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Thermal analysis and heat capacities of pyridinium and imidazolium ionic liquids

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ABSTRACT

In this work, the thermal behavior and heat capacities of four pyridinium and two imidazolium-based ionic liquids (1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, $C_2MpyNTf_2$, 3-methyl-1-propylpyridinium bis(trifluoromethylsulfonyl)imide, $C_3MpyNTf_2$, 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, $C_4MpyNTf_2$, 1-butyl-3-methylpyridinium trifluoromethanesulfonate, $C_4MpyTFO$, 1-butyl-3-methylimidazolium trifluoromethanesulfonate, $C_4MimTFO$, and 1-butyl-3-methylimidazolium dicyanamide, $C_4MimDCA$) have been experimentally determined using differential scanning calorimetry, and the obtained results have been compared and analyzed. The influence of the scan rate on the thermal analysis has been discussed along with the influence of the structure of the ionic liquid on the heat capacity.

1. Introduction

Ionic liquids (ILs) are molten salts, usually formed by a big cation and an inorganic anion, which are liquid below 100 °C. This feature along with others such as their ability to solubilize an enormous variety of compounds, good thermal stability, nonflammability, ease of recovery, and especially their negligible vapor pressure at normal conditions, makes ionic liquids good candidates for new applications [1]; among these new applications, the use of ionic liquids as replacement for heat transfer fluids is especially interesting in our case [2–6].

The thermodynamic properties of ionic liquids, such as freezing, melting, cold crystallization and glass transition temperatures and their heat capacities are very important properties which allow reflecting the stabilities and structures of these relatively new compounds; moreover, heat capacities are necessary for the design of physicochemical processing and reaction units and this property becomes vital for the application of ILs as thermal fluids. Despite this, for most ionic liquids these properties are still unknown. Due to the great number of different possible ionic liquids and besides the precise determination of such properties for each of them, it is interesting to determine the influence of the structure of the ionic liquids in such properties, especially in case that an ionic liquid of specific characteristics is needed. Differential scanning calorimetry (DSC) has proven to be a very reliable technique to obtain heat capacities in a reasonable short time with a small quantity of sample.

In this work, the thermal behavior of four pyridinium (1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)-imide, $C_2MpyNTf_2$, 3-methyl-1-propylpyridinium bis(trifluoromethylsulfonyl)imide, $C_3MpyNTf_2$, 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, $C_4MpyNTf_2$, 1-butyl-3-methylpyridinium trifluoromethanesulfonate, $C_4MpyTFO$) and two imidazolium-based (1-butyl-3-methylimidazolium trifluoromethanesulfonate, $C_4MimTFO$; and 1-butyl-3-methylimidazolium dicyanamide, $C_4MimDCA$) ionic liquids containing different anions was determined and analyzed, and their heat capacities in the liquid range were determined. Several considerations have been taken into account when selecting the ionic liquids, their relatively low viscosity, their simple and economical synthesis and that they are usually applied in several studies. Besides that, with this selection a comparative study can be made and the obtained results compared with those previously obtained for other ILs [7] to clarify the tendency followed by these thermal properties with the structure of the IL. A literature comparison was also carried out for three ionic liquids studied in this work [8–16]; for three pyridinium-based ionic liquids no literature data were found.

2. Experimental

2.1. Chemicals

The ionic liquids studied in this work were purchased from IoliTec, with a mass fraction purity higher than 0.98 for the ionic

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Table 1
Results of the thermal analysis for the studied ionic liquids and comparison with literature.

	Rate (K min^{-1})	T_g (K)	T_{f1} (K)	T_{f2} (K)	T_{cc1} (K)	T_{cc2} (K)	T_{m1} (K)	T_{m2} (K)	T_{m3} (K)
C_2MpyNTf$_2$	2		249				272		
	q + 10		239				272		
	Q + 10		187				272		
C_3MpyNTf$_2$	2	185							
	10	188							
C_4MpyNTf$_2$	2	188							
	10	191 (189)[a] (190.8)[b]							
C_4MpyTFO	2		255	256				267	303
	10	197	252		227	239	251	270	307
	Q + 10	198			228	244	253	268	307
C_4MimTFO	2		257	258			285		
	10		253 (254)[c]	[g]			289 (286)[c] (290.98)[d] (290)[e]		
	[h]	(191)[e]							
	q + 10		204				289		
C_4MimDCA	2	181			225		267		
	10	185 (183)[c]			243 (244)[c]		268 (267)[c] (270.83)[d]		
		(179)[f]			(238)[f]		(263)[f]		

[a] From Ref. [8].
[b] From Ref. [9].
[c] From Ref. [11].
[d] From Ref. [12].
[e] From Ref. [10].
[f] From Ref. [13].
[g] Not evaluable.
[h] Detected by rapid cooling.
q + 10 – quenching at 40 K min^{-1} and heating at 10 K min^{-1}.
Q + 10 – quenching at 60 K min^{-1} and heating at 10 K min^{-1}.

liquid C_4MimDCA and higher than 0.99 for the rest of them. They all were dried under vacuum ($p = 2 \times 10^{-1}$ Pa) and moderate temperature (T = 343.15 K) always prior to their use. Water content was measured using a Mettler-Toledo coulometric KF titrator, model C20, and the results showed the water content to be less than 300 ppm for each IL. To avoid moisture, ionic liquids were stored in bottles under an inert atmosphere in a glove box. Besides this purification procedure, ILs were dried *in situ* inside the DSC before each experiment.

2.2. Procedure

The thermal analyzes and the determination of heat capacities were carried out using a differential scanning calorimeter (DSC) Mettler Toledo DSC822^e, and the results were evaluated with the Star^e software, version 9.30. Samples of pure indium, zinc, water and heptane were used for the calibration of temperature and heat flow and a nitrogen flow rate of 50 mL min^{-1} was constantly passed through the furnace for an inert atmosphere. For the thermal analysis, the mass of the sample used is relatively small (4–8 mg) to avoid homogenization errors and thermal lag, and for the determination of heat capacities a higher amount is necessary, since the size of the measurement signal is proportional to the sample amount; therefore, aluminum pans hermetically sealed with a pinhole at the top with a volume of 40 and 100 μL were used, respectively. The temperatures used for the thermal analyzes range from 133.15 to 393.15 K at different cooling and heating rates. The sapphire method was chosen for the determination of the experimental heat capacities; this method consists in an initial isothermal segment for 15 min followed by a dynamic period at 20 K min^{-1} and a final isothermal segment for 15 min. The calculated standard uncertainties are ±1 K for the temperature in the thermal analysis and ±5% for the determination of the molar heat capacity. Besides the usual procedure for the purification of the ionic liquids (dried at constant stirring at moderate temperature and under vacuum), they were dried *in situ* in the DSC by heating the sample at 403.15 K for at least 1 h. The runs for c_p measurements were repeated three times for each sample.

For the thermal analysis, all the samples were subjected to a cooling and heating cycle at 2 K min^{-1}, and depending on the obtained results, the run can be repeated at 10 K min^{-1} or, if there is a freezing peak, they are subjected to a quenching in order to prevent the IL from crystallizing and thus be able to determine the glass transition. For the interpretation of the DSC curves, the melting temperature, T_m, was taken as the onset on an downward reflection of the curve peak on heating, the freezing temperature, T_f, as the onset of an upward deflection of the curve peak on cooling, the cold crystallization, T_{cc}, as the onset of an exothermic peak on heating and the glass transition temperature, T_g, as the midpoint of a heat capacity change on heating. A more detailed explanation on the experimental procedure is available in our previous paper [7].

3. Results and discussion

In general, for the imidazolium and pyridinium-based ionic liquids studied in this work (Table 1) and in a previous one [7], three behaviors when the cooling and heating rate is 2 K min^{-1} were observed: (i) the first group, formed by C_3MimNTf$_2$, C_3MpyNTf$_2$, C_4MpyNTf$_2$ and C_6MimDCA, is characterized by the presence of only a glass transition, indicating that these ionic liquids present a weak tendency for crystallization; (ii) the ionic liquids C_2MimNTf$_2$, C_2MpyNTf$_2$, C_4MpyTFO, C_4MimTFO and C_6MimTFO present the second behavior, where only freezing and melting transitions appear, presenting these ILs as very good crystal-formers. A typical supercooling is observed, with freezing temperatures markedly lower than the melting temperatures; in general, these differences