Proceeding Paper

Thermal Behaviour of Ionogels Based on Ionic Liquid Lithium Salt Mixtures †

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Abstract: The thermal behavior of the mixtures of two protic ionic liquids (ethylammonium nitrate (EAN) and ethylimidazolium nitrate ([EIm][NO₃])) with lithium nitrate salt (LiNO₃), and one aprotic ionic liquid (butyl methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMpyrr][TFSI)) with lithium bis(trifluoromethylsulfonyl)imide salt (LiTFSI), at different concentrations, was studied in this work using a Differential Scanning Calorimeter (DSC-Q2000-TA Instruments). Comparisons with the thermal behavior of silica-based ionogels of these mixtures were also performed.

Keywords: DSC; ionogel; mixture; inorganic salts

1. Introduction

There is a growing need for efficient batteries for transport, power, and industrial applications. In this field, ionic liquids (ILs) exhibit a unique combination of physicochemical properties, such as high electrochemical stability, broad liquid range, high conductivity, compatible with electrode materials—neither flammable nor volatile—that make them ideal candidates for electrolyte and energy storage applications. Amazing results have been shown in applications such as super-capacitors, Li-ion batteries, dye sensitized solar cells, sensor materials, and metal plating processes, offering the possibility of enhanced safety and stability [1]. ILs and inorganic salt mixtures are behind a new generation of active media, e.g., for electrolytes, in lithium batteries [2–4].

Nevertheless, the liquid nature of ILs can cause some difficulties, such as packaging, leakage, and movability. One way to avoid the fluidic problem is to confine ILs in nanoporous matrix, achieving optimal mechanical properties without losing the particular properties of the ILs. The incorporation of ILs into the pore structure, nanoconfined ILs, with improved mechanical properties, and ionic conductivity, constitutes a new class of hybrid materials with the intrinsic properties of ILs and the original functions of a solid matrix [5,6].

Experimental study of nanoconfined ILs is still an important challenge related to ILs in the bulk phase. In this work, changes in the thermal behavior of three ILs—as a consequence of lithium salt addition and confinement of these mixtures on silica scaffold—were studied using Differential Scanning Calorimetry (DSC). This is a technique able to measure the amount of heat absorbed, or released, during the different transitions taking place

in temperature interval; mainly, melting point (first-order endothermic phase-transition temperature), crystallization temperature (the first-order exothermic phase-transition temperature), and glass transition temperature (the second-order transition).

## 2. Materials and Methods

2.1. Chemicals

The ionic liquids selected for this work, ethylammonium nitrate (EAN), ethylimidazolium nitrate ([EIm][NO₃]), and 1-butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide ([BMpyr][TFSI]) were purchased from IoLiTec and lithium salts with the same anion were provided by Merck. Solutions of IL + lithium salt, in different concentrations, in the molality range from 0.1 mol kg^{-1} up to the saturation limit, were prepared. Table 1 shows the identification, chemical structure, purity, and provenance of the chemicals used for this work. Ionic liquid samples were dried under high vacuum for a minimum of 48 h. Residual amount of mass water was tested with a Karl Fischer titrator, and this content was shown to be less than 100 ppm. The different solutions of the salts were prepared by mixing both components with the help of an ultrasound bath during 24 to 48 h.

2.2. Gelation Routes

Two different routes of silica-based gelation of the mixtures of EAN + salt were performed in this work:

1. Formic acid route: gelation process has been performed by slightly modifying the methodology of Negre et al. [7]. Essentially, a solid ionogel-based electrolyte was synthetized using two different sol-gel agents: tetraethyl orthosilicate (TEOS) under acidic conditions (formic acid, FA) in a volumetric ratio TEOS:FA 1:2 mL. The reactants were mixed together under moderate stirring (300 rpm) at 40 °C during 18 min. Finally, the addition of 4 mL of liquid mixture of IL + salt, previously prepared following the methodology described above were added. The resulting solution was stored in sealed containers and kept at room temperature until fully gelified, approximately for a week.

2. Ethanol route: this method is based on a methodology previously reported by other authors [6,8]. A mixture of 3 mL of ethanol + 0.428 mL of TEOS + 1 mL of pure IL or IL + salt mixture was done. These mixtures were stirred for 1 h and, before gelation, transferred to adequate vials for 1–2 h to let the excess ethanol evaporate, and were finally maintained at 40 °C (lower than that in previous references since we have observed some fraction of cracking in our samples at higher temperatures) in an oven until full gelation (one week).

Table 1. Identification of compounds selected for this work, ionic liquids and metal salts: Names, molecular mass of pure salts and ionic liquid (IL), identification CAS (Chemical Abstracts Service) number, chemical structure, mass fraction purity, provenance, and water content mass.

Name Molecular Mass (g·mol^{-1})	Abbreviation CAS Number	Chemical Structure	Purity Provenance
Ethylammonium Nitrate 108.10	EAN 22113-86-6		>0.999 IoLiTec
Ethylimidazolium Nitrate 159.14	[EIm][NO₃] 501693-38-5		>0.999 IoLiTec
1-butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide	[BMpyr][TFSI] 223437-11-4		>0.99 IoLiTec
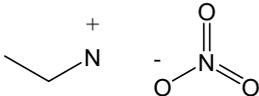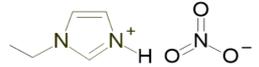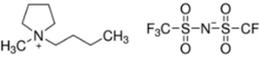
|			
422.41			
Lithium Nitrate 68.946	LiNO₃ 7790-69-4		>0.999 Merck
Lithium bis[(trifluoromethyl)sulfonyl]imide 287.09	LiTFSI 90076-65-6		>0.999 Merck
Tetraethyl orthosilicate 208.33	TEOS 78-10-4		>0.999 Sigma Al-drich
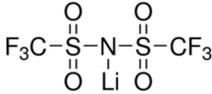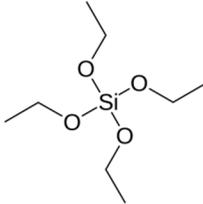
2.3. Experimental Procedure

A Differential Scanning Calorimeter (DSC Q1000 TA-Instruments) with hermetically sealed aluminum pans was used to determine the different state transitions experimented by the pure IL and salt solutions during heating and cooling cycles. All samples with mass between 5 and 8 mg were subjected to the following cooling and heating ramps: (a) heating from 25 to 120 °C at 10 °C min^{-1}; (b) isothermal step at 120 °C during 45 min to remove impurities [9] and to erase the thermal history of the sample; (c) cooling from 120 to −85 °C at 5 °C min^{-1}; (d) isothermal step at −85 °C during 5 min and (e) heating from −85 to 100 °C at 5 °C min^{-1}; and (f) cooling from 100 to −85 °C at 5 °C min^{-1}.

Transitions temperatures were determined from the DSC curves, as the onset points of the different peaks, during the reheating and re-cooling steps following the methodology used in previous papers [10].

3. Results and Discussion

The cooling and heating ramps at 5 °C min^{-1} of DSC curves in nitrogen atmosphere of pure ionic liquids are presented in Figure 1. These ILs presents a strong tendency for forming crystals in these conditions, although some important differences can be found in the behaviors of these ILs. An endothermic peak related with the melting process can be observed in all of them, whereas [EIm][NO₃] presents unique peaks in a heating ramp (endothermic melting at 35 °C), and in a cooling ramp (exothermic peak associated to crystallization process at −20 °C). EAN shows two exothermic peaks, one in a cooling ramp (crystallization at −27 °C) and the other in a heating ramp (cold crystallization at −44 °C). No peaks are observed in the cooling ramp of [BMPyrr][TFSI]. Two cold crystallization peaks (exothermic) at −57 and −28 °C are observed in the heating ramp, highlighting the different tendency of these ILs to crystallize, in spite of the fact that no evidence of amorphous phase has been observed in liquid form.
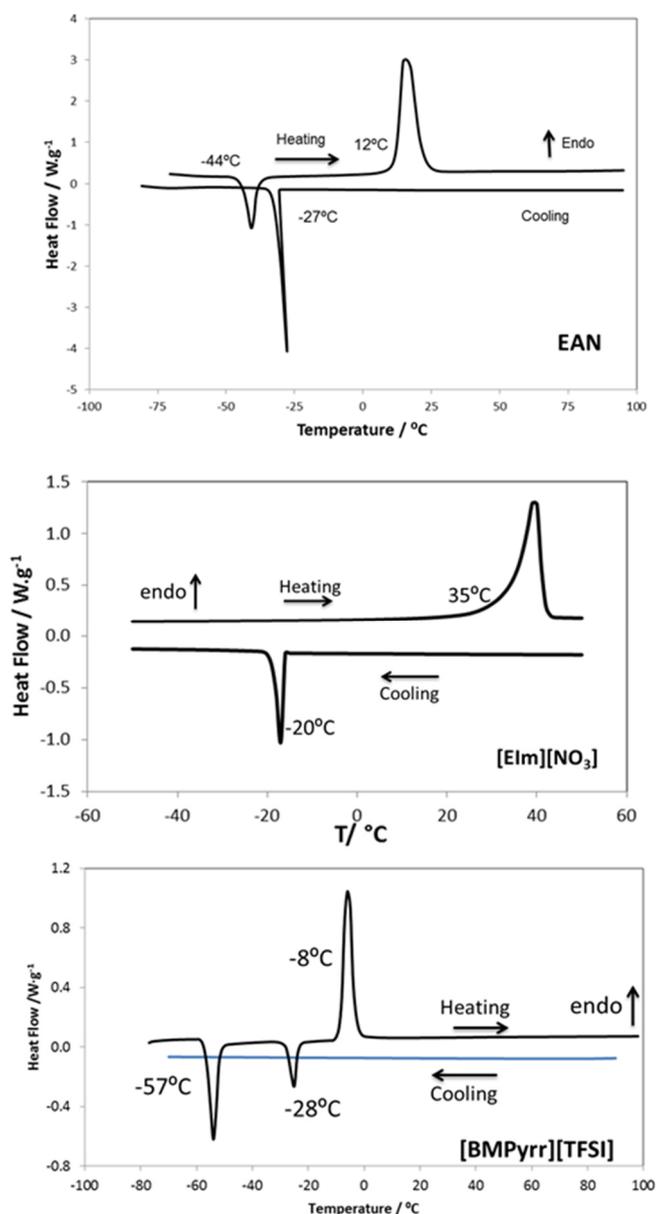
Figure 1. Differential Scanning Calorimeter (DSC) curves at 5 °C min⁻¹ of the pure ionic liquids selected for this work.

3.1. Effect of the Salt Addition

Figure 2 shows the heating ramps at 5 °C min⁻¹ of DSC curves of the IL + lithium salt at different concentrations. Results showed that, for both protic ILs (PILs), the melting transition shifts to lower temperatures upon salt addition, these peaks being broader and lower as salt concentration increases. Even for the saturated concentration of all salts, no evidence of crystalline behavior can be observed, as shown by the absence of any melting peak, accompanied with the appearance of glass transition at very low temperatures [4]. Nevertheless, the aprotic IL (APIL) shows different behavior with the salt addition, the lowest concentration also shifts melting temperature to lower values, nevertheless the melting temperature increases, and the heat associated to this peak decreases for the other concentrations with the salt addition. Moreover, a glass transition is also observed at −53 °C (see Figure 3) for the saturation concentration. These observations agree with the results of Martinelli et al. [11] who pointed out the existence of more than one phase for high concentrations of salt in this mixture.
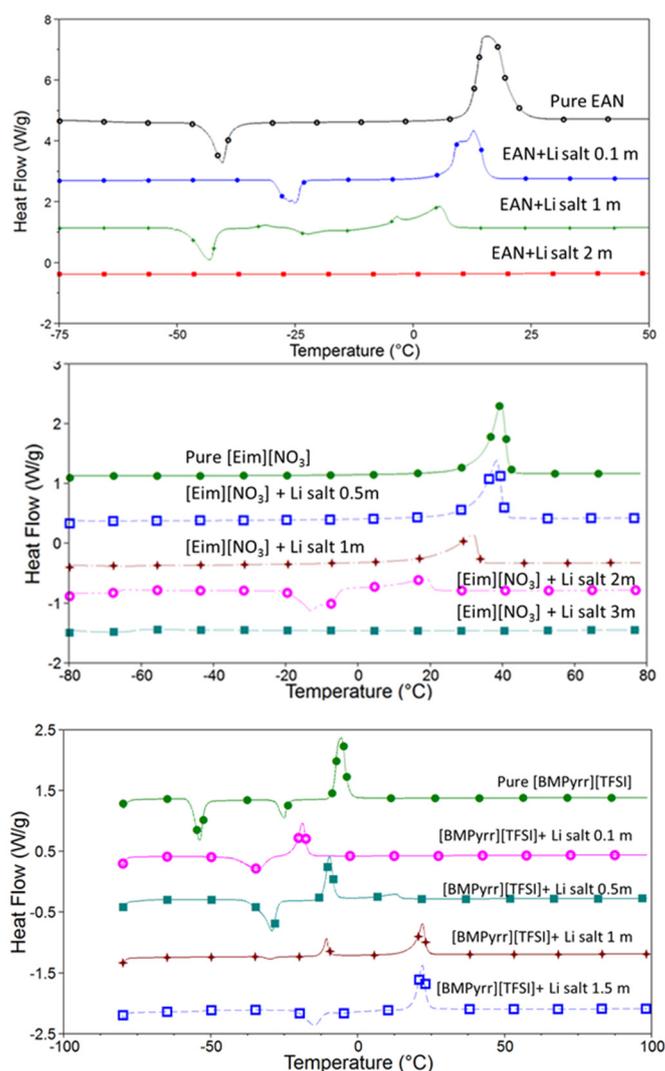
Figure 2. DSC curves at 5 °C min⁻¹ in heating ramps of the pure ionic liquids and mixtures with the corresponding lithium salt.
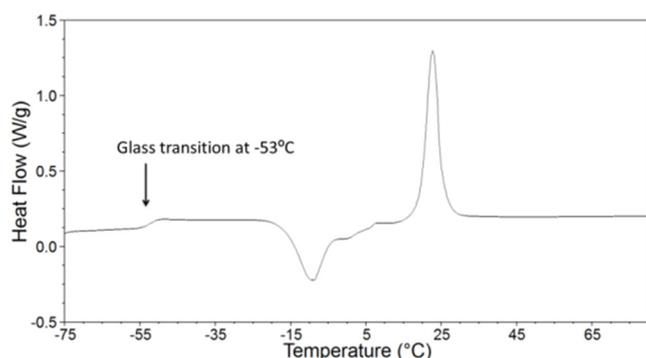
Figure 3. DSC curve of the saturated mixture [BMpyrr][TFSI] + LiTFSI.

3.2. Effect of Gelation

Figure 4 shows the heating ramps at 5 °C of the DSC curves of the ionogels prepared from the previous mixtures of IL + salt at different concentrations. PIL ionogels were made using the ethanol route and the APIL ionogel was done by the formic acid route.

The confinement of the ionic liquid in the silica matrix has a dramatic effect on DSC curves, with the disappearance of the melting and crystallization peaks, especially in EAN

and [BMPyrr][TFSI] mixtures with the lithium salts, even though the confinement did not affect the glass transition clearly visible in mixtures with the highest concentration of salt.

[EIm][NO$_3$] + salt mixture ionogels present some small endothermic and/or exothermic peaks in DSC curves that indicate the presence of crystallization and melting of a small part of the sample. This behavior is also observed by other authors who associate these discrepancies between gels to different pore sizes in the silica scaffold. A small pore size completely avoids the crystallization of the sample confined, whereas if this size increases, the sample (or part) can crystallize inside the silica network [12].
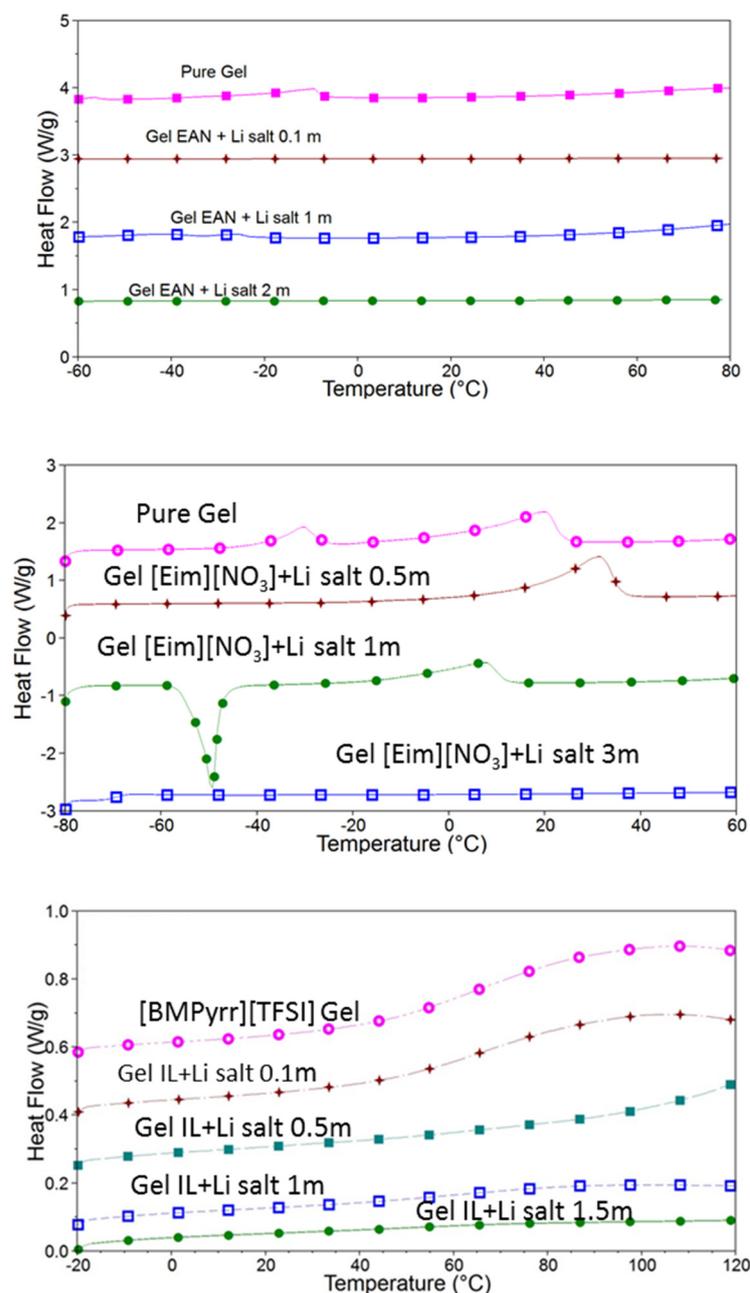
Figure 4. DSC curves at 5 °C min^{-1} in heating ramps of the gel samples of pure ionic liquids and mixtures with the corresponding lithium salt.

4. Conclusions

The thermal behavior of the mixtures of two protic ionic liquids (PILs), EAN and [EIm][NO₃], with lithium nitrate salt and one aprotic ionic liquid (APIL), [BMpyrr][TFSI], with lithium bis(trifluoromethylsulfonyl)imide salt, was studied in this work in liquid and silica based ionogel forms. Results show that the addition of the salt enlarges the amorphous phase of the fluid, especially for both protic ionic liquids and lithium nitrate mixtures. In regards to the confinement of the mixture on the silica network, one of the most remarkable effects is that thermal behavior of ionogel does not show the first-order transitions, due to the small available space for the IL crystallization. Although, as it happens in [EIm][NO₃]+LiNO₃ mixtures, the gel sample also shows similar peaks than liquid samples, but widened and shifted to lower temperatures. These differences are related to the volume of the pore wall of the ionogel.

Conflicts of Interest: The authors declare no conflict of interest.

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