

Anion Influence on Thermophysical Properties of Ionic Liquids: 1-Butylpyridinium Tetrafluoroborate and 1-Butylpyridinium Triflate

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The thermophysical properties of two pyridinium-based ionic liquids, 1-butylpyridinium tetrafluoroborate and 1-butylpyridinium triflate, have been measured. Thus, densities, refractive indices, speeds of sound, viscosities, surface tensions, isobaric molar heat capacities, and thermal properties have been experimentally determined over a wide range of temperatures. The comparison of the properties of the two ionic liquids has allowed us to analyze in detail the anion influence. Moreover, useful derived properties have been calculated from the results. On the other hand, the influence of the lack of a substituent in the cation has been evaluated when properties of 1-butylpyridinium tetrafluoroborate have been contrasted to those of 1-butyl-*n*-methylpyridinium tetrafluoroborate, (*n* = 2, 3, or 4). The study has been carried out paying special attention to interactions between ions in order to elucidate the desired relationship between properties and structural characteristics of ionic liquids.

Introduction

The study and understanding of the characteristics of ionic liquids (ILs) are the necessary previous steps for developing their potential as new solvents.^{1,2} From a theoretical point of view, their thermophysical behavior is the result of the superposition of many molecular phenomena and thus, it is very useful to have the widest possible set of properties of a given liquid to get the broadest view of the phenomena as well as the maximum molecular information possible. Additionally, the knowledge of these properties has a practical importance since they are fundamental to consider the suitability of these compounds for industrial application. Physical properties such as density and viscosity are closely related to chemical industrial processes involving heat and mass transfer phenomena. For instance, chemicals with high densities values are advantageous to the phase separation of immiscible liquids mixtures. On the other hand, high values of density or viscosity may be a limiting factor in industrial application, since this would lead to a higher power requirement of mixing. Both the refractive index and speed of sound provide some information about bulk behavior, whereas the heat capacity is important for the evaluation of these compounds from the thermal storage and heat transfer applications point of view. Besides, this property is necessary for applications in which heat has to be added or removed. The feasible temperature operating range for the study of ILs can be evaluated from the examination of their thermal behavior.

Scientists are currently carrying out a great labor in the characterization of these fluids since the huge potential of them has been discovered. Thus, the effort in the analysis of several of their properties is reflected in the number of works related with the ionic liquids.^{3–8} Nevertheless, a hardest study is still necessary to perform a rational revision of their features

depending on fundamental factors such as the ionic structures and interactions between ions. This learning will give us the possibility to design ILs in the future with specific properties.

To extend and complete a comprehensive study of several pyridinium-based ILs that our research group is developing,^{9–13} we present now the thermophysical properties of two ILs, 1-butylpyridinium tetrafluoroborate ([bpy][BF₄]) and 1-butylpyridinium triflate ([bpy][CF₃SO₃]). Several thermodynamic and transport magnitudes such as density, speed of sound, refractive index, surface tension, isobaric molar heat capacity, kinematic viscosity, and thermal properties of the studied ILs have been experimentally determined. Measurements were carried out in a wide range of temperatures from 278.15 to 328.15 K for [bpy][BF₄] and from 298.15 to 328.15 K for [bpy][CF₃SO₃]. From the experimental results, we have obtained coefficients of thermal expansion, molar refractions, and dynamic viscosities at the studied temperatures. Moreover, we have calculated entropies and enthalpies of surface formation per unit surface area from surface tension experimental data. Results for [bpy][BF₄] and [bpy][CF₃SO₃] have been compared to analyze the influence of the anion on their thermophysical properties. Furthermore, experimental data for [bpy][BF₄] have been contrasted with those obtained previously for 1-butyl-2-methylpyridinium tetrafluoroborate ([b2mpy][BF₄]), 1-butyl-3-methylpyridinium tetrafluoroborate ([b3mpy][BF₄]), and 1-butyl-4-methylpyridinium tetrafluoroborate ([b4mpy][BF₄]) to discuss how the lack of the alkyl substituent in the pyridinium cation affects to the behavior of these fluids.^{9,12} We have to mention that after revision of literature, we have found some previous references of densities, viscosities, and isobaric molar heat capacities of [bpy][BF₄] at several temperatures and therefore we also perform a comparison with these data along the paper^{14–20}

Experimental Section

The ionic liquids 1-butylpyridinium tetrafluoroborate (99%), and 1-butylpyridinium triflate (99%) were provided by IoLiTec.

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With the aim of decreasing the water content as much as possible, the ILs were dried for 24 h under a vacuum of ca. 0.05 kPa under stirring and stored before use in a desiccator. The water contents of the samples were less than 500 ppm as determined by Karl Fischer titration. The absence of significant impurities was checked by ^1H and ^{19}F NMR analyses using a Bruker AVANCE-400 spectrometer. Measurements were performed in a range of temperatures from 278.15 K for [bpy][BF₄] or 298.15 K for [bpy][CF₃SO₃] to 328.15 K with an interval of 2.5 K between each temperature.

Densities, ρ , and speed of sounds, u , of the pure compounds were determined simultaneously with an Anton Paar DSA 5000 vibrating tube densimeter and sound analyzer, automatically thermostatted within ± 0.001 K. By measuring the damping of the oscillation of the U-tube caused by the viscosity of the filled-in sample, the DSA 5000 automatically corrects viscosity related errors in the density. The calibration was carried out with ultra pure water supplied by SH Calibration service GmbH, and dry air. The final uncertainty of density and speed of sound can be estimated in $\pm 10^{-5} \text{ g}\cdot\text{cm}^{-3}$ and $\pm 0.01 \text{ m}\cdot\text{s}^{-1}$ respectively.

Refractive indices, n_D , corresponding to 589.3 nm sodium D wavelength were measured using a high precision automatic refractometer Abbemat-HP DR. Kernchen. The temperature of the sample was controlled within ± 0.01 K by a built-in Peltier device, while another Peltier thermostat was used to keep constant the temperature of the internal refractometer components. The apparatus was calibrated with deionized double-distilled water. The corresponding uncertainty is $\pm 1 \times 10^{-6}$.

Surface tensions, σ , of the pure liquids were determined using a drop volume tensiometer Lauda TVT-2.²¹ This tensiometer measures the volume of a drop detaching from a capillary of known diameter, and needs densities to calculate surface tension from volume drop determinations. The temperature was kept constant within ± 0.01 K by means of an external Lauda E-200 thermostat. Details of the experimental procedure can be found elsewhere.²² The uncertainty of the measurement is $\pm 0.01 \text{ mN}\cdot\text{m}^{-1}$ of the final value of surface tension.

Kinematic viscosities, ν , were determined using an Ubbelohde viscosimeter with a Schoot-Geräte automatic measuring unit model AVS-440. The temperature was kept constant within ± 0.01 K by means of a Schoot-Geräte thermostat. The viscosimeter constant was provided by the supplier and was $K = 0.9822 \text{ mm}^2\cdot\text{s}^{-2}$. CaCl₂ drying tubes were used to protect the samples from moisture in the air. The uncertainty of the time flow measurements is ± 0.01 s, and the corresponding uncertainty in the kinematic viscosity is $\pm 0.01 \text{ mm}^2\cdot\text{s}^{-1}$. From density and kinematic viscosity the absolute viscosity, η , can be obtained: $\eta = \rho\cdot\nu$, and the estimated uncertainty in the absolute viscosity is $\pm 0.01 \text{ mPa}\cdot\text{s}$.

Isobaric molar heat capacities of the supercooled liquid of both ionic liquids were determined using a differential scanning calorimeter Q2000 from TA Instruments equipped with a refrigerated cooling system. The melting transition (429.76 K, $3.296 \text{ kJ}\cdot\text{mol}^{-1}$) of a standard Indium sample has been used to calibrate the temperature and energy. The zero-heat flow procedure described by TA Instruments has been followed for the heat capacity measurements using, as a reference compound, a synthetic sapphire sample. All these experiments allow to estimate an overall uncertainty of ± 0.5 K in temperature, and $\pm 3\%$ in the heat capacities. The measurements were carried out using around 15 mg of sample sealed at room temperature in hermetic aluminum pans with a mechanical crimp. Previously, the sample was submitted to a drying vacuum process and it was only exposed to the air only a few minutes during the

sealing step. Once inside the calorimeter and from room temperature, the [bpy][BF₄] and [bpy][CF₃SO₃] liquid samples were cooled down to 278 and to 295 K, respectively, and after thermal equilibration a heating thermogram was performed at a scan rate of $10 \text{ K}\cdot\text{min}^{-1}$ up to 343 K.

DSC experiments were also performed in the 100–350 K temperature range, using a differential scanning calorimeter Q1000 from TA Instruments with the LNCS accessory in order to study the glass transition, solid-to-solid transition, crystallization, cold crystallization, and melting processes of both ionic liquids. In this case, the experiments were performed in a helium gas atmosphere and with around 5 mg of sample. Temperature and enthalpy calibrations were also performed using a standard sample of Indium. The same process was performed for both ionic liquids: from room or higher temperature, the liquid sample was cooled down to 100 at $10 \text{ K}\cdot\text{min}^{-1}$ and a subsequent heating up to 340 K at the same scan rate was recorded. Since the results for the [bpy][BF₄] support a slow crystallization rate, we also perform an additional measurement in which a new fresh sample from the liquid state is cooled down to 220 K, maintained during 15 min and then cooled down to 100 K. This process has allowed increase substantially the amount of crystalline phases.

Reported glass transition temperatures, T_g , have been obtained from the midpoint of the heat capacity jump on heating whereas solid–solid, melting and cold crystallization temperatures have been taken to be the maximum temperature of the endothermic and exothermic peaks on heating. For the fast crystallization on cooling shown by the triflate compound, the onset temperature is reported.

Results and Discussion

Values of density, speed of sound, refractive index, molar refraction, surface tension, isobaric molar heat capacity, kinematic viscosity, and dynamic viscosity of the ILs [bpy][BF₄] and [bpy][CF₃SO₃] at the studied temperatures can be found in the Supporting Information.

A linear relationship between thermodynamic properties and temperature for the studied ILs has been obtained. In this way, experimental results have been correlated using the following equation

$$Y = AT + B \quad (1)$$

where Y is the studied property, and A and B are adjustable parameters. The best linear fitting parameters and the standard deviations of each property for both ILs are gathered in Table 1.

Before tackling the analysis of experimental results, it is necessary to highlight several characteristics of the evaluated ions. Since both ILs share the cation, it is the choice of the anion which in this case makes the differences. Thus, size, shape, and structure of anions must be taken into account to interpret the unlike behavior of these ILs. It has been found that a higher formula weight for the triflate anion is corresponded with a greater size than that for the tetrafluoroborate anion, although tabulated volumes for such ions are not the same depending on the reference.^{23,24} The tetrafluoroborate anion seems to exhibit a low surface electrical charge density since its highly electro-negative fluorine atoms contribute to the distribution of the anionic charge of borate.³ On the other hand, the more pronounced anionic charge localization in the anionic structure of [CF₃SO₃][−] compared to [BF₄][−], makes them interacting sites with the cation.³ The effect of the positional isomeric cationic structure on properties has been previously evaluated,¹² and

TABLE 1: Fitting Parameters and Standard Deviations for the Studied Properties

property	ionic liquid	A	B	s
$\rho/\text{g}\cdot\text{cm}^{-3}$	[bpy][BF ₄]	-6.8467×10^{-4}	1.41795	0.00011
	[bpy][CF ₃ SO ₃]	-7.6688×10^{-4}	1.54295	0.00003
n_D	[bpy][BF ₄]	-2.64447×10^{-4}	1.524711	0.000014
	[bpy][CF ₃ SO ₃]	-2.81821×10^{-4}	1.542299	0.000073
$u/\text{m}\cdot\text{s}^{-1}$	[bpy][BF ₄]	-2.29100	2283.87	1.21
	[bpy][CF ₃ SO ₃]	-2.11209	2045.25	0.30
$\sigma/\text{mN}\cdot\text{m}^{-1}$	[bpy][BF ₄]	-0.06236	65.24	0.03
	[bpy][CF ₃ SO ₃]	-0.04151	48.85	0.02
$C_p/\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$	[bpy][BF ₄]	0.5271	238	1
	[bpy][CF ₃ SO ₃]	0.7392	250	1

property	ionic liquid	η_0	B	T_0	s
$\eta/\text{mPa}\cdot\text{s}$	[bpy][BF ₄]	0.124675	840.154	180.781	0.54
	[bpy][CF ₃ SO ₃]	0.135790	867.776	171.272	0.08

therefore this work is focused on the lack of the substituent group in the pyridine ring.

The linear decreasing of density values with temperature for the studied ILs is illustrated in Figure 1. This property changes with a similar slope for both ILs, being values for [bpy][CF₃SO₃] considerably greater than those for [bpy][BF₄]. It is in agreement with previous works of imidazolium-based ILs in which it has been found a direct correlation between density and formula weight of the anion.^{3,4,11} Furthermore, an analysis in terms of the substituent position reveals that [bpy][BF₄] is denser than the isomeric compounds [b2mpy][BF₄], [b3mpy][BF₄], and [b4mpy][BF₄].^{9,12} According to these results, the lack of the methyl group in the cation seems to favor a better structural organization of the ions inside the fluid, probably due to a possible relatively close approach position of the constituent ions. In this case, the preceding relationship between property and formula weight is not obeyed. A detailed revision of literature has shown that density as a function of temperature has been reported before for [bpy][BF₄].^{17–19} As can be seen in

TABLE 2: Properties of [bpy][BF₄] at Different Temperatures and Comparison with Literature Values

T/K	$\rho^{\text{exp}}/\text{g}\cdot\text{cm}^{-3}$	$\rho^{\text{lit}}/\text{g}\cdot\text{cm}^{-3}$	$\eta^{\text{exp}}/\text{mPa}\cdot\text{s}$	$\eta^{\text{lit}}/\text{mPa}\cdot\text{s}$
283.15	1.22421	1.2240 ¹⁹	457.4	247 ¹⁵ 464.49 ¹⁹
298.15	1.21370	1.2144 ¹⁷ 1.2134 ¹⁹	160.3	102 ¹⁵ 163.26 ¹⁹
313.15	1.20372	1.2053 ¹⁷ 1.203 ¹⁸ 1.2032 ¹⁹	71.1	51 ¹⁵ 70.29 ¹⁹

Table 2, their values are in a good agreement since differences between series of data are below 0.2%.

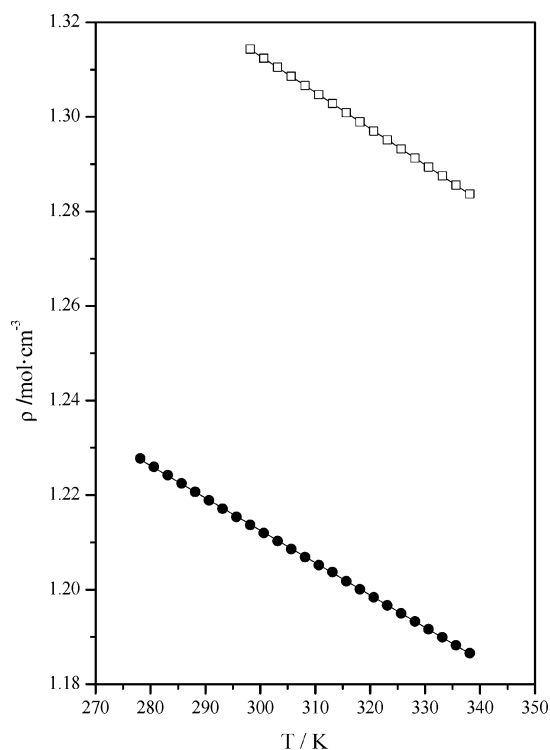
Coefficients of thermal expansion, α , have been calculated from experimental densities. A decreasing of this parameter when temperature rises is derived for the ILs and their values at 298.15 K are $5.70 \times 10^{-4}\text{ K}^{-1}$ and $5.97 \times 10^{-4}\text{ K}^{-1}$ for [bpy][BF₄] and [bpy][CF₃SO₃], respectively. They are in a similar order of magnitude than previous investigating ILs, suggesting a thermal behavior practically independent of the ionic nature.¹⁷

Just as density, refractive index also decreases with temperature, and experimental data are slightly greater when the triflate anion is joined to the cation instead of the tetrafluoroborate anion. Experimental results are represented in Figure 2. On the other hand, data for [bpy][BF₄] are lower than those for the ILs with a methyl group in the cation in their different positions.^{9,12}

A useful property such as the molar refraction, R_m , which provides an idea of the hard core volume of one mol of molecules, could be calculated from the combination of density and refractive index. Their values for both ILs are gathered in the Supporting Information together with the rest of properties. From them and taking into account the molar volume for the liquids, it is possible to derive the molar free volume, that is, the unoccupied volume by ions. As expected, the hard core volume and the free molar volume for [bpy][BF₄] are lower than those for [bpy][CF₃SO₃], [b2mpy][BF₄], [b3mpy][BF₄], and [b4mpy][BF₄].^{9,12}

Speeds of sound for the considered ILs are depicted in Figure 3. In this case, experimental data for [bpy][BF₄] are considerably greater than those for the IL containing the triflate anion. Besides, the former presents values close and between [b3mpy][BF₄] and [b4mpy][BF₄], and as the preceding compounds it shows smaller values than the isomeric IL with the methyl group in position 2.^{9,12} This fact could indicate a dissimilar structural organization for [b2mpy][BF₄].

Surface tension values are showed in Figure 4. This property is very useful from the theoretical viewpoint since it results of several phenomena that can take place not only in the surface

**Figure 1.** Density as a function of temperature. (●) [bpy][BF₄], (□) [bpy][CF₃SO₃].

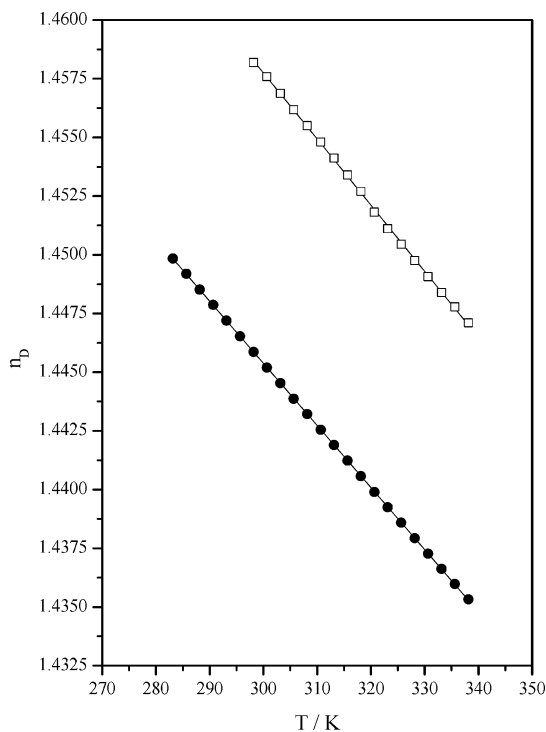


Figure 2. Refractive index as a function of temperature. (●) [bpy][BF₄], (□) [bpy][CF₃SO₃].

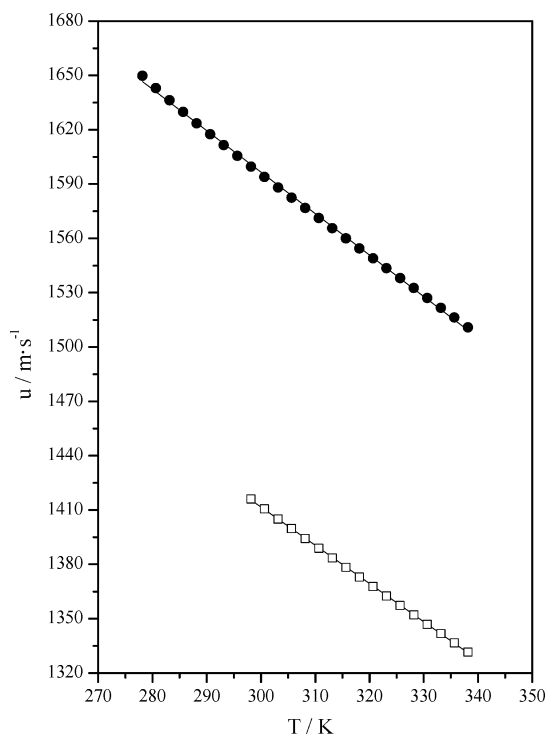


Figure 3. Speed of sound as a function of temperature. (●) [bpy][BF₄], (□) [bpy][CF₃SO₃].

of a liquid but also in the bulk.^{25–27} In this manner, it provides a better understanding of structure, which includes aspects as surface composition and molecular orientation, and cohesive forces of the pure liquids, being strongly dependent on the structural characteristics of ions. At the light of results, it can be seen that [bpy][CF₃SO₃] has significantly smaller values for this property than those for [bpy][BF₄]. In this way, it could be indicative of stronger interactions inside the fluid for the IL containing the tetrafluoroborate anion. Moreover, the spherical

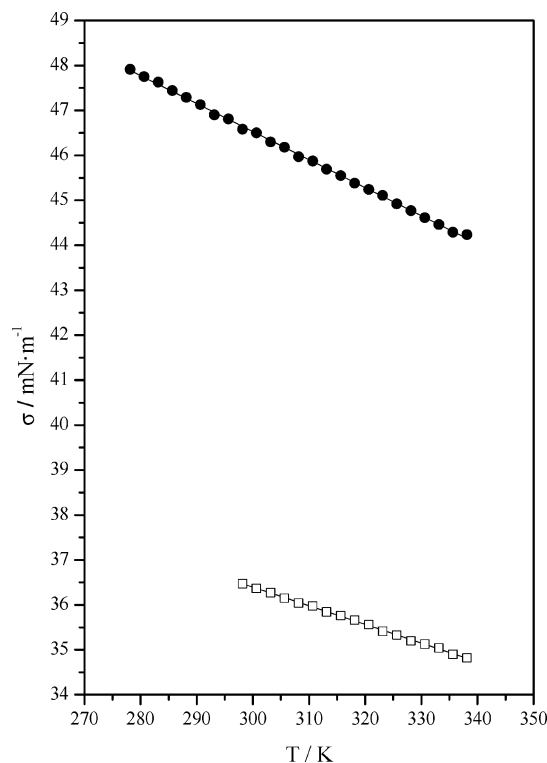


Figure 4. Surface tension as a function of temperature. (●) [bpy][BF₄], (□) [bpy][CF₃SO₃].

shape of [BF₄][−] could facilitate a better organization, an improved confinement of ions in the surface than that achieved with a larger anion as triflate. It also would be traduced in higher values for [bpy][BF₄]. In addition, greater values for the compound without a methyl group are found when the effect of introducing it is evaluated. In a similar way as in the density evaluation, it seems that a group in the cation could make difficult a good arrangement of ions, not only in the bulk, but also in the surface.^{9,12} At this point, it is not reliable to present a more detailed description of the interface; it would be necessary for most experimental measurements such as angle-resolved X-ray photoelectron spectroscopy or sum frequency generation to elucidate the mode in which they are structured.⁷ From the experimental surface tension measurements, the entropy and enthalpy of surface formation per unit surface area can be evaluated. Given that the experimental values vary linearly with temperature, the entropy of surface formation per unit surface area is in this range independent of temperature. Entropy values are 0.06 mN·m^{−1}·K^{−1} for the ionic liquid [bpy][BF₄] and 0.04 mN·m^{−1}·K^{−1} for [bpy][CF₃SO₃]. The enthalpy of surface formation per unit area changes slightly with temperature, with values of 65.43 mN·m^{−1} and 48.84 mN·m^{−1} for [bpy][BF₄] and [bpy][CF₃SO₃] at 298.15 K, respectively. Comparing the surface quantities, we notice that both surface parameters for [bpy][BF₄] are higher than for [bpy][CF₃SO₃] while they are very similar to that for [b2mpy][BF₄], [b3mpy][BF₄], and [b4mpy][BF₄].^{9,12}

As it is shown in Figure 5, temperature dependence on the dynamic viscosity values presents convex curved profiles. Thus, experimental data have been fitted to a Vogel–Fulcher–Tamman equation^{28–30}

$$\eta = \eta_0 \exp[B/(T - T_0)] \quad (2)$$

where η_0 , B , and T_0 are the adjustable parameters collected in Table 1. Results show that dynamic viscosity decreases sig-

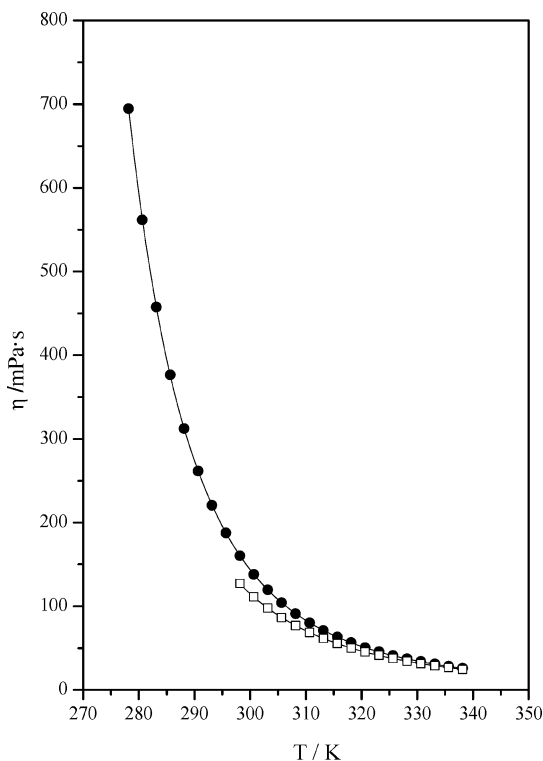


Figure 5. Viscosity as a function of temperature. (●) [bpy][BF₄], (□) [bpy][CF₃SO₃].

nificantly with temperature at low temperatures and achieves a moderate descent when temperature rises. Experimental data for [bpy][CF₃SO₃] are slightly smaller than those obtained for [bpy][BF₄], getting the greatest differences between them at 298.15 K. This property is strongly influenced by both interactions between the different types of ions and their ability to move inside the fluid. The results show that larger size and larger formula weight of the anion do not correspond with causing larger viscosity of the ILs. It is in agreement with conclusions derived from other authors when this transport property has been evaluated.^{15,31} A possible explanation proposed by Watanabe¹⁵ could describe the obtained results taking into account the nature of the anions. They indicated that the ion pairs and neutral ion aggregates formation can reduce the ionic concentration in the liquid and decreases the electrostatic forces between the ionic species, reducing in this way the viscosity of the fluid. In our case and considering the capacity of triflate for interacting with the cation, this suggestion might contribute to understand the behavior of [bpy][CF₃SO₃]. Moreover, stronger interactions between ions in [bpy][BF₄], as it has been deduced by the surface tension data, could also justify their larger values. On the other hand, the values for [bpy][BF₄] are lower than those for the isomeric compounds.^{9,12} In this case, the more spherical shape of the cation in [bpy][BF₄] due to the lack of the methyl group, can be the reason of these results, since it makes easier the flow of their ions. We have found two references in literature related to the viscosity of [bpy][BF₄] at different temperatures.^{15,19} One of them falls in the range of our measurements, being the difference between the series data of the order of ca. 2%,¹⁹ whereas our results are different from the other one.¹⁵ Comparison between experimental values and those reported earlier are shown in Table 2.

Isobaric molar heat capacities of the supercooled liquids are represented in Figure 6. This property shows a linear behavior with temperature for both compounds. The data for [bpy][BF₄] are in agreement with those reported recently by Zhang et al.

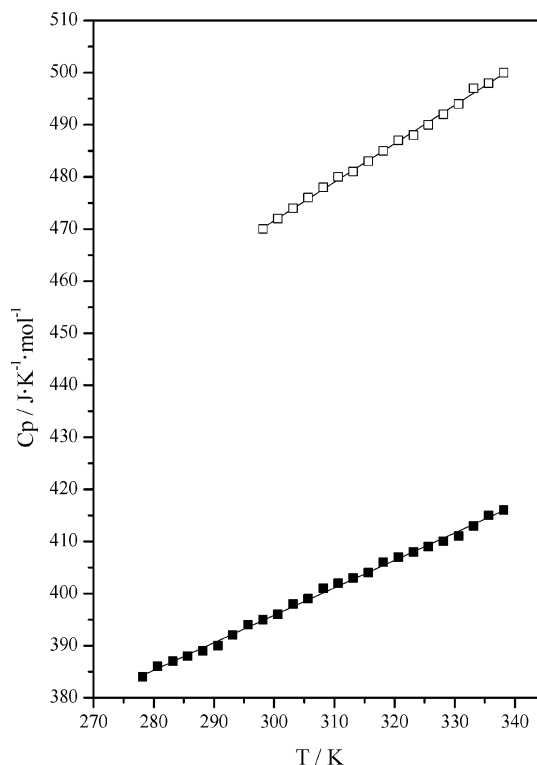


Figure 6. Isobaric heat capacity as a function of temperature. (●) [bpy][BF₄], (□) [bpy][CF₃SO₃].

that are only a 3% lower than our results.¹⁶ As expected, greater heat capacity values for the IL containing the triflate anion have been found, since a higher number of atoms are present in this anion in comparison with the tetrafluoroborate molecule resulting in an increase of the number of energy storage modes. We also want to emphasize that the additional heat capacity contribution for the [bpy][CF₃SO₃] respect to the [bpy][BF₄] (for example, 76 J·mol⁻¹·K⁻¹ at 300 K) can be nicely predicted through the group contribution method developed by Gardas and Coutinho based on experimental ionic liquid heat capacity data. Following this empirical method, only the difference between the contributions to the heat capacity of the two different anions must be evaluated since the cation is the same on both compounds and the calculation at 300 K gives 77 J·mol⁻¹·K⁻¹ in perfect accordance with the experimental value.³² On the other hand, data for [bpy][BF₄] are slightly higher than those found for [b2mpy][BF₄],¹² but the difference is around 3–4% and therefore it is not significant considering the accuracy of the heat capacity measurements. However, the presence of an additional methyl group in the cation must give an extra contribution in accordance with the previous discussion. This additional contribution was present in the [b3mpy][BF₄] and [b4mpy][BF₄] as we explained in ref 12.

Figure 7 shows the DSC curves for both compounds during cooling and successive heating at 10 K·min⁻¹. Let us first describe the [bpy][BF₄] ionic liquid. On cooling there is not crystallization peak and only a heat capacity step of ΔC_p (cooling) = 95 ± 5 J·mol⁻¹·K⁻¹ at T_g (cooling) = 185.5 ± 0.5 K is observed corresponding to its glass transition. These results indicate that the [bpy][BF₄] has a slow crystallization rate, and that at low temperature the stable supercooled liquid forms at this cooling scan rate only a glassy state. On heating and after the glass transition (T_g (heating) = 188.5 ± 1 K, ΔC_p (heating) = 105 ± 15 J·mol⁻¹·K⁻¹), the compound undergoes a cold crystallization (centered at T_{cc} = 245 K and with an enthalpy content of ΔH_{cc} ≈ 3 kJ·mol⁻¹) and finally the melting

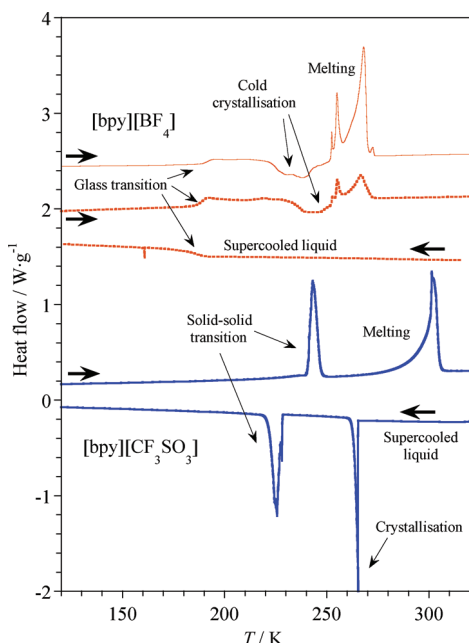


Figure 7. Differential scanning calorimetry results. (a) [bpy][BF₄], (b) [bpy][CF₃SO₃].

happens showing three peaks at $T_m = 253, 255.1,$ and 266.8 K (± 0.25 K) and with $\Delta H_m \approx 3$ kJ·mol⁻¹. The comparison with the heat capacity measurements performed by Zhang et al.¹⁶ has to be done considering the different thermal history undergone by the samples. Using the adiabatic calorimeter, a large amount of sample was slowly cooled from room temperature down to 80 K allowing the crystallization and producing a state mixture of amorphous (glassy) and crystalline phases. On heating, they report a glass transition at 194.09 K with a heat capacity step of around 70–75 J·mol⁻¹K⁻¹, the absence of cold crystallization, and the melting with only one peak at 279.79 K and with 8.45 kJ·mol⁻¹ as enthalpy content. In our sample, the fast cooling rate combined with the slow crystallization rate will increase the amount of glassy state at low temperature. This is in agreement with our larger ΔC_p , lower glass transition temperature and with the fact that $\Delta H_{cc} \approx \Delta H_m$ supporting that the crystalline fraction at low temperature is small ($\sim 100\%$ of amorphous state) and then only the crystals formed at the cold crystallization melt. On the other hand, because of the fast heating and during the cold recrystallization, defective and small crystals of different crystalline modifications or phases can be formed showing lower melting temperatures than the reported by Zhang.¹⁶ Also, Noda et al.^{14,15} have reported DSC measurements on the [bpy][BF₄] performed at 10 K·min⁻¹ on cooling and heating. During the cooling and in agreement with our results, their sample undergoes only the glass transition. On heating, this thermal process happens at 206.45 K (onset glass transition temperature of 202 K), and it is followed by the cold crystallization centered at 261 K (onset cold crystallization temperature is 251 K) with $\Delta H_{cc} = 8.35$ kJ·mol⁻¹ and finally, the solid melts at 288.45 K (onset melting temperature is 272 K) with $\Delta H_m = 10.2$ kJ·mol⁻¹. The sequence is in qualitative agreement with our experimental results although some discrepancies respect to the characteristic temperatures and enthalpies contents are present with Zhang¹⁶ and with our data. It is quite surprising the high value of T_g , and T_m , even larger than the value obtained by the slow cooling performed in the adiabatic calorimetry. Different thermal histories during the crystallization can be behind the detected differences.

To increase the crystalline fraction at low temperature and to detect possible changes in the thermal events due to a different thermal history, we cool down a new fresh [bpy][BF₄] sample from room temperature to 220 K in 3 min and after the sample was held at this temperature during 15 min and finally cooled to 100 K in 5 min. The subsequent heating thermogram is shown in Figure 7. In this case, the glass transition appears at $T_g = 192 \pm 0.5$ K with $\Delta C_p = 67 \pm 5$ J·mol⁻¹K⁻¹, the exothermic anomaly corresponding to the cold crystallization is centered at around 235 K with $\Delta H_{cc} \approx 5$ kJ·mol⁻¹, and the melting, which still keeps the complex structure, shows peaks at $T_m = 252.3, 255, 268.1,$ and 272.5 K and with $\Delta H_m \approx 10.5$ kJ·mol⁻¹. Clearly, the fact that ΔH_m is the double of ΔH_{cc} and the decrease of the heat capacity step at the glass transition indicates that a higher fraction of the sample was allowed to crystallize during the cooling process. Additionally, the glass transition temperature has increased from 188 to 192 K, approaching, as expected, the value reported by Zhang.¹⁶ This increase is in accordance with the reduction of the species (anions and cations) mobility due to the confined effect produce by the crystalline part. The melting process shows the same peaks detected previously (with higher total enthalpy content) but an additional small peak appears at 272.5 K, close to the melting temperature reported by Zhang.¹⁶ In accordance with these results, we can suppose that if the sample during the cooling would spend more time in the 200–250 K temperature range (as probably happens in the work of Zhang using adiabatic calorimetry), the different crystalline phases or modifications could evolve to a most stable crystalline form and then during the subsequent heating, the melting peak at around 272 K would increase while the others would disappear. The [bpy][CF₃SO₃] behaves differently as it is shown in Figure 7. During the cooling from 340 at 10 K·min⁻¹, the sample maintains the liquid state down to $T_c = 265.25$ K (onset crystallization temperature) where the compound easily crystallizes. During this process, fast and energetic, a self-heating of the sample is produced since the peak maximum temperature is higher than the observed peak onset.^{33,34} The crystallization enthalpy content is $\Delta H_c = 10.8$ kJ·mol⁻¹. The [bpy][CF₃SO₃] seems to reach, after crystallization, a state that is almost fully crystalline since no glass transition is detected down to 100 K. However, a solid–solid transition is observed at $T_{ss} = 225.7$ K with $\Delta H_{ss} = 7.05$ kJ·mol⁻¹, which may correspond to the transformation to a different crystalline phase more stable at low temperature. Also note that the 1-butyl-3-methylimidazolium trifluoromethanesulfonate [bmim][CF₃SO₃]^{3,4} and the 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [emim][CF₃SO₃]³⁵ also undergo a crystallization without glass transition indicating that the triflate anions seems to favor the crystallization may be due to stronger interaction between the anion and cation. During the subsequent heating, this phase transition appears at $T_{ss} = 243.1$ K (hysteresis of 17.4 K) with $\Delta H_{ss} = 6.4$ kJ·mol⁻¹ and finally the melting happens as a single peak at $T_m = 301.4$ K and with $\Delta H_m = 12$ kJ·mol⁻¹.

Conclusions

A thermophysical characterization of two pyridinium-based ILs, 1-butylpyridinium tetrafluoroborate and 1-butylpyridinium triflate, has been performed in structural and energetic terms by means of the experimental determination of several properties such as density, viscosity, or isobaric molar capacity in a broad range of temperatures, paying special attention to the effect of the anion nature on the features of the compounds. Thus, size, shape, and structure of ions have been taken into account to

interpret the unlike behavior of these ILs. Moreover, the effect of the lack of a substituent in the cationic structure in this family of ILs has been analyzed in detail when results have been contrasted with those previously obtained by our investigation group.

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Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.

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