][$N(CN)_2$]; □, [HMim][$N(CN)_2$].

cation, in their study with pyridinium-based ILs with $[NTf_2]^-$ anion. Gardas et al.[50] studied structure–property relationships for pyrrolidinium-based ILs with $[NTf_2]^-$ anion detecting the same tendency, similar to that observed for imidazolium-based ILs in their previous works.[51] Moreover, Kolbeck et al.[52] explained, in their work with imidazolium-based ILs with $[NTf_2]^-$ anion, the decrease of the density as a result of the nonpolar regions size; these regions take more space as the alkyl chain elongates, resulting in a lower overall density.

Regarding to the refractive indices, an increase in the alkyl chain length of pyridinium-based ILs with $[NTf_2]^-$ anion leads to an increase of the refractive index, as can be seen in Figure 3. A similar behavior was observed for imidazolium-based ILs with $[NTf_2]^-$ and $[TFO]^-$ anions, which was also found by

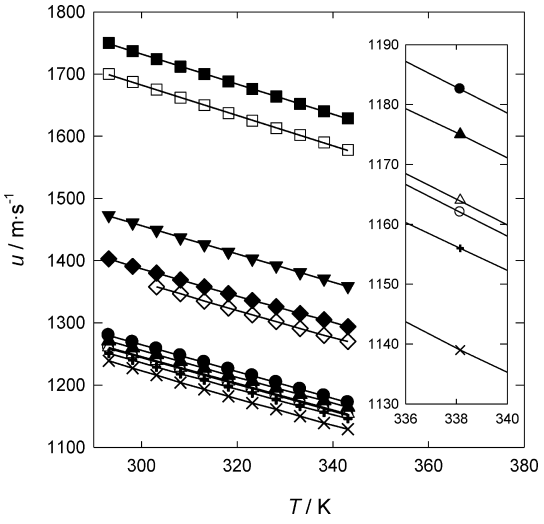

Figure 4. Speed of sound, u, and fitted curves from eq 3 (—) of the studied ionic liquids as a function of temperature: ▲, [EMpy][NTf_2]; △, [PMpy][NTf_2]; ○, [BMpy][NTf_2]; +, [EMim][NTf_2]; ×, [HMim][NTf_2]; ●, [BMpyr][NTf_2]; ▼, [BMpyr][TFO]; ♦, [BMim][TFO]; ◊, [HMim][TFO]; ■, [BMim][$N(CN)_2$]; □, [HMim][$N(CN)_2$].

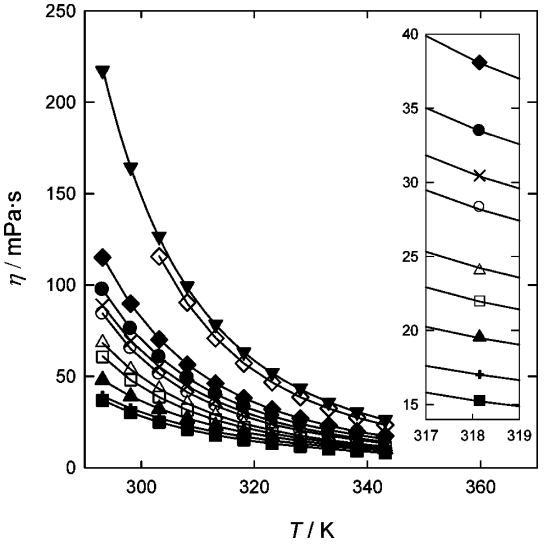

Figure 5. Viscosity, η, and fitted curves from eq 7 (—) of the studied ionic liquids as a function of temperature: ▲, [EMpy][NTf_2]; △, [PMpy][NTf_2]; ○, [BMpy][NTf_2]; +, [EMim][NTf_2]; ×, [HMim][NTf_2]; ●, [BMpyr][NTf_2]; ▼, [BMpyr][TFO]; ♦, [BMim][TFO]; ◊, [HMim][TFO]; ■, [BMim][$N(CN)_2$]; □, [HMim][$N(CN)_2$].

Tariq et al.[14] On the contrary, it is worth highlighting that an increase in the alkyl chain length of imidazolium-based ILs with $[N(CN)_2]^-$ anion leads to a decrease of the refractive index.

In contrast to density and speed of sound, viscosity increases in pyridinium-based ILs with $[NTf_2]^-$ anion and imidazolium-based ILs with $[NTf_2]^-$, $[TFO]^-$, and $[N(CN)_2]^-$ anions, as the alkyl chain in the cation elongates, in accordance with experimental data obtained by several authors.[26,36,55−58] Tokuda et al.[55] found that the increase of the viscosity due to the increase of the van der Waals interactions is due to an ionic dissociation or "ionicity". The justification put forward by Bonhôte et al.[56] is based on the van der Waals interactions; an increase in the alkyl chain length leads to bigger van der Waals interactions and

dx.doi.org/10.1021/ie2029255 | Ind. Eng. Chem. Res. 2012, 51, 2492−2504

thus, to higher viscosities. This behavior is also explained by Jacquemim et al.[57] as the formation of microstructures that are responsible of the increase in viscosity.

3.3. Effect of the Anion. The effect of the anion on the physical properties was studied comparing the pyrrolidinium-based ILs [BMpyr][NTf_2]/[BMpyr][TFO] and the imidazolium-based ILs [BMim][TFO]/[BMim][$N(CN)_2$] and [HMim][NTf_2]/[HMim][TFO]/[HMim][$N(CN)_2$]. From the experimental data it was possible to conclude that the anions have a strong influence on the density, as shown in Figure 2, since the value of this property decreases with the molecular weight of the anion in the order $[NTf_2]^-$ > $[TFO]^-$ > $[N(CN)_2]^-$. This behavior was also observed by Tariq et al.,[14] who reported density data for ILs with $[BMim]^+$ cation and $[TFO]^-$ and $[NTf_2]^-$ as anions, Fröba *el at.*[27] in their study on ILs including $[EMim]^+$ cation and $[NTf_2]^-$ and $[N(CN)_2]^-$ anions, and Bandrés et al.,[59] who found this behavior in pyridinium-based ILs with $[TFO]^-$ and $[BF_4]^-$ anions. Fredlake et al.[49] have already described this dependency for the ILs [BMim][TFO] and [BMim][NTf_2], among others, attributing the high values of density to the nature of the anions, which can occupy nearby positions around the cation, and this leads to higher density values.

On the other hand, refractive index and speed of sound increase their values with a decrease of the molecular weight of the anion. This is in agreement with Tariq et al.,[14] who found a strong dependence of the anion on the refractive index for imidazolium- and phosphonium-based ILs with $[TFO]^-$, $[MeSO_4]^-$, $[OAc]^-$ and $[NTf_2]^-$ anions. This was also observed by Fröba et al.[27] in their work with $[EMim]^+$-based ILs with $[NTf_2]^-$, $[N(CN)_2]^-$, and $[EtSO_4]^-$ anions.

Viscosity is not influenced by the molecular weight of the anion, and decreases in the order $[TFO]^-$ > $[NTf_2]^-$ > $[N(CN)_2]^-$, as observed by other authors.[28,38,56,59,60] For instance, Tokuda et al.[60] compared imidazolium-based ILs with $[TFO]^-$ and $[NTf_2]^-$ anions finding the same behavior. According to Bandrés et al.,[59] in their study with pyridinium-based ILs with $[TFO]^-$ and $[BF_4]^-$ anions, a larger size and formula weight of the anion do not correspond with causing larger viscosity values of the ILs. Moreover, Bonhôte et al.[56] took into account the fact that viscosity is strongly governed by van der Waals forces and hydrogen bonding. They proved that ILs with $[NTf_2]^-$ anions have lower viscosities than ILs with $[TFO]^-$ anions because in the latter one hydrogen bonding interactions are dominant.

3.4. Effect of the Cation. Finally, the study of the effect of the cation was carried out comparing the behavior of the pairs [BMpy][NTf_2]/[BMpyr][NTf_2], [EMpy][NTf_2]/[EMim]-[NTf_2] and [BMpyr][TFO]/[BMim][TFO]. From the pair [BMpy][NTf_2]/[BMpyr][NTf_2] it is possible to conclude that pyrrolidinium-based ILs present lower densities and refractive indices than pyridinium-based ILs. In the same way, Gardas et al.[50] found this behavior in their study with pyridinium- and pyrrolidinium-based ILs with $[NTf_2]^-$ anion.

On the contrary, speed of sound and viscosity are higher for pyrrolidinium-based ILs, as can be inferred from Figures 4 and 5. It is worth noting that [BMpyr][NTf_2] and [BMpy][NTf_2] are different cations with their alkyl chains in different positions: while [BMpyr][NTf_2] has the two alkyl substituent groups in the nitrogen atom (1-butyl-1-methylpyrrolidinium), [BMpy][NTf_2] has each alkyl chain in different atoms (1-butyl-3-methylpyridinium). If we assume that the studied properties cannot distinguish between structural and positional isomers and that the effect of the different lengths and positions of the alkyl substituent groups can be lumped into a single chain, as stated by Oliveira et al.[26] in their work with pyridinium-based ILs, then [BMpyr][NTf_2] and [BMpy][NTf_2] can be compared accurately even with their alkyl chains placed in different ways.

Taking into account the ILs [EMim][NTf_2]/[EMpy][NTf_2], it is possible to observe that imidazolium-based ILs exhibit a slightly higher density than pyridinium-based ILs. This behavior is in accordance with that published by Sánchez et al.[38] for the ILs $[BMim]^+$ and $[BMpy]^+$ with $[N(CN)_2]^-$ and $[BF_4]^-$ anions. According to these authors the effect of the cation on the density appears to be linked to the kind of atomic associations that a given cation exerts on the counteranion. Besides, pyridinium-based ILs with $[NTf_2]^-$ anions exhibit a higher speed of sound and refractive index than the imidazolium-based ILs with the same anion. Regarding viscosity, it is possible to remark that the studied imidazolium-based ILs exhibit slightly lower values than pyridinium-based ILs. This behavior was also observed by Sánchez et al.[38] comparing [BMim][$N(CN)_2$] and [BMpy][$N(CN)_2$], and Crosthwaite et al.,[28] comparing [HMpy][NTf_2] and [HMim][NTf_2].

Finally, considering the data belonging to the ILs [BMpyr]-[TFO]/[BMim][TFO], imidazolium-based ILs show higher density and refractive index than pyrrolidinium-based ILs, as can be inferred from Figures 2 and 3. This behavior was also found by Sánchez et al.,[38] who analyzed density data for imidazolium- and pyrrolidinium-based ILs with $[SCN]^-$ anion. With respect to viscosity and speed of sound, imidazolium-based ILs show lower values than pyrrolidinium-based ILs. This is in agreement with the data published by Tokuda et al.,[60] who studied density and viscosity data for imidazolium- and pyrrolidinium-based ILs with the $[NTf_2]^-$ anion.

3.5. Comparison with Literature. *3.5.1. Density.* Figure 6 shows the deviations of experimental density of [EMim][NTf_2], [HMim][NTf_2], [BMim][TFO], [BMpyr][NTf_2], [BMpy]-[NTf_2], and [PMpy][NTf_2] calculated from eq 3 as well as for that available in the literature.[14,26,27,30−32,34,50,51,53,54,61−64] The main sources of deviations can be the difference in the level of water content, impurities due to the starting material in the synthesis, and the level of accuracy of the method of measurements.

[EMim][NTf_2] was compared with the data published by Fröba et al.,[27] Gardas et al.,[51] Tariq et al.,[14] and Jacquemin et al.,[54] showing a good agreement with the experimental data obtained in this work, with maximum deviations lower than 0.02%, 0.16%, 0.27%, and 0.06%, respectively.

It is important to point out that [HMim][NTf_2] is considered and used as a reference ionic liquid in the IUPAC project "Thermodynamics of ionic liquids, ionic liquid mixtures, and the development of standardized systems" (IUPAC Project 2002-005-1-100),[61] where samples of high purity, termed IUPAC samples, were distributed to the participating laboratories to measure different thermophysical properties.[30,61−63] Among these laboratories, Seddon et al.,[61] Widegren et al.,[30] Esperança et al.,[62] and Kandil et al.[63] have used different models of the vibrating tube densimeter Anton Paar, with estimated uncertainties of 0.05, 1.4, and 1.5 $g \cdot cm^{-3}$ and 0.3%, respectively. In a comparison of our density data with those obtained in this project an excellent agreement was observed, with deviations of about 0.07%. Among the compared data, a maximum deviation of 0.44% was observed with respect to the data provided by Azevedo et al.[53] Considering that these densities were measured using an Anton Paar DMA 512P densimeter and that the water content of their sample is slightly higher than ours, these negative deviations

dx.doi.org/10.1021/ie2029255 | *Ind. Eng. Chem. Res.* 2012, 51, 2492−2504

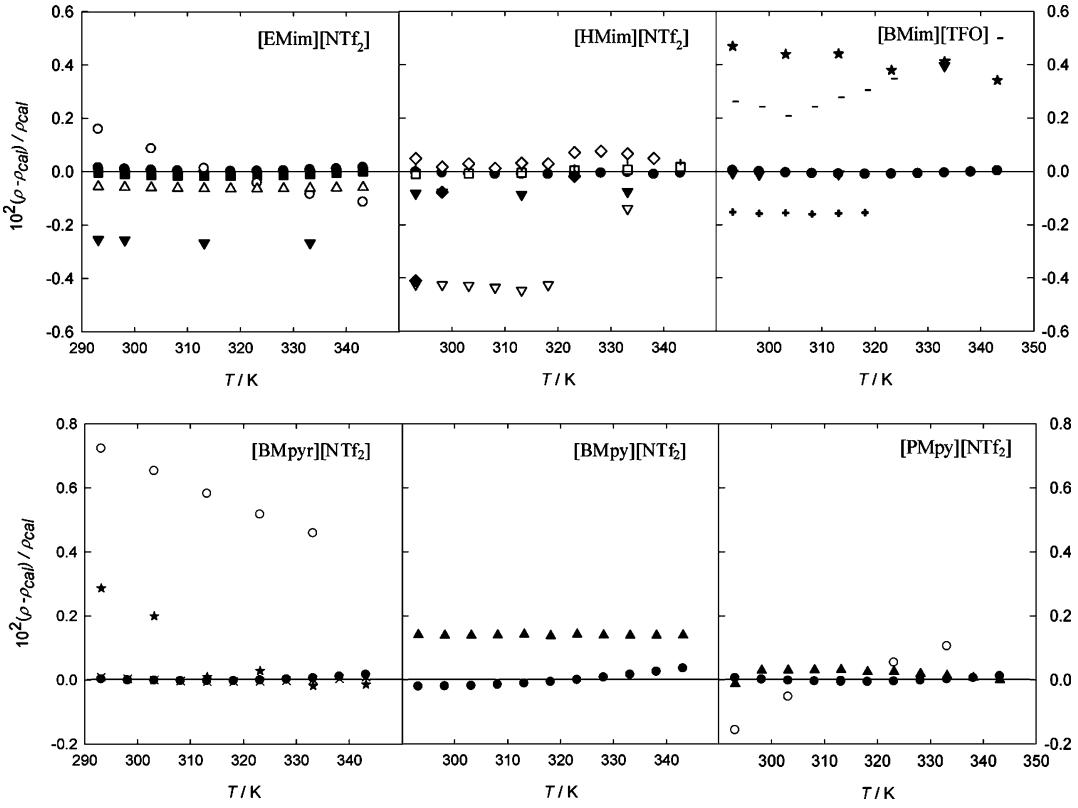

Figure 6. Relative deviations of our experimental density data from eq 3 as well as for that available in the literature as a function of temperature for [EMim][NTf_2]: (●) this work; (▼) Tariq et al.;[14] (■) Fröba et al.;[27] (○) Gardas et al.;[51] (△) Jacquemin et al.[54] [HMim][NTf_2]: (●) this work; (▼) Tariq et al.;[14] (|) Widegren et al.;[30] (▽) Azevedo et al.;[53] (□) Marsh et al.;[61] (◊) Esperança et al.;[62] (♦) Kandil et al.[63] BMim][TFO]: (●) this work; (▼) Tariq et al.;[14] (★) Shamsipur et al.;[32] (+) García-Miaja et al.;[34] (—) Ge et al.[64] [BMpyr][NTf_2]: (●) this work; (×) Pereiro et al.;[31] (★) Shamsipur et al.;[32] (○) Gardas et al.[50] [BMpy][NTf_2]: (●) this work; (▲) Oliveira et al.[26] [PMpy][NTf_2]: (●) this work; (▲) Oliveira et al.;[26] (○) Gardas et al.[50]

could be attributed to the different IL purity or to the adopted experimental techniques.

Concerning the deviations between experimental and literature data for [BMim][TFO], the maximum deviation found for density data is about 0.46% with respect to Shamsipur et al.,[32] who used a SVM 3000 Anton Paar digital double-tube viscosimeter-densimeter with a precision of about 2×10^{-4} g·cm^{-3}. The data supplied by Ge et al.[64] for [BMim][TFO] were obtained using a pycnometer, of which the uncertainty was not specified, and the sample was prepared in a traditional way in the laboratory. These data show a maximum difference of 0.49% at T = 340 K, although this difference is reduced to 0.26% at lower temperatures, while the density data published by García-Miaja et al.[34] and Tariq et al.[14] show deviations between 0.01 and 0.39%.

For the ILs [BMpyr][NTf_2], [BMpy][NTf_2], and [PMpy][NTf_2] scarce literature was found. Oliveira et al.[26] used a vibrating U-tube instrument SVM 3000 Anton Paar rotational Stabinger viscosimeter-densimeter with a relative uncertainty of 5×10^{-4} g·cm^{-3}. Gardas et al.[50] employed a DMA 60 Anton Paar, and Pereiro et al.[31] measured with a DSA-5000 Anton Paar with an uncertainty lower than $\pm 2 \times 10^{-6}$ g·cm^{-3}. Since the deviations of experimental properties are small, being in the range of 0.8 and −0.2%, it can be concluded that our measurements show a good agreement with the data reported by these authors. It is worth noticing that the higher deviations are found with the data presented by Gardas et al.;[50] a possible explanation for this difference is that the equipment used in literature does not correct the influence of viscosity on the measured density or the presence of possible impurities.

3.5.2. Viscosity. In Figure 7, the deviations of experimental viscosity and literature values of [EMim][NTf_2], [HMim][NTf_2], [BMpy][NTf_2], [BMpyr][NTf_2], [BMim][TFO], and [PMpy][NTf_2] from the values obtained in the fitting are plotted. The fitting used for this comparison is that obtained with the VFT equation, since it is the equation that gave the lower deviations.

As can be observed, our viscosity data for [EMim][NTf_2] are in agreement with those reported in literature, the highest deviation at low temperatures being about 9% for Crosthwaite et al.,[28] who used a rheometer (Brookfield model DV-III) with an accuracy of approximately 2%. Viscosity data measured by Tariq et al.[65] with an automated SVM 3000 Anton Paar rotational Sabinger viscodensimeter, of which the uncertainty in the measurements is 2%, show a maximum difference of 4.3% from our fit. Viscosity data for [EMim][NTf_2] supplied by Fröba et al.[27] using a surface light scattering (SLS) method with an uncertainty less than 3% and Tokuda et al.,[60] who have not specified the equipment, are in excellent agreement, showing deviations between 0.01 and 1.67%.

Viscosity measurements of [HMim][NTf_2] were also performed in the IUPAC project.[30,61,63] A maximum difference of 15% was observed at 308.15 K from the values reported by Marsh et al.[61] using a viscometer (Brookfield model LCDV-II), although it is reduced to 11% at higher temperatures. On the other hand, the data reported by Widegren et al.[30] using a

dx.doi.org/10.1021/ie2029255 | *Ind. Eng. Chem. Res.* 2012, 51, 2492−2504

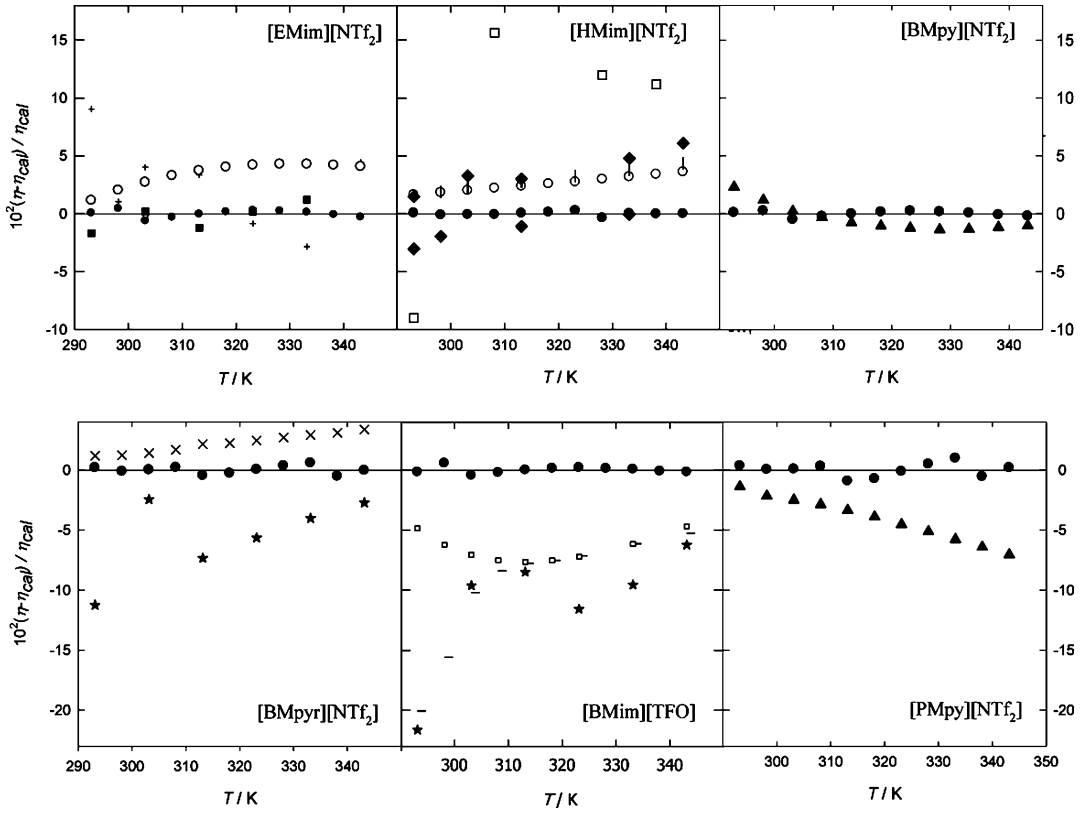

Figure 7. Relative deviations between our experimental viscosity data from eq 7 and available literature data as a function of temperature for [EMim][NTf_2]: (●) this work; (■) Fröba et al.;[27] (+) Crosthwaite et al.;[28] (□) Tokuda et al.;[60] (○) Tariq et al.[65] [HMim][NTf_2]: (●) this work; (l) Widegren et al.;[30] (□) Marsh et al.;[61] (♦) Kandil et al.;[63] (○) Tariq et al.[65] [BMpy][NTf_2]: (●) this work; (▲) Oliveira et al.[26] [BMpyr][NTf_2]: (●) this work; (×) Pereiro et al.;[31] (★) Shamsipur et al.[32] [BMim][TFO]: (●) this work; (★) Shamsipur et al.;[32] (□) Tokuda et al.;[33] (—) Ge et al.[64] [PMpy][NTf_2]: (●) this work; (▲) Oliveira et al.[26]

Stabinger viscometer (Anton Paar model SVM3000) and by Kandil et al.[63] using a vibrating wire viscometer, both for an IUPAC sample, showed maximum differences of 3.83% and 6.10%, respectively, being in better agreement with our fit. Tariq et al.[65] also provided viscosity data for [HMim][NTf_2], and they are in good agreement with those reported in this work, reaching maximum deviations around 3.6%.

Oliveira et al.[26] determined viscosity data for the ILs [BMpy][NTf_2] and [PMpy][NTf_2], being in good agreement with our data for the IL [BMpy][NTf_2], as can be inferred for the very low deviations. Nevertheless, there are higher mismatches at high temperatures for [PMpy][NTf_2]. The large deviations between the different data sets may be explained by different or undefined impurities.

The temperature viscosity dependence is in good agreement with the data presented by Pereiro et al.[31] for the IL [BMpyr][NTf_2] using an automatic viscosimeter Lauda PVS1 with two Ubbelholde capillaries. However, there are mismatches between our data and those from Shamsipur et al.[32] for this IL at low temperatures. These authors employed an automated SVM 3000 Anton Paar rotational Stabinger viscosimeter−densimeter with a precision about 1×10^{-4} mPa·s.

In the case of [BMim][TFO], the differences at low temperatures between Shamsipur et al.[32] and Ge et al.[64] with our data reached 21% at 293 K, although these deviations are reduced to 5−6% at 343.15 K in both cases. The differences, as occurred with other properties, can be due to the sample purity and/or the equipment employed. Ge et al.[64] employed an Ubbelohde capillary viscodensimeter with an uncertainty of ±0.01, and in both cases the ILs were synthetized in their laboratory. On the other hand, a relative agreement is observed between our data and those obtained by Tokuda et al.[33] using a Toki RE80 cone−plate viscometer under nitrogen atmosphere, with a maximum difference about 7.6%. The IL used by Tokuda et al.[33] was prepared in a traditional way and the water content was not indicated.

4. CONCLUSIONS

Experimental density, refractive index, speed of sound, and dynamic viscosity data for [EMpy][NTf_2], [PMpy][NTf_2], [BMpy][NTf_2], [EMim][NTf_2], [HMim][NTf_2], [BMpyr]-[NTf_2], [BMpyr][TFO], [BMim][TFO], [HMim][TFO], [BMim][$N(CN)_2$], and [HMim][$N(CN)_2$] ILs are presented as a function of temperature at atmospheric pressure. From the experimental densities, the coefficients of thermal expansion were calculated.

As expected, a linear dependence of the thermodynamic properties density, refractive index, and speed of sound with the temperature was found in the studied range. The viscosity values were fitted using the Arrhenius-like Law, Vogel−Fulcher−Tamman (VFT) equation, modified VFT, Litovitz equation, and fluidity. It was found that, overall, the VFT equation provides the best fit for the studied ILs.

In all cases, the values of the studied properties decrease when the temperature increases. From the experimental density and speed of sound for a given anion and cation, it is observed that as the alkyl chain length increases in imidazolium-based ILs with $[NTf_2]^-$, $[TFO]^-$, or $[N(CN)_2]^-$ anions and pyridinium-based ILs

dx.doi.org/10.1021/ie2029255 | Ind. Eng. Chem. Res. 2012, 51, 2492−2504

with $[NTf_2]^-$ anion, the value of these properties decreases. Regarding to the refractive indices, an increase in the alkyl chain length of pyridinium-based ILs with $[NTf_2]^-$ anion and imidazolium-based ILs with $[NTf_2]^-$ or $[TFO]^-$ anion leads to an increase of the refractive index, while an increase in the alkyl chain length of imidazolium-based ILs with $[N(CN)_2]^-$ anion leads to a decrease of the refractive index. In contrast to density and speed of sound, viscosity increases in pyridinium-based ILs with $[NTf_2]^-$ anion and imidazolium-based ILs with $[NTf_2]^-$, $[TFO]^-$, or $[N(CN)_2]^-$ anion as the alkyl chain in the cation elongates.

The nature of the anions have influence on density, since the value of this property decreases with the molecular weight of the anion in the order $[NTf_2]^-$ > $[TFO]^-$ > $[N(CN)_2]^-$. However, the refractive index and speed of sound increase their values with a decrease of the molecular weight of the anion. Viscosity exhibits a different behavior, the imidazolium-based ILs with $[N(CN)_2]^-$ anion being the least viscous and the ILs with $[TFO]^-$ anion being the most viscous compounds.

Finally, we can observe that pyrrolidinium-based ILs with the $[NTf_2]^-$ anion have lower densities and refractive indices than pyridinium-based ILs with the $[NTf_2]^-$ anion. On the contrary, the speed of sound and viscosity values are higher for pyrrolidinium-based ILs. On one hand, the imidazolium-based IL with the $[NTf_2]^-$ anion shows lower viscosity, speed of sound, and refractive index and higher density than the pyridinium-based IL with the $[NTf_2]^-$ anion; on the other hand, the pyrrolidinium-based IL with the $[TFO]^-$ anion has lower density and refractive index and higher viscosity and speed of sound values than the imidazolium-based IL with the $[TFO]^-$ anion.

Taking the obtained outcomes of the structural influence on the thermophysical properties into consideration, we can conclude that the anion is the part of the IL which exercises more influence over the thermophysical properties.

A critical evaluation and comparison with available literature data was also carried out. In general, our measurements show a good agreement with the data reported by other authors.

AUTHOR INFORMATION

Corresponding Author

*E-mail: elenagc@uvigo.es.

ACKNOWLEDGMENTS

The authors are grateful to Xunta de Galicia (Spain) for the financial support via the project INCITE09314258PR and to the Ministerio de Ciencia e Innovación from Spain (Project ZTQ2010-18147). N. Calvar and E. J. González acknowledge the financial support from Fundação para a Ciência e a Tecnologia (Portugal) through their postdoctoral grants (SFRH/BPD/37775/2007 and SFRH/BPD/70776/2010, respectively) and E. Gómez is also thankful to Xunta de Galicia for the financial support through Ángeles Alvariño Programme.

REFERENCES

(1) Zhao, H. Innovative Applications of Ionic Liquids as "Green" Engineering Liquids. *Chem. Eng. Commun.* **2006**, *193*, 1660−1677.

(2) Gan, Q.; Rooney, D.; Xue, M.; Thompson, G.; Zou, Y. An Experimental Study of Gas Transport and Separation Properties of Ionic Liquids Supported on Nanofiltration Membranes. *J. Membr. Sci.* **2006**, *280*, 948−956.

(3) Olivier-Bourbigou, H.; Magda, M.; Morvan, D. Ionic Liquids and Catalysis: Recent Progress from Knowledge to Applications. *Appl. Catal. A* **2010**, *373*, 1−56.

(4) Torimoto, T.; Tsuda, T.; Okazaki, K. I.; Kuwabata, S. New Frontiers in Materials Science Opened by Ionic Liquids. *Adv. Mater.* **2010**, *22*, 1196−1221.

(5) Sun, P.; Armstrong, D. W. Ionic Liquids in Analytical Chemistry. *Anal. Chim. Acta* **2010**, *661*, 1−16.

(6) Moniruzzaman, M.; Nakashima, K.; Kamiya, N.; Goto, M. Recent Advances of Enzymatic Reactions in Ionic Liquids. *Biochem. Eng. J.* **2010**, *48*, 295−314.

(7) Quijano, G.; Couvert, A.; Amrane, A. Ionic Liquids: Applications and Future Trends in Bioreactor Technology. *Bioresour. Technol.* **2010**, *101*, 8923−8930.

(8) Jiang, T.; Han, B. Ionic Liquid Catalytic Systems and Chemical Reactions. *Curr. Org. Chem.* **2009**, *13*, 1278−1299.

(9) Reddy, R. G. Novel Applications of Ionic Liquids in Materials Processing. *J. Phys.: Conf. Ser.* **2009**, *165*, 012076.

(10) Plechkova, N. V.; Seddon, K. R. Applications of Ionic Liquids in the Chemical Industry. *Chem. Soc. Rev.* **2008**, *37*, 123−150.

(11) Wei, D.; Ivaska, A. Applications of Ionic Liquids in Electrochemical Sensors. *Anal. Chim. Acta* **2008**, *607*, 126−135.

(12) Earle, M. J.; Esperança, J. M. M. S.; Gilea, M. A.; Canongia Lopes, J. N.; Rebelo, L. P. N; Magee, J. W.; Seddon, K. R.; Widegren, J. A. The Distillation and Volatility of Ionic Liquids. *Nature* **2006**, *439*, 831−834.

(13) Aparicio, S.; Atilhan, M.; Karadas, F. Thermophysical Properties of Pure Ionic Liquids: Review of Present Situation. *Ind. Eng. Chem. Res.* **2010**, *49*, 9580−9595.

(14) Tariq, M.; Forte, P. A. S.; Gomes, M. F. C.; Lopes, J. N. C.; Rebelo, L. P. N. Densities and Refractive Indices of Imidazolium and Phosphonium Based Ionic Liquids: Effect of Temperature, Alkyl Chain Length, and Anion. *J. Chem. Thermodyn.* **2009**, *41*, 790−798.

(15) Gardas, R. L.; Coutinho, J. A. P. Estimation of Speed of Sound of Ionic Liquids Using Surface Tensions and Densities: A Volume Based Approach. *Fluid Phase Equilib.* **2008**, *267*, 188−192.

(16) Sadeghi, R.; Shekaari, H.; Hosseini, R. Volumetric and Isentropic Compressibility Behavior of Ionic Liquid, 1-Propyl-3-Methylimidazolium Bromide in Acetonitrile, Dimethylformamide, and Dimethylsulfoxide at T = (288.15 to 308.15) K. *Int. J. Thermophys.* **2009**, *30*, 1491−1509.

(17) Gómez, E.; Calvar, N.; Domínguez, A.; Macedo, E. A. Synthesis and Temperature Dependence of Physical Properties of Four Pyridinium-Based Ionic Liquids: Influence of the Size of the Cation. *J. Chem. Thermodyn.* **2010**, *42*, 1324−1329.

(18) Gómez, E.; González, B.; Calvar, N.; Tojo, E.; Domínguez, A. Physical Properties of Pure 1-Ethyl-3-methylimidazolium Ethylsulfate and Its Binary Mixtures with Ethanol and Water at Several Temperatures. *J. Chem. Eng. Data* **2006**, *51*, 2096−2102.

(19) González, B.; Calvar, N.; Gómez, E.; Domínguez, A. Physical Properties of the Ternary System (Ethanol+Water+1-Butyl-3-Methylimidazolium Methylsulphate) and Its Binary Mixtures at Several Temperatures. *J. Chem. Thermodyn.* **2008**, *40*, 1274−1281.

(20) Gómez, E.; González, B.; Calvar, N.; Domínguez, A. Excess Molar Properties of Ternary System (Ethanol+Water+1,3-Dimethylimidazolium Methylsulphate) and Its Binary Mixtures at Several Temperatures. *J. Chem. Thermodyn.* **2008**, *40*, 1208−1216.

(21) González, B.; Calvar, N.; Gómez, E.; Macedo, E. A.; Domínguez, A. Synthesis and Physical Properties of 1-Ethyl 3-Methylpyrindium Ethylsulfate and Its Binary Mixtures with Ethanol and Water at Several Temperatures. *J. Chem. Eng. Data* **2008**, *53*, 1824−1828.

(22) González, B.; Calvar, N.; Gómez, E.; Domínguez, I.; Domínguez, A. Synthesis and Physical Properties of 1-Ethylpyridinium Ethylsulfate and its Binary Mixtures with Ethanol and 1-Propanol at Several Temperatures. *J. Chem. Eng. Data* **2009**, *54*, 1353−1358.

(23) González, B.; Gómez, E.; Domínguez, A.; Milas, M.; Tojo, E. Physicochemical Characterization of New Sulfate Ionic Liquids. *J. Chem. Eng. Data* **2011**, *56*, 14−20.

(24) Gómez, E.; González, B.; Domínguez, A.; Tojo, E.; Tojo, J. Dynamic Viscosities of a Series of 1-Alkyl-3-Methylimidazolium Chloride Ionic Liquids and Their Binary Mixtures with Water at Several Temperatures. *J. Chem. Eng. Data* **2006**, *51*, 696−701.

(25) Widegren, J. A.; Laesecke, A.; Magee, J. W. The Effect of Dissolved Water on the Properties of Room-Temperature Ionic Liquids. *Chem. Commun.* **2005**, 1610−1612.
(26) Oliveira, F. S.; Freire, M. G.; Carvalho, P. J.; Coutinho, J. A. P.; Lopes, J. N. C.; Rebelo, L. P. N; Marrucho, I. M. Structural and Positional Isomerism Influence in the Physical Properties of Pyridinium NTf_2-Based Ionic Liquids: Pure and Water-Saturated Mixtures. *J. Chem. Eng. Data* **2010**, *55*, 4514−4520.
(27) Fröba, A. P.; Kremer, H.; Leipertz, A. Density, Refractive Index, Interfacial Tension, and Viscosity of Ionic Liquids [EMIM][$EtSO_4$], [EMIM][NTf_2], [EMIM][$N(CN)_2$], and [OMA][NTf_2] in Dependence on Temperature at Atmospheric Pressure. *J. Phys. Chem. B* **2008**, *112*, 12420−12430.
(28) Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, J. F. Phase Transition and Decomposition Temperatures, Heat Capacities, and Viscosities of Pyridinium Ionic Liquids. *J. Chem. Thermodyn.* **2005**, *37*, 559−568.
(29) Frez, C.; Diebold, G. J. Determination of Thermal Diffusivities, Thermal Conductivities, and Sound Speeds of Room-Temperature Ionic Liquids by the Transient Grating Technique. *J. Chem. Eng. Data* **2006**, *51*, 1250−1255.
(30) Widegren, J. A.; Magee, J. W. Density, Viscosity, Speed of Sound, and Electrolytic Conductivity for the Ionic Liquid 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide and Its Mixtures with Water. *J. Chem. Eng. Data* **2007**, *52*, 2331−2338.
(31) Pereiro, A. B.; Veiga, H. I. M.; Esperança, J. M. M. S.; Rodríguez, A. Effect of Temperature on the Physical Properties of Two Ionic Liquids. *J. Chem. Thermodyn.* **2009**, *41*, 1419−1423.
(32) Shamsipur, M.; Beigi, A. A. M.; Teymouri, M.; Pourmortazavi, S. M.; Irandoust, M. Physical and Electrochemical Properties of Ionic Liquids 1-Ethyl-3-methylimidazolium Tetrafluoroborate, 1-Butyl-3-methylimidazolium Trifluoromethanesulfonate and 1-Butyl-1-methyl-pyrrolidinium Bis(trifluoromethylsulfonyl)imide. *J. Mol. Liq.* **2010**, *157*, 43−50.
(33) Tokuda, H.; Hayamizu, K.; Ishii, K. Physicochemical Properties and Structures of Room Temperature Ionic Liquids. *J. Phys. Chem. B* **2004**, *108*, 16593−16600.
(34) García-Miaja, G.; Troncoso, J.; Romaní, L. Excess Molar Properties for Binary Systems of Alkylimidazolium-Based Ionic Liquids + Nitromethane. Experimental Results and ERAS-Model Calculations. *J. Chem. Thermodyn.* **2009**, *41*, 334−341.
(35) Stoppa, A.; Hunger, J.; Buchner, R. Conductivities of Binary Mixtures of Ionic Liquids with Polar Solvents. *J. Chem. Eng. Data* **2009**, *54*, 472−479.
(36) Yoshida, Y.; Baba, O.; Saito, G. Ionic Liquids Based on Dicyanamide Anion: Influence of Structural Variations in Cationic Structures on Ionic Conductivity. *J. Phys. Chem. B* **2007**, *111*, 4742−4749.
(37) Esperança, J. M. S. S.; Guedes, H. J. R.; Blesic, M.; Rebelo, L. P. N. Densities and Derived Thermodynamic Properties of Ionic Liquids. 3. Phosphonium-Based Ionic Liquids over an Extended Pressure Range. *J. Chem. Eng. Data* **2006**, *51*, 237−242.
(38) Sánchez, L. G.; Espel, J. R.; Onink, F.; Meindersma, G. W.; de Haan, A. B. Density, Viscosity, and Surface Tension of Synthesis Grade Imidazolium, Pyridinium, and Pyrrolidinium Based Room Temperature Ionic Liquids. *J. Chem. Eng. Data* **2009**, *54*, 2803−2812.
(39) Andrade, E. N. A Theory of the Viscosity of Liquids. *Phil. Mag.* **1934**, *17*, 698−732.
(40) Vogel, H. The Law of the Relation Between the Viscosity of Liquids and the Temperature. *Phys. Z.* **1921**, *22*, 645−646.
(41) Fulcher, G. S. Analysis of Recent Measurements of the Viscosity of Glasses. *J. Am. Ceram. Soc.* **1925**, *8*, 339−355.
(42) Tammann, G.; Hesse, W. Z. The Dependence of Viscosity upon the Temperature of Supercooled Liquids. *Anorg. Allg. Chem.* **1926**, *156*, 245−257.
(43) Litovitz, T. A. Temperature Dependence of the Viscosity of Associated Liquids. *J. Chem. Phys.* **1952**, *20*, 1088−1089.
(44) Ghatee, M. H.; Zare, M.; Moosavi, F.; Zolghadr, A. R. Temperature-Dependent Density and Viscosity of the Ionic Liquids 1-Alkyl-3-methylimidazolium Iodides: Experiment and Molecular Dynamics Simulation. *J. Chem. Eng. Data* **2010**, *55*, 3084−3088.
(45) Seddon, K. R.; Starck, A. S.; Torres, M. J. Viscosity and density of 1-alkyl-3-methylimidazolium ionic liquids. In *Ionic Liquids III: Fundamentals, Progress, Challenges, and Opportunities*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 901; American Chemical Society: Washington DC, 2004.
(46) Wilkes, J. S. Properties of Ionic Liquid Solvents for Catalysis. *J. Mol. Catal. A* **2004**, *214*, 11−17.
(47) Otokuro, O. O.; Vandernoot, J. J. Temperature Dependence of Viscosity for Room Temperature Ionic Liquids. *J. Electroanal. Chem.* **2004**, *568*, 167−181.
(48) Ghatee, M. H.; Zare, M.; Zolghadr, A. R.; Moosavi, F. Temperature Dependence of Viscosity and Relation with the Surface Tension of Ionic Liquids. *Fluid Phase Equilib.* **2010**, *291*, 188−194.
(49) Fredlake, C. P.; Croshthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. Thermophysical Properties of Imidazolium-Based Ionic Liquids. *J. Chem. Eng. Data* **2004**, *49*, 954−964.
(50) Gardas, R. L.; Costa, H. F.; Freire, M. G.; Carvalho, P. J.; Marrucho, I. M.; Fonseca, I. M. A.; Ferreira, A. G. M.; Coutinho, J. A. P. Densities and Derived Thermodynamic Properties of Imidazolium-, Pyridinium-, Pyrrolidinium-, and Piperidinium-Based Ionic Liquids. *J. Chem. Eng. Data* **2008**, *53*, 805−811.
(51) Gardas, R. L.; Freire, M. G.; Carvalho, P. J.; Marrucho, I. M.; Fonseca, I. M. A.; Ferreira, A. G. M.; Coutinho, J. A. P. $P\rho T$ Measurements of Imidazolium-Based Ionic Liquids. *J. Chem. Eng. Data* **2007**, *52*, 1881−1888.
(52) Kolbeck, C.; Lehmann, J.; Lovelock, K. R. J.; Cremer, T.; Pappe, N.; Wasserscheid, P.; Fröba, A. P.; Maier, F.; Steinrück, H. P. Density and Surface Tension of Ionic Liquids. *J. Phys. Chem. B* **2010**, *114*, 17025−17036.
(53) Azevedo, R. G.; Esperança, J. M. S. S.; Szydlowski, J.; Visak, Z. P.; Pires, P. F.; Guedes, H. J. R.; Rebelo, L. P. N Thermophysical and Thermodynamic Properties of Ionic Liquids Over an Extended Pressure Range: [Bmim][NTf_2] and [Hmim][NTf_2]. *J. Chem. Thermodyn.* **2005**, *37*, 888−899.
(54) Jacquemin, J.; Husson, P.; Mayer, V.; Cibulka, I. High-Pressure Volumetric Properties of Imidazolium-Based Ionic Liquids: Effect of the Anion. *J. Chem. Eng. Data* **2007**, *52*, 2204−2211.
(55) Tokuda, H.; Hayamizu, K.; Kunikazu, I.; Susan, M. A. B. H.; Watanabe, M. Physicochemical Properties and Structures of Room Temperature Ionic Liquids. 2. Variation of Alkyl Chain Length in Imidazolium Cation. *J. Phys. Chem. B* **2005**, *109*, 6103−6110.
(56) Bonhôte, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. *Inorg. Chem.* **1996**, *35*, 1168−1178.
(57) Jacquemin, J.; Husson, P.; Padua, A. A. H.; Majer, V. Density and Viscosity of Several Pure and Water-Saturated Ionic Liquids. *Green. Chem.* **2006**, *8*, 172−180.
(58) Ziyada, A. K.; Wilfred, C. D.; Bustam, M. A.; Man, Z.; Murugesan, T. Thermophysical Properties of 1-Propyronitrile-3-alkylimidazolium Bromide Ionic Liquids at Temperatures from (293.15 to 353.15) K. *J. Chem. Eng. Data* **2010**, *55*, 3886−3890.
(59) Bandrés, I.; Royo, F. M.; Gascón, I.; Castro, M.; Lafuente, C. Anion Influence on Thermophysical Properties of Ionic Liquids: 1-Butylpyridinium Tetrafluoroborate and 1-Butylpyridinium Triflate. *J. Phys. Chem. B* **2010**, *114*, 3601−3607.
(60) Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M. Physicochemical Properties and Structures of Room-Temperature Ionic Liquids. 3. Variation of Cationic Structures. *J. Phys. Chem. B* **2006**, *110*, 19593−19600.
(61) Marsh, K. N.; Brennecke, J. F.; Chirico, R. D.; Frenkel, M.; Heintz, A.; Magee, J. W.; Peters, C. J.; Rebelo, L. P. N; Seddon, K. R. Thermodynamic and Thermophysical Properties of the Reference Ionic Liquid: 1-Hexil-3-Methylimidazolium Bis[(Trifluoromethyl)-Sulfonyl]Amide (Including Mixtures) Part 1. Experimental Methods and Results. *Pure Appl. Chem.* **2009**, *81*, 781−790.

(62) Esperança, J. M. S. S.; Guedes, H. J. R.; Lopes, J. N. C.; Rebelo, L. P. N Pressure−Density−Temperature ($P-\rho-T$) Surface of [C_6mim][NTf_2]. *J. Chem. Eng. Data* **2008**, *53*, 867−870.
(63) Kandil, M. E.; Marsh, K. N. Measurement of the Viscosity, Density, and Electrical Conductivity of 1-Hexyl-3-methylimidazolium Bis(trifluorosulfonyl)imide at Temperatures between (288 and 433) K and Pressures below 50 MPa. *J. Chem. Eng. Data* **2007**, *52*, 2382−2387.
(64) Ge, M. L.; Zhao, R. S.; Yi, Y. F.; Zhang, Q.; Wang, L. S. Densities and Viscosities of 1-Butyl-3-methylimidazolium Trifluoromethanesulfonate + H_2O Binary Mixtures at T = (303.15 to 343.15) K. *J. Chem. Eng. Data* **2008**, *53*, 2408−2411.
(65) Tariq, M.; Carvalho, P. J.; Coutinho, J. A. P.; Marrucho, I. M.; Lopes, J. N. C.; Rebelo, L. P. N. Viscosity of (C_2−C_{14}) 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquids in an Extended Temperature Range. *Fluid Phase Equilib.* **2011**, *301*, 22−32.