Structural and Positional Isomerism Influence in the Physical Properties of Pyridinium NTf_2-Based Ionic Liquids: Pure and Water-Saturated Mixtures[†]

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Density and viscosity data for six pyridinium-based ionic liquids combined with the bis[(trifluoromethyl)-sulfonyl]amide anion were measured at atmospheric pressure in the (278 to 363) K temperature range. The fundamental aim of this work is to study the effect of the structure of the pyridinium-based cation, namely, its alkyl chain length and structural isomers, and the position of the second alkyl substitution on the measured properties. Albeit many studies exist on the physical properties of ionic liquids in what concerns the nature of the anion and the length of the cation alkyl side chain, the effect of structural and positional isomerism on those properties is much less known. In addition—and since small amounts of water influence the phase equilibrium and thermophysical properties of ionic liquids—water-saturated ionic liquid samples were also studied in the (298 to 363) K temperature range. The Vogel−Tammann−Fulcher (VTF) method was applied to describe the viscosity data, and novel group contribution parameters are proposed for the ionic liquid cations presented here, thus broadening its applicability.

Introduction

In recent years ionic liquids (ILs) have grown to be one of the most studied classes of solvents and are considered as valid potential substitutes of many volatile organic solvents. ILs are salts, thus ionic compounds, that are liquid at or near room temperature. This is due to the asymmetry and charge dispersion of their organic and inorganic ions. Among other unique thermophysical properties, usually ILs do not evaporate at ambient temperature[1] and present relatively high thermal stability, high ionic conductivity, and a large liquidus temperature range. Moreover, ILs exhibit excellent solvent quality for many types of compounds, a fact that stems from the notion that their physical and chemical properties can be finely adjusted by a careful selection of ions, which, in turn, determines an interplay among Coulombic, van der Waals, and specific, mainly space-oriented, interactions.[2] This fact enables their fine-tuning for specific purposes, optimizing yield, selectivity, substrate solubility, product separation, and even enantioselectivity.[1−5]

To design ILs with suitable properties for a desired industrial application,[6] the accurate knowledge of their thermophysical properties is required. The study of these properties can provide information not only about the IL structure but also yield qualitative insights concerning their interactions at a molecular level. Because of the wide variety of ILs that can be synthesized, the available data are still scarce to provide a well-informed choice of the most suitable IL for a specific purpose. Additionally, among different authors, some discrepancies in the thermophysical properties are still found.[7,8] Those differences are usually attributed to impurities in ILs (halides and water content), the experimental technique adopted, and measurement conditions. Two major reviews are available in literature regarding the effect of impurities on the IL properties.[9,10] Besides changing the physical properties of ILs, water can also act as a cosolvent, increasing the miscibility between IL and alcohol mixtures,[11] and has an effect on the rates and selectivity of reactions carried out in IL media.[12]

The most studied ILs are those based on the imidazolium cation.[8,13−24] Fewer studies have been devoted to the viscosities and densities of pyridinium-based ILs.[19,25−31] As for the anion, bis(trifluoromethylsulfonyl)amide-based ILs are one of the most interesting classes as far as water stability,[18] high thermal stability, enhanced hydrophobicity,[17] and relatively low viscosity are concerned.

In this work, viscosity and density data of six pyridinum-based ILs with the bis[(trifluoromethyl)sulfonyl]amide anion were measured in the temperature range between (278 and 363) K and at atmospheric pressure. Albeit most authors have studied the anion nature and the cation alkyl chain length influence on the IL thermophysical properties, there are almost no studies on the effect of both the structural and the positional isomerism of ILs. Thus, the purpose of this study is to address the effect of the alkyl chain length of the cation and also the positional and structural isomerism of the IL cation on density and viscosity.

Given the importance of the water content on the IL physical properties, water-saturated ILs samples were also evaluated for the six pyridinium-based ILs studied in the temperature range from (298 to 363) K, and at atmospheric pressure.

Finally, aiming at correlating the experimental data obtained, the group contribution Vogel−Tammann−Fulcher (VTF) method[32] was used to describe the viscosity data for the pure ILs. As a result, novel group contribution parameters are proposed for the IL cations studied in this work.

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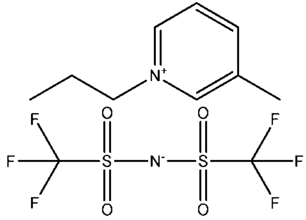
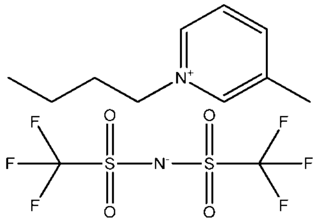
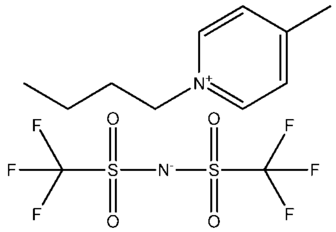
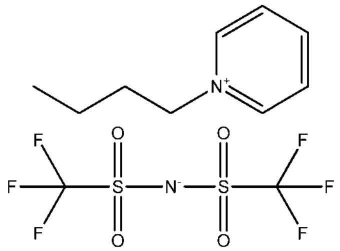
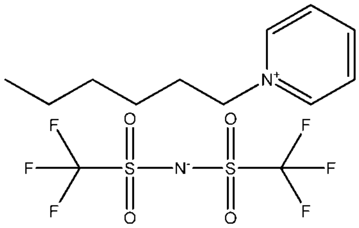
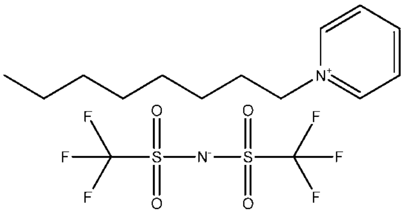
Table 1. Ionic Structures of the Studied ILs and Corresponding Designations

Ionic Liquid Designation	Ionic Structure
1-propyl-3-methylpyridinium bis[(trifluoromethyl)sulfonyl]amide [C_3-3-C_1pyr] [NTf_2]	
1-butyl-3-methylpyridinium bis[(trifluoromethyl)sulfonyl]amide [C_4-3-C_1pyr] [NTf_2]	
1-butyl-4-methylpyridinium bis[(trifluoromethyl)sulfonyl]amide [C_4-4-C_1pyr] [NTf_2]	
1-butylpyridinium bis[(trifluoromethyl)sulfonyl]amide [C_4pyr] [NTf_2]	
1-hexylpyridinium bis[(trifluoromethyl)sulfonyl]amide [C_6pyr] [NTf_2]	
1-octylpyridinium bis[(trifluoromethyl)sulfonyl]amide [C_8pyr] [NTf_2]	

Experimental Section

Materials and Procedure. The ionic structures of the studied ILs and corresponding designations are presented in Table 1. 1-Propyl-3-methylpyridinium bis[(trifluoromethyl)sulfonyl]amide [C_3-3-C_1pyr][NTf_2], 1-butyl-3-methylpyridinium bis[(trifluoromethyl)sulfonyl]amide [C_4-3-C_1pyr][NTf_2], 1-butyl-4-methylpyridinium bis[(trifluoromethyl)sulfonyl]amide [C_4-4-C_1pyr][NTf_2], 1-butylpyridinium bis[(trifluoromethyl)sulfonyl]amide [C_4pyr][NTf_2], 1-hexylpyridinium bis[(trifluoromethyl)sulfonyl]amide [C_6pyr [NTf_2], and 1-octylpyridinium bis[(trifluoromethyl)sulfonyl]amide [C_8pyr][NTf_2] were acquired at IoLiTec with mass fraction purities higher than 0.99. The purities of the ILs were further checked by ^1H, ^{13}C, and ^{19}F NMR spectra. All of the IL samples (circa 10 mL) were dried under constant stirring,

Table 2. Molecular Weight (M_{IL}), Mole Fraction Solubility (x_w), and Weight Fraction (w_w) Saturation of Water in Each IL at 298.15 K and Atmospheric Pressure

IL	M_{IL} $g \cdot mol^{-1}$	x_w	w_w
[C_3-3-C_1pyr][NTf_2]	416.37	0.238	0.013
[C_4-3-C_1pyr][NTf_2]	430.39	0.214	0.011
[C_4-4-C_1pyr][NTf_2]	430.39	0.244	0.013
[C_4pyr][NTf_2]	416.37	0.248	0.014
[C_6pyr][NTf_2]	444.42	0.233	0.012
[C_8pyr][NTf_2]	472.48	0.197	0.009

Table 3. Experimental Densities, ρ, for Both Pure and Water-Saturated (at 298.15 K) ILs [C_3-3-C_1pyr][NTf_2], [C_4-3-C_1pyr][NTf_2], and [C_4-4-C_1pyr][NTf_2] as a Function of Temperature and at Atmospheric Pressure

	[C_3-3-C_1pyr][NTf_2]		[C_4-3-C_1pyr][NTf_2]		[C_4-4-C_1pyr][NTf_2]	
	$\rho/(g \cdot cm^{-3})$		$\rho/(g \cdot cm^{-3})$		$\rho/(g \cdot cm^{-3})$	
T/K	dried	saturated	dried	saturated	dried	saturated
278.15	1.4671		1.4312		1.4310	
283.15	1.4623		1.4266		1.4263	
288.15	1.4575		1.4219		1.4216	
293.15	1.4528		1.4174		1.4169	
298.15	1.4475	1.4407	1.4128	1.4076	1.4122	1.4024
303.15	1.4428	1.4359	1.4082	1.4029	1.4076	1.3976
308.15	1.4381	1.4311	1.4036	1.3982	1.4029	1.3928
313.15	1.4334	1.4263	1.3990	1.3936	1.3983	1.3881
318.15	1.4288	1.4216	1.3945	1.3890	1.3936	1.3834
323.15	1.4241	1.4168	1.3899	1.3843	1.3890	1.3786
328.15	1.4195	1.4121	1.3854	1.3797	1.3844	1.3739
333.15	1.4149	1.4074	1.3809	1.3751	1.3798	1.3693
338.15	1.4103	1.4028	1.3764	1.3706	1.3753	1.3646
343.15	1.4057	1.3981	1.3719	1.3660	1.3707	1.3599
348.15	1.4011	1.3935	1.3674	1.3615	1.3662	1.3553
353.15	1.3966	1.3889	1.3629	1.3570	1.3617	1.3507
358.15	1.3921	1.3843	1.3585	1.3525	1.3572	1.3461
363.15	1.3877	1.3797	1.3541	1.3480	1.3527	1.3415

Table 4. Experimental Densities, ρ, for Both Pure and Water-Saturated (at 298.15 K) ILs [C_4pyr][NTf_2], [C_6pyr][NTf_2], and [C_8pyr][NTf_2] as a Function of Temperature and at Atmospheric Pressure

	[C_4pyr][NTf_2]		[C_6pyr][NTf_2]		[C_8pyr][NTf_2]	
	$\rho/(g \cdot cm^{-3})$		$\rho/(g \cdot cm^{-3})$		$\rho/(g \cdot cm^{-3})$	
T/K	dried	saturated	dried	saturated	dried	saturated
278.15	1.4676		1.4125		1.3472	
283.15	1.4628		1.4078		1.3427	
288.15	1.4581		1.4032		1.3382	
293.15	1.4534		1.3987		1.3338	
298.15	1.4487	1.4421	1.3942	1.3865	1.3295	1.3246
303.15	1.4440	1.4374	1.3897	1.3819	1.3252	1.3202
308.15	1.4393	1.4326	1.3852	1.3774	1.3209	1.3158
313.15	1.4346	1.4278	1.3807	1.3728	1.3166	1.3115
318.15	1.4300	1.4231	1.3763	1.3683	1.3123	1.3071
323.15	1.4254	1.4183	1.3718	1.3638	1.3080	1.3027
328.15	1.4207	1.4136	1.3673	1.3592	1.3037	1.2984
333.15	1.4161	1.4089	1.3629	1.3547	1.2995	1.2940
338.15	1.4116	1.4042	1.3585	1.3502	1.2952	1.2897
343.15	1.4070	1.3996	1.3540	1.3457	1.2909	1.2854
348.15	1.4025	1.3950	1.3496	1.3412	1.2867	1.2811
353.15	1.3980	1.3904	1.3453	1.3367	1.2825	1.2769
358.15	1.3935	1.3858	1.3409	1.3323	1.2783	1.2726
363.15	1.3890	1.3813	1.3366	1.3280	1.2741	1.2684

at moderate temperatures (below 333 K) and under moderate vacuum (0.1 Pa), for a minimum of 24 h, before their thermophysical property measurements. This step is extremely important to reduce the amount of volatile impurities, as well as the water content, since both contaminants greatly influence the viscosity and density results. Water content was measured in all samples after the drying procedure, using a Karl Fischer titration (Metrohm 831 Karl Fischer coulometer), and it was found to be smaller than 100 ppm (mass fraction content). Moreover, the water quantification was also performed after each series of measurements and variations of the water content is within a mass fraction of ± 10 ppm suggesting therefore that no significant adsorption of water from the atmosphere occurred during the measurements. The halide content was quantified by ion chromatography and shown to be smaller than 100 ppm (mass fraction). No further purification of the ILs was carried out.

The water used for the preparation of the saturated solutions was double-distilled, passed through a reverse osmosis system, and finally treated with a Milli-Q plus 185 water purification apparatus. The saturation of the IL-rich phase was accomplished by mixing water and the respective IL in excess (approximately 10 cm^3 of each). The two phases were left to equilibrate for at least 24 h for the ILs with smaller cation alkyl chains, and 48 h for the ILs with longer alkyl chains, respectively [C_6pyr][NTf_2] and [C_8pyr][NTf_2]. The vials containing the samples were maintained at 298.15 K (± 0.01 K) using an air bath previously developed for the purpose. Further details on the equilibration conditions can be found elsewhere.[17,33]

All of the samples were taken from the liquid−liquid equilibrium immediately before performing density and viscosity measurements to prevent the loss of water by air−liquid equilibration. The mole fraction solubility and weight fraction saturation of water in each IL at 298.15 K are presented in Table 2. Moreover, the molecular weight of each IL is presented in Table 2.

The measurements of viscosity and density were performed using an automated SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter. The temperature uncertainty is ± 0.02 K, the relative uncertainty of the dynamic viscosity ± 0.35 %, and the absolute uncertainty of the density ± 0.0005 $g \cdot cm^{-3}$. Further details about the equipment, methodology, and associated uncertainties can be found elsewhere.[34]

Results and Discussion

Densities. Tables 3 and 4 report the density data obtained for the six pyridinium-based ILs studied in this work (both dried and water-saturated ILs). Density measurements for pure ILs were performed in the (278.15 to 363.15) K temperature range. Density measurements of water-saturated IL samples were measured in the (298.15 to 363.15) K temperature range. The water saturation process was carried out at 298.15 K. It should be pointed out that density/viscosity measurements of the IL water-saturated samples were not determined at temperatures below 298.15 K to avoid phase splitting and changes in the binary composition.

From the inspection of Tables 3 and 4, the density of the ILs proved to be essentially dependent on the IL cation alkyl chain length and, to a lower extent, on the temperature (in the evaluated temperature range). In general, the densities decrease with the increase of the alkyl chain of the cation, as shown in Figure 1. It is interesting to notice that the densities of [C_4pyr][NTf_2] and [C_3-3-C_1pyr][NTf_2] are very similar. The same is also true for [C_4-3-C_1pyr][NTf_2] and [C_4-4-C_1pyr][NTf_2]. This fact indicates that this property 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. In fact, the density of ILs is merely an additive property with ion-independent[35] molar volume increments of 17.1 $cm^3 \cdot mol^{-1}$ at 298.15 K per each $-CH_2$ group,[2,19,20] as it can be observed in Table 5. As expected, the molar volumes for the series [$C_n$pyr][NTf_2] increase with a constant increment of approximately 17 $cm^3 \cdot mol^{-1}$ per each

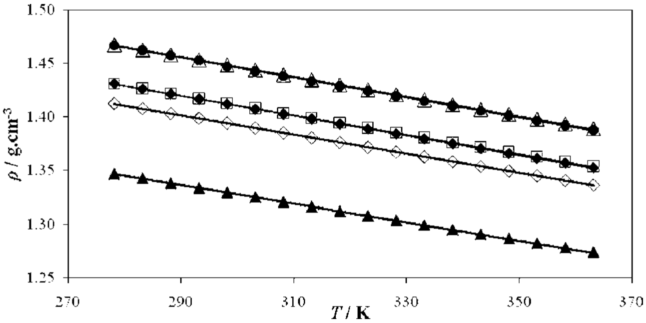


Figure 1. Densities (ρ) of the dried pyridinium-based ILs as a function of temperature: ●, [C_3-3-C_1pyr][NTf_2]; ♦, [C_4-3-C_1pyr][NTf_2]; □, [C_4-4-C_1pyr][NTf_2]; △, [C_4pyr][NTf_2]; ◇, [C_6pyr][NTf_2]; ▲, [C_8pyr][NTf_2]. The solid lines represent the correlation of the experimental data using eq 1.

Table 5. Molar Volumes for Both Dried and Water-Saturated ILs, at 298.15 K

IL	V_m/(cm^3·mol^{-1}) dried	saturated
[C_3-3-C_1py][NTf_2]	287.65	223.15
[C_4-3-C_1py][NTf_2]	304.64	242.94
[C_4-4-C_1py][NTf_2]	304.77	235.24
[C_4py][NTf_2]	287.41	220.18
[C_6py][NTf_2]	318.76	248.74
[C_8py][NTf_2]	355.38	289.03

$-CH_2$ group, and the molar volumes for positional and structural isomers are identical.

Figure 2 compares the density data obtained in this work with the data available in literature.[19,31] The measurements show good agreement with the data reported by Gardas et al.[19] and Yunus et al.[31] with relative average deviation of 0.10 % for [C_3-3-C_1pyr][NTf_2] and 0.07 % and 0.20 % for [C_4pyr][NTf_2] and [C_8pyr][NTf_2], respectively. Both positive and negative deviations were observed, and it seems that our results do not present systematic errors. Moreover, the temperature density dependence agrees well with the data presented by Yunus et al.[31]

As mentioned before, in the range of temperatures studied, the density of both dried and water-saturated samples decreases linearly with increasing temperature, thus allowing the use of the following equation,

$$\ln \rho = a + b(T/\mathrm{K}) \qquad (1)$$

where ρ is the density in g·cm^{-3}; a and b are characteristic parameters; and T is the temperature in K. The parameters a and b for each IL, as well as the respective correlation coefficient, are given in Table 6. Maximum relative deviations between experimental values from those calculated by eq 1 are in the order of 0.03 % for both dried and water-saturated ILs.

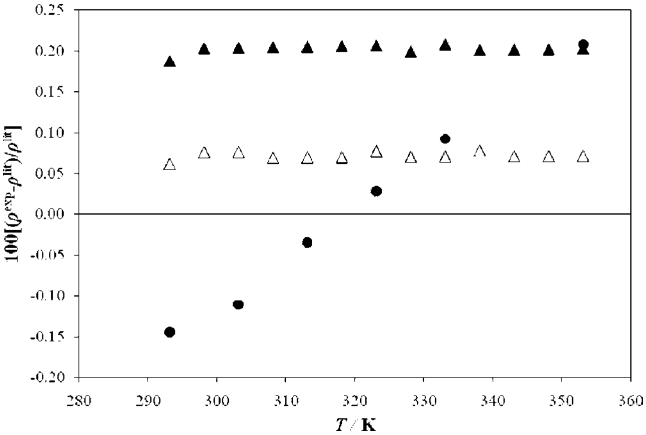


Figure 2. Relative deviations between this work's experimental data and density data available in the literature as a function of temperature. ●, [C_3-3-C_1pyr][NTf_2] from Gardas et al.;[19] △, [C_4pyr][NTf_2] and ▲, [C_8pyr] [NTf_2] from Yunus et al.[31]

Table 6. Correlation Parameters a and b, for Both Dried and Water Saturated ILs, Derived from Equation 1, and the Respective Correlation Coefficient (R^2)

IL	a dried	a saturated	b/(10^{-4} K^{-1}) dried	b/(10^{-4} K^{-1}) saturated	R^2 dried	R^2 saturated
[C_3-3-C_1pyr][NTf_2]	0.5656	0.5646	−6.56	−6.69	0.9999	1.0000
[C_4-3-C_1pyr][NTf_2]	0.5402	0.5414	−6.53	−6.69	1.0000	1.0000
[C_4-4-C_1pyr][NTf_2]	0.5429	0.5429	−6.63	−6.87	1.0000	1.0000
[C_4pyr][NTf_2]	0.5640	0.5652	−6.49	−6.68	1.0000	1.0000
[C_6pyr][NTf_2]	0.5261	0.5261	−6.50	−6.68	1.0000	1.0000
[C_8pyr][NTf_2]	0.4804	0.4813	−6.56	−6.71	1.0000	1.0000

Table 7. Coefficients of Thermal Expansion (α_p) for Both Pure and Water-Saturated (at 298.15 K) ILs as a Function of Temperature and at Atmospheric Pressure

IL	α_p/(10^{-4} K^{-1}) dried	saturated
[C_3-3-C_1py][NTf_2]	6.55	6.65
[C_4-3-C_1py][NTf_2]	6.52	6.65
[C_4-4-C_1py][NTf_2]	6.62	6.83
[C_4py][NTf_2]	6.48	6.64
[C_6py][NTf_2]	6.49	6.65
[C_8py][NTf_2]	6.55	6.68

Although some controversy exists between the application of a linear correlation or a second polynomial equation to the density dependence on temperature, we have used a linear equation since it satisfactorily describes the experimental data obtained in the temperature range and pressure conditions evaluated. Furthermore, for the IL−water saturated samples the density data are also well-described by eq 1, a fact that can arise from the presence of only small amounts of water. It should be noted that an increase in the composition of water in the binary systems would lead to a nonlinear density dependence on temperature.[23,36] Nevertheless, this is mainly relevant for hydrophilic ILs and high water content regimes, thus being out of the scope of this work.

As expected, and since the densities of all ILs are greater than that of water, the water-saturated samples present lower densities than the respectively dried ILs. Despite the fact that in terms of density the dried-saturated density difference is minimal (less than 1 %), this change of conditions obviously significantly affects the molar volume.

Table 7 presents the isobaric thermal expansion coefficients, $\alpha_p = -((\partial \ln \rho)/\partial T)_p$, where α_p is the thermal expansion coefficient in K^{-1} and ρ is the density in g·cm^3. For the IL set, the α_p values range from (6.5 to 6.8)·10^{-4} K^{-1}, which are in the same order of magnitude with those displayed by Jacquemin et al.[8] and in with good agreement with those displayed by Yunus et al.[31] Nevertheless, the α_p values obtained are lower than typical expansivities presented by organic solvents. In common to what was observed in another IL family (alkylmethylimidazolium-based), for the monosubstituted pyridinium-based ILs, α_p values increase with the alkyl chain length increase. On the other hand, for the disubstituted cations the values of α_p follow the rank: [C_4-3-C_1pyr][NTf_2] < [C_3-3-C_1pyr][NTf_2] < [C_4-4-C_1pyr][NTf_2]. In addition, the presence of water in the samples are proven to slightly increase the thermal expansion coefficients, a fact that is also shown by Jacquemin et al.[8]

Viscosities. The viscosity data obtained are reported in Tables 8 and 9 and illustrated in Figures 3 and 4 for all of the dried and

Table 8. Experimental Viscosities, η, for Both Pure and Water-Saturated (at 298.15 K) ILs [C_3-3-C_1pyr][NTf_2], [C_4-3-C_1pyr][NTf_2], and [C_4-4-C_1pyr][NTf_2] as a Function of Temperature and at Atmospheric Pressure

	[C_3-3-C_1pyr][NTf_2]		[C_4-3-C_1pyr][NTf_2]		[C_4-4-C_1pyr][NTf_2]	
	η/(mPa·s)		η/(mPa·s)		η/(mPa·s)	
T/K	dried	saturated	dried	saturated	dried	saturated
278.15	159.860		195.430		169.900	
283.15	117.810		142.730		124.190	
288.15	89.221		107.150		93.266	
293.15	69.105		82.194		71.723	
298.15	54.942	39.448	64.359	48.932	56.330	34.101
303.15	44.221	32.288	51.387	39.539	45.071	27.937
308.15	36.146	26.831	41.640	32.470	36.670	23.215
313.15	29.982	22.583	34.263	27.031	30.279	19.549
318.15	25.197	19.225	28.566	22.791	25.340	16.654
323.15	21.433	16.534	24.103	19.429	21.453	14.338
328.15	18.410	14.357	20.572	16.736	18.365	12.464
333.15	15.969	12.571	17.712	14.552	15.865	10.926
338.15	13.968	11.089	15.379	12.754	13.824	9.648
343.15	12.314	9.851	13.470	11.265	12.127	8.583
348.15	10.933	8.809	11.897	10.016	10.725	7.680
353.15	9.769	7.922	10.560	8.930	9.540	6.914
358.15	8.782	7.162	9.440	8.031	8.531	6.255
363.15	7.937	6.503	8.484	7.260	7.673	5.688

Table 9. Experimental Viscosities, η, for Both Pure and Water-Saturated (at 298.15 K) ILs [C_4pyr][NTf_2], [C_6pyr][NTf_2], and [C_8pyr][NTf_2] as a Function of Temperature and at Atmospheric Pressure

	[C_4pyr][NTf_2]		[C_6pyr][NTf_2]		[C_8pyr][NTf_2]	
	η/(mPa·s)		η/(mPa·s)		η/(mPa·s)	
T/K	dried	saturated	dried	saturated	dried	saturated
278.15	181.810		322.080		398.720	
283.15	133.340		229.050		281.380	
288.15	100.650		167.560		204.350	
293.15	77.715		125.560		151.980	
298.15	61.249	43.970	96.206	63.143	115.550	79.903
303.15	49.154	35.859	75.215	50.410	89.603	63.087
308.15	40.087	29.684	59.862	40.912	70.721	50.632
313.15	33.172	24.899	48.419	33.686	56.766	41.243
318.15	27.811	21.133	39.742	28.104	46.230	34.058
323.15	23.589	18.131	33.039	23.728	38.144	28.470
328.15	20.230	15.706	27.794	20.244	31.863	24.071
333.15	17.508	13.728	23.642	17.430	26.909	20.569
338.15	15.279	12.091	20.298	15.157	22.955	17.726
343.15	13.440	10.725	17.579	13.285	19.765	15.412
348.15	11.907	9.576	15.354	11.743	17.162	13.511
353.15	10.620	8.603	13.508	10.434	15.018	11.921
358.15	9.528	7.768	11.964	9.327	13.234	10.584
363.15	8.594	7.047	10.663	8.382	11.740	9.454

water-saturated pyridinum-based ILs studied. Figure 5 compares the viscosity results obtained in this work with the available literature data (Yunus et al.,[31] Tokuda et al.,[37] and Crosthwaite et al.[28]). In general, there are mismatches between our data and those of Crosthwaite et al.,[28] except for [C_4-3-C_1pyr][NTf_2], while good agreement is obtained with the other authors.

Both the IL structure and the temperature affect the viscosity values; nevertheless, the effect of temperature is much more pronounced. From the experimental data, and at the same temperature, the viscosity follows the order [C_8pyr][NTf_2] > [C_6pyr][NTf_2] > [C_4-3-C_1pyr][NTf_2] > [C_4pyr][NTf_2] > [C_4-4-C_1pyr][NTf_2] > [C_3-3-C_1pyr][NTf_2]. From Figure 3, a clear distinction can be observed between the viscosity values of [C_6pyr][NTf_2] and [C_8pyr][NTf_2] and the remaining ILs, since they present viscosities substantially higher than the others. In addition, for the monosubstituted ILs, and not considering isomerism effects, a general trend is observed: the longer the cation's alkyl chain, the higher the viscosity of the IL. This behavior follows the results obtained by other groups.[8,37]

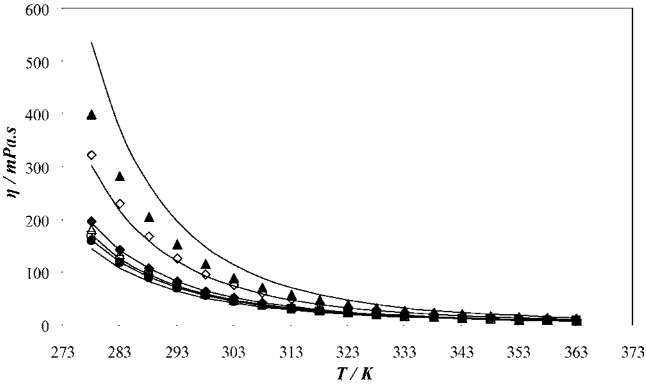


Figure 3. Experimental viscosities (η) of all of the dried pyridinium-based ILs as a function of temperature: ●, [C_3-3-C_1pyr][NTf_2]; ♦, [C_4-3-C_1pyr][NTf_2]; □, [C_4-4-C_1pyr][NTf_2]; △, [C_4pyr][NTf_2]; ◇, [C_6pyr][NTf_2]; ▲, [C_8pyr][NTf_2]. The solid lines represent the prediction of the experimental data using eq 2 and with the parameters proposed in Tables 10 and 11.

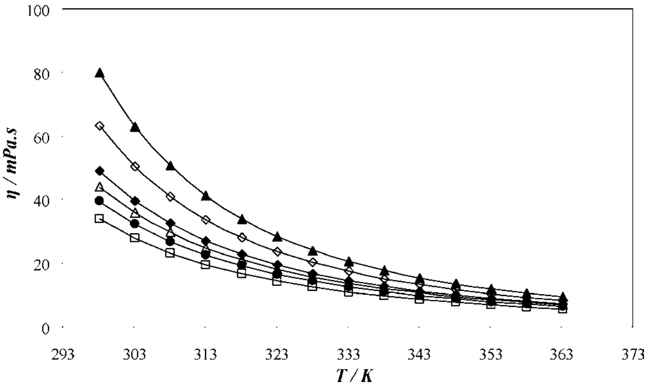


Figure 4. Experimental viscosities (η) for all of the water-saturated pyridinium-based ILs as a function of temperature: △, [C_4pyr][NTf_2]; ◇, [C_6pyr][NTf_2]; ▲, [C_8pyr][NTf_2]; ●, [C_3-3-C_1pyr][NTf_2]; ♦, [C_4-3-C_1pyr][NTf_2]; □, [C_4-4-C_1pyr][NTf_2]. The solid lines represent the prediction of the experimental data using eq 2 and with the parameters proposed in Table 10.

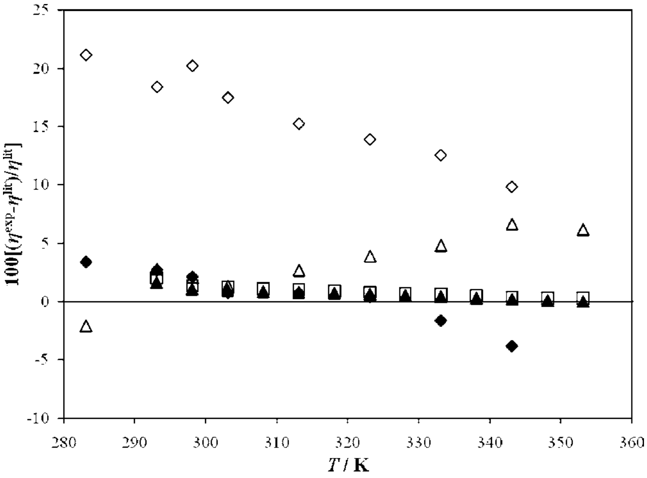


Figure 5. Relative deviations between this work's experimental data and viscosity data available in the literature as a function of temperature: △, [C_4pyr][NTf_2] from Tokuda et al.;[37] □, [C_4pyr][NTf_2] and ▲, [C_8pyr][NTf_2] from Yunus et al.;[31] ♦, [C_4-3-C_1pyr][NTf_2] and ◇, [C_6pyr][NTf_2] from Crosthwaite et al.[28]

Jacquemin et al.[8] attributed it to the formation of microstructures in the IL, in which the alkyl chains form nonpolar domains and, at the same time, the charged parts tend to form ionic domains. Indeed, computer simulation studies showed that imidazolium-based ILs with side chains above butyl exist in the pure liquid phases as nanostructured fluids.[38,39] Therefore, these microstruc-

Table 10. Correlation Parameters A_η and B_η for the Viscosity of Dried and Water-Saturated ILs as a Function of Temperature Determined from Experimental Measurements between (293.15 and 363.15) K for the Dried Samples and between (298.15 and 363.15) K for the Water-Saturated Samples

	A_η		B_η/K	
IL	dried	saturated	dried	saturated
$[C_3\text{-}3\text{-}C_1pyr][NTf_2]$	−8.851	−8.718	782.02	729.73
$[C_4\text{-}3\text{-}C_1pyr][NTf_2]$	−8.926	−8.823	822.94	772.05
$[C_4\text{-}4\text{-}C_1pyr][NTf_2]$	−8.873	−8.828	796.956	724.66
$[C_4pyr][NTf_2]$	−8.886	−8.696	804.62	741.03
$[C_6pyr][NTf_2]$	−9.036	−8.915	886.46	818.21
$[C_8pyr][NTf_2]$	−9.187	−9.030	968.30	865.16

Table 11. Correlation and Predictive Parameters $a_{i,\eta}$ and $b_{i,\eta}$ for the Viscosity of Dried ILs

	VTF method[32]	
cations/anions/groups	$a_{i,\eta}$	$b_{i,\eta}$/K
1-methylpyridinium (+)	−7.541[32]	587.66[32]
1,3-dimethylpyridinium (+)	−7.581	605.98
1,4-dimethylpyridinium (+)	−7.528	580.00
$[NTf_2]$ (23)	−1.119[32]	94.20[32]
$-CH_2$	−0.075[32]	40.92[32]

tures are likely to be responsible for this increase in the viscosity with the alkyl chain length increase.

Comparing the structural isomers, $[C_3\text{-}3\text{-}C_1pyr][NTf_2]$ and $[C_4pyr][NTf_2]$, it is evident that the viscosity values differ. Higher viscosities are observed for the disubstituted IL. The presence of two shorter alkyl chains instead of a single longer alkyl chain enhances the charge density of the IL cation, favoring thus the anion−cation Coulombic forces, and increasing therefore the viscosity of the IL. The positional isomerism, the position of the second alkyl side chain on the cation, also affects the viscosity. The presence of a methyl group on the *para* position of the pyridinium's ring proved to decrease the IL's viscosity, while on the position *meta* the IL's viscosity increased. As mentioned above, this effect can be understood taking into account the distribution of the charge in the pyridinium's ring, since the second substitution on the *para* position of the cation leads to more resonance structures than on the *meta* position. $[C_4\text{-}4\text{-}C_1pyr][NTf_2]$ clearly possesses stronger IL−IL interactions responsible for the decrease in the viscosity values. Indeed, Bandrés et al.[26] studied several thermophysical properties of the isomers $[C_4\text{-}4\text{-}C_1pyr][BF_4]$ and $[C_4\text{-}3\text{-}C_1pyr][BF_4]$, such as density and viscosity, and show that on the position *para* the methyl group was more capable of storing energy. On the contrary of what was observed for density, the presence of structural and positional isomers in the IL cation leads to significant differences on viscosity values. As a result, group contribution methods should be carefully employed to viscosity predictions, and additional care must be taken when isomeric effects are present.

In Tables 8 and 9 the effect of water on the viscosity values is visible. The presence of water significantly decreases the viscosity of the samples. The effect of the water content is much more pronounced than that previously witnessed for densities. The rank of the water-saturated sample viscosity follows the same order as the dried samples with one exception: the viscosity of the water-saturated $[C_4\text{-}4\text{-}C_1pyr][NTf_2]$ is smaller than the viscosity of the water-saturated $[C_3\text{-}3\text{-}C_1pyr][NTf_2]$, a mere consequence of the water saturation difference. From a practical standpoint, the presence of even small quantities of water allows one to decrease the usually high viscosities presented by most ILs. Note that this issue is especially relevant at low working temperatures.

The VTF method[32] (eq 2) was applied to correlate the viscosity experimental data as the following,

$$\ln \eta = A_\eta + \frac{B_\eta/\text{K}}{(T/\text{K} - T_{0\eta})} \tag{2}$$

where η is the viscosity in mPa·s; T is the temperature in K; and A_η, B_η, and $T_{0\eta}$ are adjustable parameters, and the parameter $T_{0\eta}$ is similar for all of the ILs studied with a constant value of 165.06 K.[32] The VTF method was employed with the group contribution method previously reported[32] aiming at using such a combination in a predictive way. Parameters A_η and B_η can be obtained by a group contribution method, accordingly to eqs 3 and 4,

$$A_\eta = \sum_{i=1}^{k} n_i a_{i,\eta} \tag{3}$$

$$B_\eta = \sum_{i=1}^{k} n_i b_{i,\eta} \tag{4}$$

where n_i is the number of groups of type i, k is the total number of different groups in the molecule, and $a_{i,\eta}$ and $b_{i,\eta}$ are estimated parameters. For both dried and water-saturated samples the value of $T_{0\eta} = 165.06$ K was used. For the 1,3-dialkypyridinium-based cation, additional experimental data taken from literature[25−30] were used, aiming at obtaining a more global group contribution estimation.

Experimental data together with the correlation obtained from eq 2 are illustrated in Figure 3 for the pure ILs. Figure 4 presents the same correlation for water-saturated samples. Table 10 presents the parameters A_η and B_η. Maximum relative deviations between experimental values and those calculated by eq 2 are in the order of 7.40 % for the dried ILs and 0.10 % for the water-saturated. Both dried and water-saturated samples showed higher deviations for the minimum temperature.

New group contributions for positional isomers were estimated, taking into account different substitution positions for the alkyl chains at the pyridinium cation. Figure 3 shows that the group contribution method coupled to the VTF method[32] yields satisfactory results for the studied ILs. Larger deviations were observed for $[C_8pyr][NTf_2]$. Although this method was developed specifically for ILs, it does not take into account the formation of nano- and microdomains, a situation that becomes increasingly relevant with increasing alkyl chain length. The new parameters calculated for the group contribution method are displayed in Table 11.

Conclusions

The results presented in this work add useful data on a number of new ILs to the growing database of IL properties, a database which is essential for the many applications of these liquids currently under exploration. With that aim, in this work, experimental data for the density and viscosity of dried and water-saturated samples of six pyridinium-based ILs, combined with the anion bis[(trifluoromethyl)sulfonyl]amide, in the temperature range between (298.15 and 363.15) K and at atmospheric pressure, were presented.

As expected, the increase of the alkyl chain length in the pyridinium cation promotes an increase in the viscosity and a decrease in density. The presence of structural and positional isomerism was shown to largely affect the viscosity, while no significant differences were observed in density. In density this effect can be seen as a single longer alkyl chain, independent of the position of the second substituted group, being therefore an exclusively additive property. On the other hand, care must be taken when dealing with properties such as viscosities, since they largely depend on the intermolecular interactions (hydrogen-bonding, dispersive, and Coulombic interactions). The VTF method combined with a group contribution was found to be very successful in the prediction of the viscosity data, and new groups were proposed aiming at completing such a database.

Finally, the water content has strong effect on the viscosity, but only a very small effect on density was observed. In fact, since these isomers present different water saturation contents, the viscosities and densities can be altered.

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