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Influence of the alkyl chain cation position on thermal behaviour: (1,2) and (1,4) pyridinium Bis(trifluoromethylsulfonyl)imide - Based ionic liquids

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ABSTRACT

This work focuses on the influence of the position of the alkyl chain cation on the thermal behavior and on the values of the heat capacities, for ionic liquids with pyridinium cation and bis(trifluoromethylsulfonyl)imide anion To achieve this objective, thermal properties such as, melting, freezing, cold crystallization and glass transition temperatures and heat capacities (in the temperature range from 293.15K to 363.15K) have been experimentally determined for several ionic liquids using differential scanning calorimetry. The ionic liquids chosen were: 1-alkyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide (1,2) $C_nMpyNTf_2$ (n = 2,3,4) and 1-alkyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide (1,4) $C_nMpyNTf_2$ (n = 2,3,4). The results obtained were compared with those published by the group in a previous paper concerning 1-alkyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide (1,3) $C_nMpyNTf_2$ (n = 2,3,4) ionic liquids. Moreover, the results from this essay were also compared with literature values. Three thermal behaviors were found for the studied ionic liquids: those characterized by the presence only glass transition, those presenting only freezing and melting transitions and those with subcooling phenomenon.

1. Introduction

Ionic liquids (ILs) are compounds composed entirely of ions that are liquid at temperatures close to room temperature and they are called “green” because they have negligible vapor pressure. Another important characteristic of ionic liquids is that by adequate selection of the anion and cation, an ionic liquid suitable for a specific application can be synthesized.

In addition to the two mentioned aspects of ionic liquids, other properties well known as thermal stability and high solubility are also important. Their low melting points and their high values of heat capacities must be highlighted. These last two features make them possible substitutes for conventional heat transfer fluids (synthetic organic fluids and silicone based fluids). There is some work where the use of ionic liquids as fluids for heat transfer operations has been reported [1,2], such as their application as an alternative means for thermal storage in solar thermal energy systems [3].

Due to the multiple possibilities of synthesizing ionic liquids and the challenge to synthesize the appropriate ionic liquid for a specific application, it is important to determine and to know the properties of the largest possible number of ionic liquids.

Thermal properties are needed to set the feasible temperature operation range for a particular fluid and heat capacities are necessary to estimate heating and cooling requirement as well as heat-storage capacity.

The aim of this work is to study the influence of the position of the ethyl, propyl or butyl substituent of the cation of the ionic liquid on the thermal behavior and on heat capacities of 1-alkyl-X-methylpyridinium bis(trifluoromethylsulfonyl)imide (1,X) $C_nMpyNTf_2$ (n = 2,3,4) ionic liquids, because although there are several studies about these ionic liquids, they concern substituents with (1,3) position the radicals [4,5]. Regarding the (1,2) and (1,4) positions there are only two studies available in the literature [6,7].

Thermal behavior of several pyridinium bis(trifluoromethylsulfonyl)imide-based ionic liquids was analyzed and their heat capacities were determined as function of temperature using differential scanning calorimetry (DSC). To assess the influence of the alkyl chain position, the thermal behavior of 1-alkyl-2-methylpyridinium

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bis(trifluoromethylsulfonyl)imide (1,2) ($C_nMpyrNTf_2$) with n = 2,3,4 and 1-alkyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide (1,4) ($C_nMpyrNTf_2$) with n = 2,3,4 has been analyzed, and the heat capacities of the same ionic liquids measured. Besides, the results obtained in this study were compared with those from a previous publication of the group, for the 1-alkyl-3-methylpyridinium bis(-trifluoromethylsulfonyl)imide (1,3) ($C_nMpyrNTf_2$) with n = 2,3,4ionic liquids [8]. Finally, both obtained results of thermal analysis and heat capacities were further compared with literature values [6,7].

2. Experimental

2.1. Chemicals

The structure, abbreviations and CAS number of the IL used in this work and those of the ILs used in a previous work [8], are presented in Table 1.

All the ionic liquids used in this work were acquired to IoLitec. The mole fraction purity, given by the source, and the water content determined in the laboratory after purification are shown in Table 2. The ionic liquids were purified by vacuum drying (at 343K and 0.2 Pa) for at least 48 h before use. It is important to mention that in this case, the ionic liquids have also been dried in situ within DSC before each experiment, the sample was heated at $T = 393.15$ K for 30 min inside the furnace. The water content was determined using a Coulometric KF titrator, model C20 using Hydranal-Coulomat CG and Hydranal-Coulomat AG as cathodic and anodic titrant. The standard uncertainty of the measurement of water content is ±5%.

2.2. Apparatus and procedure

The Mettler-Toledo differential scanning calorimeter (DSC), model DSC822e and the Mettler-Toledo STAR^e software version 9.30 were used to determine and evaluate the experimental data of thermal behavior and the measurement of heat capacities of the pure ionic liquids. This DSC is connected to a liquid nitrogen cooling system in order to reach temperatures as low as 133.15K. Moreover, dry nitrogen is constantly flowing at 50 mL/min for maintain dry and inert atmosphere.

For the thermal analyses, 40 μL aluminum pans hermetically sealed with a pinhole at the top were used for the samples and a similar empty pan also with a pinhole was used as the reference in the furnace. The masses of the samples were among 4 and 8 mg. All the samples were weighed using a Mettler-Toledo AX-205 Delta Range balance with an uncertainty in the measurement of $\pm 3 \times 10^{-4}$ g.

The working protocol followed for the determination of transition temperatures was the following: the samples of ionic liquids were cooled from to 393.15K−133.15K at a rate of 2K·min^{-1} and after this, they were heated from 133.15K to 393.15K at the same rate. Only for the samples presenting a freezing temperature, these were quenched (cooling at 40K min^{-1} and heating at 10K·min^{-1}) with the objective of being able to determine if these samples also had a glass transition temperature. It is important to mention that the rate used in heating and cooling influences some transition temperatures, as reported in a previous study [8] and it is the most important factor in thermal analysis, as crystallization transitions strongly depend on the cooling and heating rate. Due to the special nature of ionic liquids, variations upon heating and cooling rates are useful to study their thermal transitions. Taking into account that at fast rates the phase transition peaks can appear overlapped, while at slow rates these peaks can move apart from each other, a recommended practice is to begin the study of a sample by a scan carried out at a relatively slow heating rate of 2 K min^{-1} to gain better information about the thermal behavior of the sample [9]. For this reason, the protocol and the rates chosen in this study are the same from this previous work [8].

Regarding the understanding of the thermal scans, the melting temperature (T_m) was taken as the onset of an endothermic peak

Table 1
Structure, abbreviations, CAS number and names of ionic liquids.

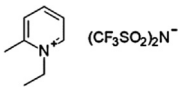
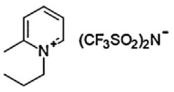
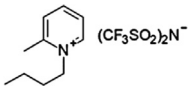
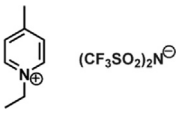
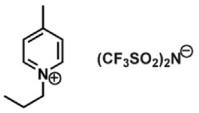
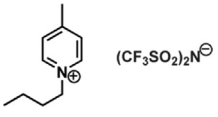
Name	Abbreviation	CAS number	Molecular weight	Structure
1-ethyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide	(1,2) $EMpyNTf_2$	712354-99-9	402.33	
1-propyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide	(1,2) $PMpyNTf_2$	n.a (not applicable)	416.36	
1-butyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide	(1,2) $BMpyNTf_2$	387347-09-5	430.39	
1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide	(1,4) $EMpyNTf_2$	712355-03-8	402.33	
1-propyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide	(1,4) $PMpyNTf_2$	1456878-01-5	416.36	
1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide	(1,4) $BMpyNTf_2$	475681-62-0	430.39	

Table 2
Purity and sources of ionic liquids.

Name	Source	Initial Mole Fraction Purity[a]	Analysis Method[a]	Purification	Water content[b]
1-ethyl-2-methylpyridinium bis(trifluoromethylsulfonyl) imide	IoLitec	0.99	NMR[c]	Vacuum drying (at 343K and 0.2 Pa)	<50 ppm
1-propyl-2-methylpyridinium bis(trifluoromethylsulfonyl) imide	IoLitec	0.99	NMR	Vacuum drying (at 343K and 0.2 Pa)	<85 ppm
1-butyl-2-methylpyridinium bis(trifluoromethylsulfonyl) imide	IoLitec	0.99	NMR	Vacuum drying (at 343K and 0.2 Pa)	<70 ppm
1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl) imide	IoLitec	0.99	NMR	Vacuum drying (at 343K and 0.2 Pa)	<60 ppm
1-propyl-4-methylpyridinium bis(trifluoromethylsulfonyl) imide	IoLitec	0.99	NMR	Vacuum drying (at 343K and 0.2 Pa)	<80 ppm
1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl) imide	IoLitec	0.99	NMR	Vacuum drying (at 343K and 0.2 Pa)	<65 ppm

[a] Initial mole fraction purity and analysis method given by the company.
[b] Standard uncertainty u (water content) = ±5%.
[c] Nuclear magnetic resonance.

(downward deflection of the curve peak) on heating, the freezing temperature (T_f) as the onset of an exothermic peak (upward deflection of the curve peak) on cooling, the glass transition temperature (T_g) as the midpoint of a small heat capacity change on heating from the amorphous glass state to a liquid state, the cold crystallization temperature (T_{cc}) as the onset of an exothermic peak on heating from a subcooled liquid state to a crystalline solid state, the solid-solid transition (T_{s-s}) as the onset of an exothermic or endothermic peak on heating from a crystalline solid state.

For the determination of heat capacities, the sapphire method was used, which consists of an initial isothermal segment for 15 min followed by a dynamic period at 20K·min^{-1} and a final isothermal segment for 15 min; 100 μL aluminum pans hermetically sealed with a pinhole at the top were used.

The Mettler-Toledo differential scanning calorimeter was calibrated for temperature and heat flow using pure zinc, indium, water and heptane and for tau lag by determining onset temperatures at different heating rates [8]. The calculated standard uncertainties are ±1K for the temperature in the thermal analysis, and ±5% for the determination of the molar heat capacity. A more detailed explanation about the procedure can be found in Ref. [9], as well as the calculation of the standard uncertainties [10].

3. Results and discussion

3.1. Thermal analysis

In this work, the determination of the thermal transition temperatures for six 1-alkyl-X-methylpyridinium bis(trifluoromethylsulfonyl)imide ionic liquids was carried out. Table 3 summarizes the results of the thermal analysis of the 1-alkyl-2-methylpyridinium and 1-alkyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ionic liquids determined in this study, together with the values obtained in our previous work for 1-alkyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide the ionic liquids [8] and literature results found in the literature [6,7]. Besides, Fig. 1a) and b) and c) show an example of a thermal scan of each of the three thermal behaviors found.

As can be observed in Table 3, the influence of the position of the alkyl chain cation of the ionic liquid on the thermal behavior does not follow a trend depending on the position of the alkyl chain. Three thermal behaviors were found for the six ionic liquids studied in this work and the for the ionic liquids presented in a previous work when the cooling and heating rate is 2K·min^{-1}.

- Behavior type 1 corresponds to the following ionic liquids: 1-propyl-3-methylpyridinium, 1-butyl-3-methylpyridinium and 1-butyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide.

Ionic liquids that exhibit behavior type 1 are characterized by presenting only vitreous transition; this type of ionic liquids has neither freezing nor melting temperature, that is, they have very little tendency to form crystals, and they are liquids in the entire range of temperatures covered.

An example of behavior type 1 is shown in the thermal scan presented in Fig. 1 a) for the 1-butyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide ionic liquid.

- Ionic liquids 1-ethyl-2-methylpyridinium, 1-propyl-2-methylpyridinium, 1-ethyl-4-methylpyridinium, 1-propy-4-methylpyridinium and 1-ethyl-3-methylpyridinium, bis(trifluoromethylsulfonyl)imide are those that exhibit behavior type 2, as can be seen from Fig. 1b) (thermal scan for the (1,2) PMpyNTf$_2$) and in Table 3. These ionic liquids exhibit freezing and fusion, therefore opposite to the ionic liquids with the behavior type 1, are good crystal formers.

As above commented in the experimental section, when samples presented a freezing temperature, these were quenched (cooling at 40K min^{-1} and heating at 10K·min^{-1}) with the objective of being able to determine if these samples also had a glass transition temperature. The ionic liquids with ethyl alkyl chain ((1,2) EMpyNTf$_2$, (1,3) EMpyNTf$_2$ and (1,4) EMpyNTf$_2$) continued to show a freezing point after quenching. For the (1,2) PMpyNTf$_2$ ionic liquid it was possible to avoid crystallization.

Finally, the third behavior was found for the (1,4) BMpyNTf$_2$ ionic liquid. As can be seen in Fig. 1c) (example of behavior type 3 for (1,4) BMpyNTf$_2$ ionic liquid), ionic liquids that exhibit behavior type 3 are those that are characterized by presenting a cold crystallization, they do not show tendency to crystallize on cooling; however, on heating they show cold crystallization.

Therefore, in summary, the influence of the position of the cation alkyl chain of the ionic liquid on the thermal properties of the 1-alkyl-X-methylpyridinium bis (trifluoromethylsulfonyl) imide ionic liquids is as follows:

- When the alkyl chain is ethyl, the position of alkyl chain cation of the ionic liquid has not influence on the thermal properties.
- If the alkyl chain is propyl, then alkyl chains in position (1,3) lead to ILs presenting behavior type 1 and alkyl chains in position (1,2) and (1,4) result in Ils with behavior type 2.

Table 3
Results of the thermal analysis for the studied ionic liquids and comparison with literature.[a].

Ionic Liquid	Rate/K·min^{-1}	T_g/K	T_f/K	T_{cc}/K	T_{s-s}/K	T_m/K
(1,2) EMpyNTf$_2$	2		250 (250)[c]		284 (285)[c]	289 (289)[c]
	q+10[b]		190		278	289
(1,2) PMpyNTf$_2$	2		246 (249)[c]		284 (249)[c]	289 (295)[c]
	q+10	199				
(1,2) BMpyNTf$_2$	2	199				
(1,4) EMpyNTf$_2$	2		266		284	288
	q+10		221		281	289
(1,4) PMpyNTf$_2$	2		250		267	301
	q+10		211		273	301
(1,4) BMpyNTf$_2$	2	188 (193)[e]		218	n.a[d]	289 (283)[e]
(1,3) EMpyNTf$_2$[f]	2		249			272
	q+10		239			272
(1,3) PMpyNTf$_2$[f]	2	185				
(1,3) BMpyNTf$_2$[f]	2	188				

[a] Standard uncertainty $u(T) = \pm 1$K.
[b] Cooling with quenching at 40K·min $^{-1}$and heating at 10K·min $^{-1}$.
[c] From Ref. [6] at 10K·min^{-1} rate.
[d] Not readable with accuracy enough from thermal scan.
[e] From Ref. [7] at 10K·min^{-1} rate.
[f] From Ref. [8] from the our group.

- And finally, when the alkyl chain is butyl, ionic liquids with the alkyl chains in positions (1,4) present behavior type 3, while when the substituent are in position (1,2) and (1,3) the behavior found is of type 1.

Table 3 also shows the experimental data found in the literature obtained by other authors [6,7] for the (1,2) EM pyNTf$_2$, (1,2) PMpyNTf$_2$ and (1,4) BMpyNTf$_2$.

The results presented in Table 3 for reference [6] for (1,2) EMpyNTf$_2$, (1,2) PMpyNTf$_2$ were determined using a differential scanning calorimeter Q1000 and the liquid sample was cooled down from room temperature to 100K at 10K·min^{-1}and subjected to a subsequent heating up to 320K at the same scan rate [6]. Although the authors do not report glass transition temperature for (1,2) PMpyNTf$_2$, in this work, it was possible to confirm that the (1,2) PMpyNTf$_2$ shows T_g if the ionic liquid is subjected to a sub-cooling process, furthermore, the authors refer that during cooling they observed a solid-solid transition (T_{s-s} = 231.09K) that in the thermal analysis performed in this work was not observed (Fig. 1b)), the other values reported by the authors [6], are in agreement with ours, although cooling and heating rates used are not the same.

Respect to (1,2) BmpyNTf$_2$, the only difference observed is that García-Mardones et al. [6] mention that during the heating cycle the (1,2) EMpyNTf$_2$ presents a double melting point, differently to our understanding this corresponds to a T_{s-s}. We carried out studies to confirm that the peak corresponds to a T_m or T_{s-s}. Accordingly, the studies we performed consisted in obtaining the thermograms at different cooling and heating rates. From reading these thermograms, it is possible to check the transition temperature of this peak. If the temperature of the peak changes, it means that this peak is a T_{s-s} and not a T_m, as it is well known that heating and cooling rate do not influence [8] the melting temperature.

Regarding the comparison of (1,4) BMpyNTf$_2$, only T_g and T_m values are presented in the literature [7], and no T_{cc} is reported. Taking into account that both the equipment and method used were different from those used in this study, values agree.

3.2. Heat capacities

Table S1 and Fig. 2 present the experimental heat capacities for the all ionic liquids studied in this work in the temperature range T = (308.15−353.15) K, except for (1,4) PmpyNTf$_2$. In Fig. 2 the heat capacities of (1,3) 1-alkyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide with n = 2,3 and 4 ionic liquids determined in our previous work [8] are also presented, in order to better evaluate the influence of the alkyl chain position of the cation of the ionic liquid in the value of the heat capacity.

Heat capacities were determined from (293.15−363.15) K. However, only data from 308.15K to 356.15K are presented since at the temperature range limits, the samples were not fully thermally conditioned [9]. The heat capacities for the ionic liquid (1,4) 1-propyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide were determined from (303.15−373.15) K because this ionic liquid presents a melting point at 301K, and the C_p measurements were carried out in the liquid range of the ILs, but only data from 317.15K to 361.15K are presented.

In Fig. 2 it can be observed that the C_p value increases with the increase of the cation alkyl chain of ionic liquids for all series of ionic liquids studied. This behavior agrees with that reported previously in literature by other authors [11,12] and with the results of our previous work [8] (as also shown in Fig. 2).

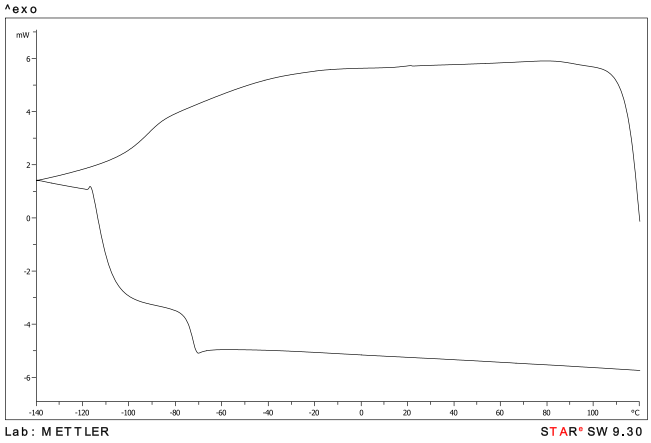
To represent the heat capacities values as a function of temperature, a quadratic polynomial equation like was used:

$$C_p = y_0 + aT + bT^2 \quad (1)$$

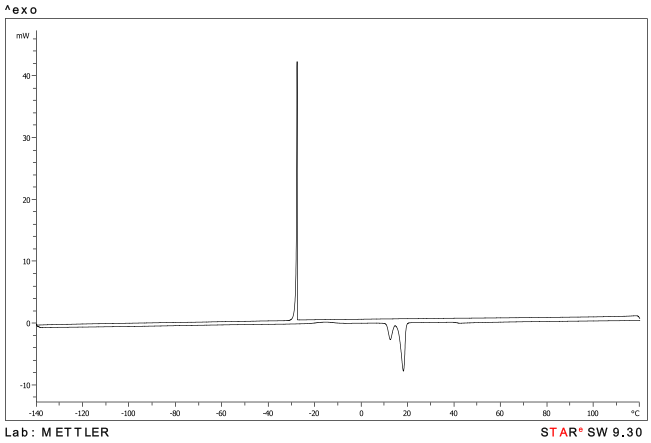
The parameters (y_0, a and b) of equation (1) together with the correlation factor, R^2, and the mean absolute percentage deviation, MAPD, are presented in Table 4, and this fitting can also be observed in Fig. 2. From the value of the correlation factors (R^2) in Table 4 and by inspection of Fig. 2 it can be concluded that the heat capacities have a quadratic linear trend with the temperature for all ionic liquids presented in this work and in the temperature range studied.

Respect to the influence of the position of the cation alkyl chain of the ionic liquid on the heat capacities values, the C_p values follow the order: Cp (1-alkyl-2-methylpyridinium bis (trifluoromethylsulfonyl) imide) > Cp (1-alkyl-3-methylpyridinium bis (trifluoromethyls ulfonyl) imide) > Cp (1-alkyl-4-methylpyridinium bis (trifluoromethylsulfonyl) imide) for the ionic liquids with butyl alkyl chain. For the ionic liquids with ethyl and butyl alkyl chain, in general, the values of the heat capacities were similar. More specifically: for the ionic liquids with propyl alkyl chain the trend is (1,2) PmpyNTf2 > (1,4) PmpyNTf2 > (1,3) PmpyNTf2 from 317.15 to

a)



b)



c)

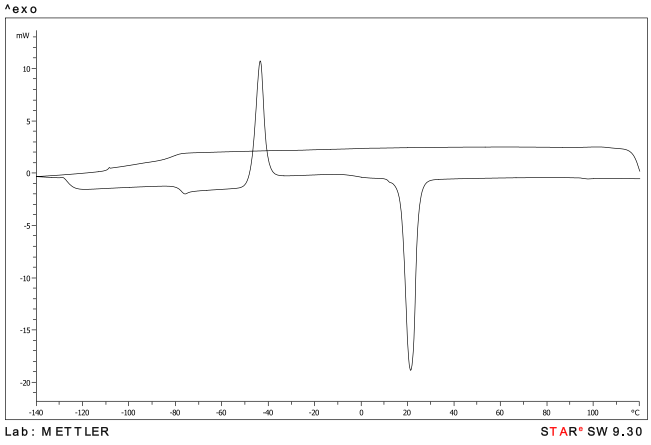


Fig. 1. Thermal scan cooling the sample from 393.15K to 133.15K at a rate of 2K·min^{-1} and after were heating from 133.15K to 393.15K at the same rate for a) (1,2) BMpyNTf$_2$, b) (1,2) PMpyNTf$_2$ and c) (1,4) BMpyNTf$_2$.

330.15K; (1,4) PmpyNTf2 = (1,2) PmpyNTf2 > (1,3) PmpyNTf2 from 330.15 to 350.15K and (1,4) PmpyNTf2 > (1,2) PmpyNTf2 > (1,3) PmpyNTf2 from 350.15K.

For the ionic liquids with ethyl alkyl chain the values of C_ps are very similar for all temperature range.

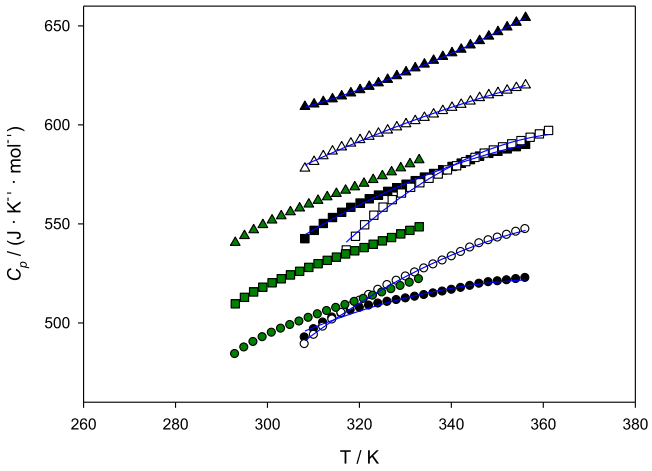


Fig. 2. Experimental molar heat capacities, c_p, determined in this work and in previous works as a function of temperature. Symbols: ●, (1,2) EMpyNTf$_2$ (this work); ■, (1,2) PMpyNTf$_2$ (this work); ▲, (1,2) BMpyNTf$_2$ (this work); ○, (1,4) EMpyNTf$_2$ (this work); □, (1,4) PMpyNTf$_2$ (this work); △, (1,4) BMpyNTf$_2$ (this work); ● (1,3) EMpyNTf$_2$ (reference 8); ■, (1,3) PMpyNTf$_2$ (reference 8); ▲, (1,3) BMpyNTf$_2$ (reference 8); (−), solid blue lines represent the fitting using eq (1).

Table 4
Fitting parameters for the fitting ($C_p = y_0 + aT + bT^2$) of the experimental heat capacities, correlation factor, R^2, and mean absolute percentage deviation, MAPD.

IL	y_0	a	b	R^2	MAPD[a]
(1,2) EMpyNTf$_2$	−617.1	6.2710	−0.0086	0.9812	0.03591
(1,2) PMpyNTf$_2$	−732.7	6.9112	−0.0090	0.9979	0.00065
			0		
(1,2) BMpyNTf$_2$	903.4	−2.5961	0.0053	0.9999	0.00854
(1,4) EMpyNTf$_2$	−1189	9.1631	−0.0120	0.9982	0.02496
(1,4) PMpyNTf$_2$	−2248	15.429	−0.0209	0.9927	0.09914
(1,4) BMpyNTf$_2$	−201.9	4.0067	−0.0048	0.9981	0.00381

[a] $$\text{MAPD} = 100\,\frac{1}{n_{dat}}\sum_{i}^{n}\left(\frac{(Cp_i^{exp} - Cp_i^{cal})}{Cp_i^{exp}}\right)$$

(n_{dat} is the number of experimental data points, Cp_i^{exp} and Cp_i^{cal} are the values of the experimental and calculated heat capacity, respectively).

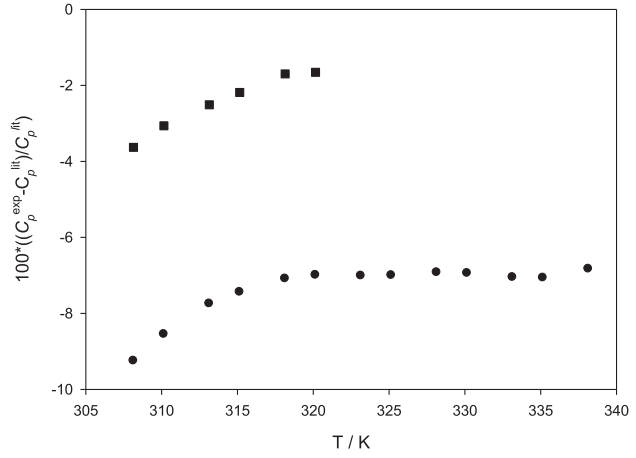


Fig. 3. Comparison of literature [6] molar heat capacities, c_p, with those obtained in this work: ●, (1,2) EMpyNTf$_2$ and ■, (1,2) PMpyNTf$_2$.

In Fig. 3, the deviation of literature values [6] from our experimental heat capacities as function of the temperature is presented for (1,2) $PMpyNTf_2$ and (1,2) $BMpyNTf_2$ ionic liquids. The deviations values are around 8% for the (1,2) $PMpyNTf_2$ and 4% (1,2) $BMpyNTf_2$. The uncertainty in the measurement of the heat capacities is ±5%. The differences found may be due to the different methods used for the experimental determination or of heat capacities. In this work the C_p has been determined from 293.15 to 363.15 K and with shappire method. In the literature [6], the heat capacities were determined using a differential scanning calorimeter Q2000 and the method was described as: the liquid samples were cooled down to 278.15K and, after thermal equilibration, a heating thermogram was performed at a scan rate of $10K \cdot min^{-1}$ up to 323.15K. Therefore, the C_p from the literature were not only determined in the liquid range, as in our case.

4. Conclusions

Thermal analysis and heat capacities of the 1-alkyl-2 −methylpyrridinium -bis (trifluoromethylsulfonyl) imide) and 1-alkyl-3-methylpyridinium bis (trifluoromethylsulfonyl) imide) were determined with a Mettler-Toledo differential scanning calorimeter (DSC). To study the influence of the position of the alkyl chain of the ionic liquid on the thermal transition temperatures and heat capacities, the results obtained in this work were compared with those reported in a previous paper from our group, for the 1-alkyl-4-methylpyridinium bis (trifluoromethylsulfonyl) imide ionic liquids.

The thermal behavior found for the ionic liquids studied can be divided into three types: behavior type 1 corresponds to ionic liquids characterized by only presenting a glass transition; behavior type 2 is characterized by presenting freezing, forming crystals on cooling and finally, behavior type 3 appears in the ILs that present a subcooling phenomenon. The experimental results were compared with those found in the literature, and the comparison showed a satisfactory agreement in several.

Heat capacity values increased quadratic linearly with temperature and increase as the alkyl-side chain of the cation increases for all studied ionic liquids. Regarding the influence of the position of alkyl chain cation on the heat capacities of ILs, the ionic liquids with substituents in position (1,2) present higher heat capacities than ILs with radicals in position (1,3) and these present higher heat capacities than ILs with alkyl chains in (1,4) for the ionic liquids with butyl as alkyl chain and for the ILs with ethyl and propyl the heat capacities are similar.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Elena Gómez: Conceptualization, Methodology, Supervision, Formal analysis, Writing - original draft, Visualization. **Patricia F. Requejo:** Validation, Investigation. **Ángeles Domínguez:** Project administration, Writing - review & editing. **Eugénia A. Macedo:** Funding acquisition, Project administration, Supervision, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fluid.2020.112658.

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