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Ternary mixtures of N-butyl-pyrrolidinium bis (trifluoromethanesulfonyl) imide, lithium bis (trifluoromethanesulfonyl) imide and carbonate as advanced electrolytes for lithium-ion batteries

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Abstract:

Thermophysical properties of the ternary liquid mixtures IL + lithium salt + carbonate were studied in this work in terms of thermal transition temperatures, thermal stability and electrical conductivity of mixtures against pure compounds. The selected ionic liquid is the N-butyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide; the lithium salt with common anion, lithium bis(trifluoromethanesulfonyl)imide salt and two different carbonates (dimethyl carbonate or diethyl carbonate) were used to prepare the ternary mixtures. The main results were the cryoscopic decrease in IL with the salt addition, a reduction of crystallinity of ternary mixtures with regards to pure IL and IL+salt samples, and an increase of the electric conductivity of mixtures with temperature, following Bahe-Varela model in terms of volumetric fraction and a decrease with the increasing chain length of carbonate.

Keywords: Energy storage; ionic liquid mixtures; carbonate.

1. Introduction

The electrochemical energy storage plays a crucial role towards the decarbonisation of the electricity sector by improving the integration and exploitation of renewable energy sources.

The design of novel electrolytes and electrodes for electrochemical devices is currently one of the major topics of both fundamental and applied research.

Commercially available electrolytes for lithium-ion batteries are based on organic carbonates with lithium salts [1], offering good electrical conductivities although the safety of these devices is limited because of its high volatility and flammability, that is a problem also presented with organic solvents. During the last years new smart electrolytes based on mixtures of ionic liquids (ILs) with inorganic salts have been proposed with regards to their good electrical properties, good thermal and chemical stabilities and low toxicity [2–4].

Ionic liquids, also designed as room-temperature molten salts, are a novel class of nanostructured tunable solvents with multiple applications on different fields, as for example in lubrication [5] or in biology as active compounds [6]. They are also conventionally between the most promising materials for electrochemical applications, and they are considered optimal candidates for 4th and 5th generation batteries.

A wide set of ILs meet all the requirements to be classified as smart materials, since they usually present large variations in their properties with the modification of external variables such as water content, temperature, electric field, etc.

High viscosities and low ionic conductivities are common disadvantages for highly concentrated electrolytes on their practical use in devices requiring their fluidification with the addition of low-viscosity solvents. In this last decade, ternary mixtures of ILs, metallic salts and molecular cosolvents, including water, alcohols, acetonitrile, DMSO or carbonates [7–11], among others, have started being used for this proposal.

In this work, we determine the thermal behavior and electrical conductivity of two ternary mixtures of an IL with lithium salt with the same anion and two carbonates with different alkyl chain length, specifically 1-butyl-1methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide + Lithium bis(trifluoromethanesulfonyl)imide + Dimethyl Carbonate and 1-butyl-1methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide + Lithium bis(trifluoromethanesulfonyl)imide + Diethyl Carbonate.

2. Materials and methods

2.1. Chemicals

In this work, the thermal behavior and the electrical conductivity of ternary mixtures of ionic liquid + lithium salt + dialkyl carbonate were determined. Table 1 summarizes the used compounds.

Taking into account previous results of conductivity of the binary mixture IL+Li salt we decided to use the following procedure:

- Binary mixture of the IL [BMPyr][NTf$_2$] and [Li][NTf$_2$] salt at 0.2 m (moles of salt per kg of IL) was firstly prepared.
- Ternary mixtures of [BMPyr][NTf$_2$] + [Li][NTf$_2$] (0.2 m) + DMC and [BMPyr][NTf$_2$] + [Li][NTf$_2$] (0.2 m) + DEC in all the concentration range of carbonates were prepared.

Table 1. Identification of Chemicals used in this work

Name	Molecular Mass ($g \cdot mol^{-1}$)	Short Name CAS Number	Purity Supplier
1-butyl-1methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide	422.41	[BMPyr][NTf$_2$] 223437-11-4	>99 % IoLiTec
Lithium bis(trifluoromethanesulfonyl)imide	287.09	[Li][NTf$_2$] 90076-65-6 >99	>99 % Sigma Aldrich
Dimethyl Carbonate	90.08	DMC 616-38-6	>99 % Sigma Aldrich
Diethyl Carbonate	118.13	DEC 105-58-8	>99 % Sigma Aldrich

2.2. Experimental procedure

A differential scanning calorimeter (DSC Q2000 TA-Instruments) with hermetically sealed aluminum pans was used to determine the different state transitions experimented by pure IL and binary and ternary mixtures. Mass samples were ranged between 6-10 mg. Heating and cooling ramps were programed as follows:

- Heating ramp at 125ºC at 20ºC·min^{-1}
- Isothermal step at 125ºC during 45 min for removing impurities and erasing the thermal story of the samples
- Cooling ramp from 125ºC to -80ºC at 5ºC·min^{-1}
- Isothermal step at -80ºC during 5 min
- Heating ramp from -80ºC to 100ºC at 5ºC·min^{-1}.

Thermal stability of these samples was analysed by a thermogravimetric device TGA-DTA Metter Toledo under dynamic mode, nitrogen atmosphere and heating rate of 10ºC·min^{-1} between 50ºC and 600ºC.

Electrical conductivity was measured using two conductimeters, Crison Basic 30 and Crison GLP 31 operating under a frequency of 500Hz in a temperature range from -10ºC to 50ºC in heating and cooling ramps.

3. Results

3.1. Thermal behaviour

The effect of salt addition on the thermal behaviour of pure ILs is reflected in numerous papers [3,12] and basically corresponds to a loss of crystallinity characterized by a loss of definition of melting and crystallization peaks and the presence of glass transitions with the increasing concentration of salt in the mixture. Specifically, in a previous work [13], we pointed out a decrease in melting temperature of the mixture [BMPyr][NTf_2] + [Li][NTf_2] for low salt concentrations. Figure 1 shows the comparison between the thermal behaviour of the pure IL, the binary mixture IL+ Li salt 0.2 m and the ternary mixtures (IL + 0.2 m Li salt)+ 0.2 m carbonates. Beside of the crioscopic decrease and loss of definition peaks with salt addition, changes on crystalinity are evident as consequence of the carbonate adition through the vanishing of peaks, turning out a completely vitrious ternary mixture with both carbonates.

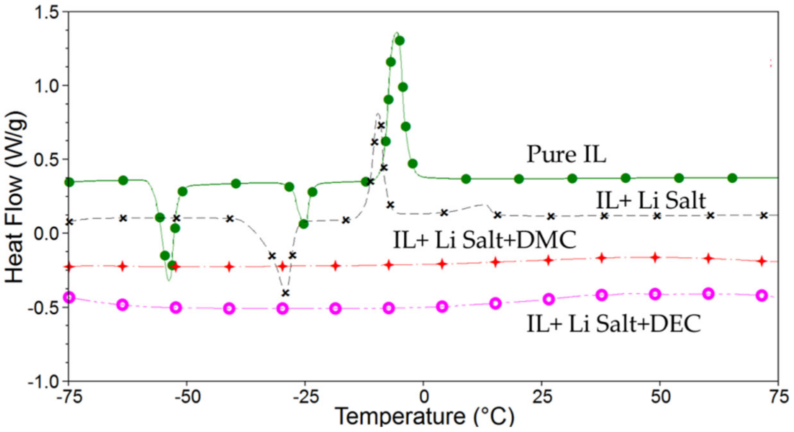

Figure 1. DSC curves (heating ramp at 5ºC·min^{-1}) of the pure IL, binary mixture IL + 0.2 m Li salt of salt and the ternary mixtures IL + 0.2 m Li salt + 0.2 m carbonates.

Moreover, one of the most general and mentioned properties in the scientific literature of ionic liquids is its high thermal stability, although is highly dependent on the anion; in particular $[NTf_2]^-$ provides, generally, the highest stability for a specific cation. Salgado et al. (2014) [14] carried out a thermal stability study of several ILs with common $[BMPyr]^+$ cation, observing that $[BMPyr][NTf_2]$ is the most stable with an onset temperature of 417ºC in dynamic mode and a maximum operating temperature in isothermal regime of 280ºC.

On the other hand, recent studies conclude that the addition of salts, namely lithium, does not show significant differences in the stability of the mixture with respect to the pure IL [3]. However, up to our knowledge the effect of the cosolvent on the mixture has not been studied in any articles published so far. Figure 2 shows the TGA and DTA curves of the two carbonates. The endothermic character of the peaks at the temperatures (58ºC for DMC and 80ºC for DEC) can be associated with evaporation processes.

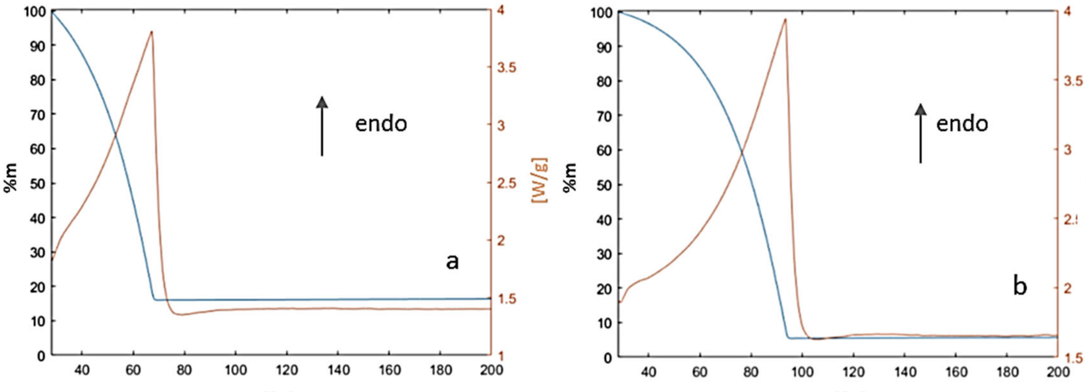

Figure 2. TGA (**blue**) and DTA (**orange**) curves of the carbonates DCM (a) and DEC (b)

Figure 3 shows the TGA and DTA curves of ternary $[BMPyr][NTf_2]$ + $Li[NTf_2]$ + DEC where the two evaporation processes (both endothermic) of carbonate (at temperatures below 100ºC) and IL + salt can be seen around 400ºC.

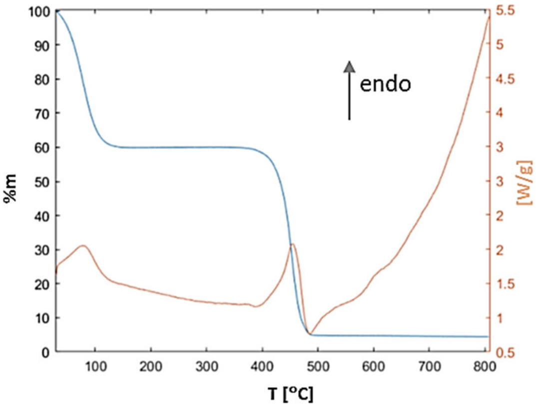

Figure 3. TGA (**blue**) and DTA (**orange**) curves of the ternary mixture $[BMPyr][NTf_2]$ + $Li[NTf_2]$ +DEC

3.2. Electrical conductivity

The experimental results of electrical conductivity of the ternary mixtures IL + salt + carbonate against volumetric fraction of carbonate at different temperatures are presented in Figure 4. Conductivity increases with temperature, following the behaviour of the VFT Vogel-Fulcher-Tamman) equation [15], as can be expected due to transport is dominated by a self-diffusion phenomena (the particles move randomly, with all direction of motion), and the higher the temperature, the higher the kinetic energy particles of the fluid. In addition, an increase in the conductivity with addition of carbonates until volumetric fractions of up to 0.5 was also observed. This behavior is in accordance with the Bahe-Varela model [16], being slighly higher the values corresponding to the ternary mixture with DMC than the corresponding to DEC. The increase conductivity was higher in DMC than in DEC.

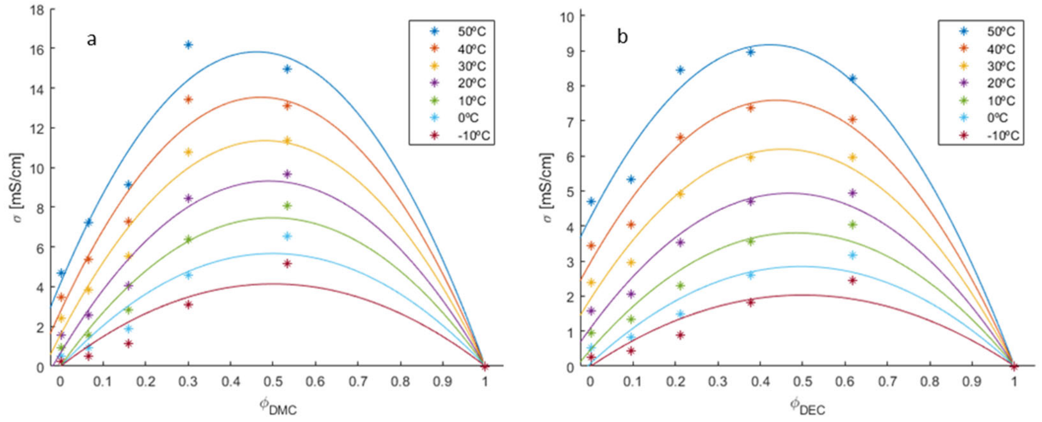

Figure 4. Conductivity of the thermary mixtures of IL + salt + carbonates (a) DMC, b) DEC) against the volumetric fraction of carbonate.

Conclusions:

Ternary mixtures of [BMPyr][NTf$_2$] + Li[NTf$_2$] + two different carbonates (DMC and DEC) are described on this study. The main observations are:

- Phase transitions of the ternary mixtures showed the change to a vittrous phase with both carbonates at 0.2 m of them on IL + salt 0.2 m.
- Thermal stability of this ternary mixtures is defined by the thermal stability of the carbonates.
- The electrical conductivity increases with temperature following the VFT model and with the carbonate following Bahe-Varela model, being the biggest increase the corresponding to the addition of the carbonate with the lowest alkyl chain length.

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Conflicts of Interest: The authors declare no conflict of interest

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