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Transport properties of alkali/alkaline earth cations in ionic-liquid based electrolytes

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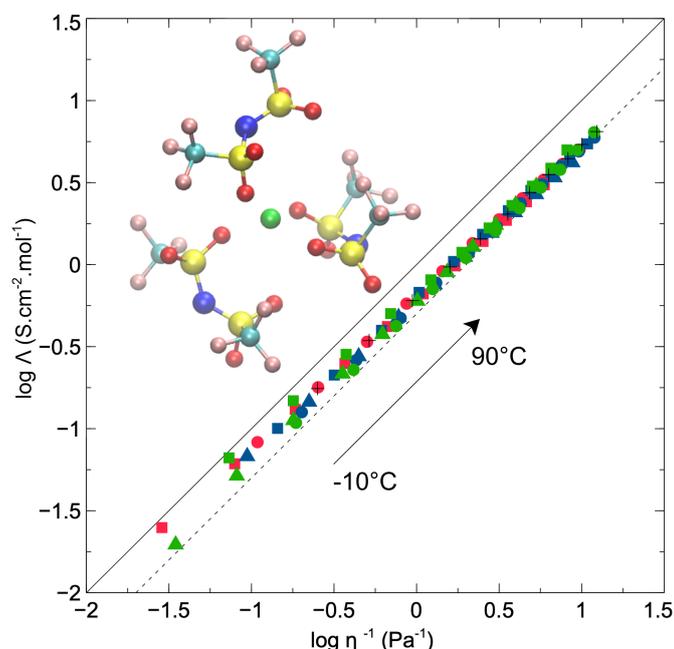
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Highlights :

- Large amounts of alkali or earth alkaline salts (Li^+ , Na^+ , K^+ , Cs^+ and Mg^{2+}) can be dissolved in ionic liquids.
- Mixtures of alkali salts with IL are 'good ionic conductors'.
- These results are confirmed from self-diffusion coefficients which also allows to retrieve contributions of each species to ionic transport and then dissociation ratio inside these mixtures. Slight differences between alkali and earth alkali ions may be related to solvation mechanisms, as proposed from infrared spectroscopy measurements.
- Transport properties of these electrolytes are deciphered from viscosity, ionic conductivity and individual self-diffusion coefficients.

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Abstract :

The increasing need of portable electrical resources requires to develop post-Li batteries, in which redox reactions are then based on the different alkali or earth alkaline ions. Keeping in mind the specific advantages of electrolytes based on ionic liquid (electrochemical properties, safety, stability ...), this paper focuses on the specific properties of those obtained by mixing alkali or earth alkaline salts (Li^+ , Na^+ , K^+ , Cs^+ and Mg^{2+}) in a prototypical ionic liquid, the 1-butyl-3-methyl imidazolium bis(trifluoromethyl sulfonyl) imide (BMImTFSI). Transport properties of these electrolytes are deciphered from viscosity, ionic conductivity and individual self-diffusion coefficients. At room temperature, change of electrolyte composition (nature of ion, concentration) induces some large variations of these transport properties. However, if these measurements are scaled towards glass transition temperatures, master curves are obtained with only slight differences between monovalent alkali and divalent earth alkaline ions. Further information is obtained from the Walden approach and evidences that these electrolytes are 'good ionic conductors'. These results are confirmed from self-diffusion coefficients which also allows to retrieve contributions of each species to ionic transport and then dissociation ratio inside these mixtures. Slight differences between alkali and earth alkali ions may be related to solvation mechanisms, as proposed from infrared spectroscopy measurements.

Keywords: ionic liquid electrolytes, alkali salts, ionic conductivity, PFG-NMR, self-diffusion coefficients, Walden diagram, post-Li battery

I. Introduction

Ionic liquids (ILs) are liquids composed only from ions, and since the past few years, they are considered as promising alternative solvents to electrolytes based on conventional liquids or polymer for battery applications.^{1,2,3,4} Unique properties of ionic liquids⁵ such as non-volatility, non-flammability, thermal and electrochemical stabilities make these materials good candidates for safer battery technologies. Synthesis flexibility also allows to get ionic liquid electrolytes which are still liquid at room-temperature or even below (Room Temperature Ionic Liquid, abbr. RTIL), and enable to dissolve consequent amount of lithium salt with acceptable ionic conductivities at low temperatures.⁶ Another unique feature of this class of materials derive from their specific molecular architecture because two antagonist counterparts are strongly linked together through a stable chemical bond : an ionic core (cationic head + anion) and an apolar aliphatic chain. This molecular architecture leads *i*) to a strong local demixing and to a very specific nanoscale organization⁷, which have strong consequences on ionic mobility processes⁸ and *ii*) to unique ability to dissolve either ionic compounds (salts), or organic molecules allowing to design materials able to fulfill specific needs for energy, catalysis, organic synthesis, magnetism, luminescence ...⁹

Taking advantage from these peculiar properties, the reliability of IL based electrolytes was already recently demonstrated in advanced lithium batteries which may be used as power source even in extreme environmental conditions such as for instance orbital microsatellites.¹⁰ However, lithium battery market is growing so quickly and for such a large range of applications (mobile equipment, automotive transportation, stationary power sources) that lithium mineral resource may become out of stock soon. Then, post-lithium batteries are already proposed for the next future.^{11,12} Most specifically rechargeable batteries working at room temperature and based on sodium¹³, potassium¹⁴ magnesium¹⁵ or calcium¹⁶ are already considered as good alternatives in respect to low cost, high performance and sustainability. In the frame of these research and development stages, the quest for suitable and compatible electrolytes is a keypoint to get high performance devices and ionic liquids are already successfully reported to be used for sodium^{17,18,19}, potassium²⁰, magnesium^{21,22,23} or even aluminium or zinc rechargeable batteries.²⁴ In most of these studies, versatility of synthesis and structure design is taken as an advantage to tune viscosity and ionic conductivity, as well as to optimize stability in electrochemical devices. On a broader approach, the ability of ILs to solubilize salts has also a strong implication for other issues such as purification and extraction technologies.²⁵

In parallel to these studies dealing with the properties and optimization towards specific applications, more fundamental studies are also reported to decipher the behavior of alkali/earth alkaline ions dissolved in IL in *i*) using multi-technique experiments and spectroscopies²⁶ and/or *ii*) molecular simulation approaches (first principle or molecular dynamic).²⁷ Obviously, most of such studies are dealing with ILs doped with Li⁺ cations,^{28,29,30} because of the current interest to use these

electrolytes for lithium batteries, while only fewer are dealing with Na^+ , Mg^{2+} or even to more systematic comparison of the behavior of different alkali^{31,32} or multicharged cations³³ inside a common IL. However, it appears that some effects of cation are evidenced on solubility, viscosity and ionic conductivity of the electrolytes. They may be related to some local structural modifications as it could be evidenced from IR/Raman spectroscopy³⁴, and also confirmed from molecular simulations^{26,35,36,37}: *i*) modification of alkali coordination shell (number of TFSI⁻ anion around the alkali); *ii*) formation of clusters in which two (or more) alkali ions are connected together through anion(s) and *iii*) equilibrium constant and lifetime of complex species. These modifications are related to the differential Soft/Hard characteristics of the components³⁸ which may be described as well in terms of size, surface charge density, polarizability or electronegativity of the different alkali/alkaline earth cations (Table 1).

Table 1: some properties of alkali/earth alkaline cation^{39,40}

	Li^+	Na^+	K^+	Cs^+	Mg^{2+}	Ca^{2+}
ionic radius (pm)	76	102	138	167	72	100
electronegativity (Pauling scale)	0.98	0.93	0.82	0.79	1.31	1.00
polarizability (\AA^3)	0.03	0.18	0.81	2.02	0.08	0.44

As systematic studies about the modulation of transport properties with the nature of dissolved alkali/earth-alkaline cation are very scarce⁴¹, the main objective of this paper is an attempt to fill this gap in proposing an experimental approach to compare transport properties of alkali (Li^+ , Na^+ , K^+ and Cs^+) and earth alkaline cations (Mg^{2+} , Ca^{2+}) dissolved inside a prototypical ionic liquid: 1-butyl-3-methyl imidazolium bis(trifluoromethyl sulfonyl) imide (abbr. BMIm TFSI). To validate their use as electrolytes in post-lithium batteries, an innovative approach based on a set of different techniques is proposed in this study. First, the determination of solubility limits shown different behaviors depending on the cations tested. Then, their physico-chemical properties such as thermal transitions, room temperature viscosities and ionic conductivities are presented. Large variations are measured depending on the nature and concentration of salt introduced. In order to explain these results, the impact of the cation was first studied by infrared spectroscopy which allows to study local interactions of the cations with its solvating medium. From these studies three different cations have been selected for more detailed investigations: the smallest and the largest alkali (Li^+ , Cs^+) as well as the soluble alkaline-earth Mg^{2+} . Let's note that Cs^+ based electrolytes can not be considered as an option in a battery, but is only an interesting model in the frame of this study to extend variations on the dissolved cation. For these three cations, viscosities and ionic conductivities were determined on a large temperature range (-10°C/90°C) in order to determine Walden's relationship. Finally, thanks to the NMR properties of all the nuclei present, we were able to obtain a better insight into

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the molecular transport mechanisms for Li⁺ and Cs⁺ based electrolytes. These measurements, based on pulsed field gradient nuclear magnetic resonance (PFG-NMR), are limited to a small number of elements/nuclei: hydrogen (¹H) and fluorine (¹⁹F) to determine BMIm and TFSI behavior, respectively, with lithium (⁷Li) and cesium (¹³³Cs) being the only two alkali cations that allow such measurements (other alkali/alkaline earth cations possess detrimental nuclear properties such as low NMR-accessible nuclei abundance, low gyromagnetic ratio and/or short relaxation times). These studies converge to show that such ionic liquids-based electrolytes are good ionic conductors (i.e. they have a high dissociation) and then promising electrolytes for post-Li batteries for the various alkali/earth alkali cations.

II. Materials and methods.

II.1 Material preparation

1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMImTFSI) and cesium bis (tri fluoromethylsulfonyl)imide (CsTFSI) were purchased from Solvionic, lithium bis (trifluoromethylsulfonyl) imide (LiTFSI) from Aldrich and used without any additional purification (purities are 98% for BMImTFSI and CsTFSI and 99% for LiTFSI). Sodium, potassium, magnesium and calcium bis (trifluoromethylsulfonyl)imides (NaTFSI, KTFSI, Mg(TFSI)₂, and Ca(TFSI)₂ respectively) were synthesized from an acid-base reaction and purified following procedure described in Table S1.

Electrolytes (blends of IL and alkali/earth alkaline salt) were prepared by mixing the required amount of BMImTFSI and alkali-TFSI salt in an argon filled glovebox. Mixtures were stirred at 80 °C until homogenous solutions are obtained and then cooled down to RT to check the complete dissolution of the salt. To establish the phase diagram, solubility was assessed if the solution remains clear without any cloud or solid particles after 72h.

In this work, the electrolytes are named [X][BMIm][TFSI] (where X stands for the alkali/earth alkaline cation) and the molar fraction of dissolved salt, noted f is defined as the number of Mⁿ⁺ ions per the number of BMIm⁺ cations ($f = M/BMIm$) and was varied between 0.05 and 1.0.

II.2 Density

Density of the blends IL-salts were measured in an argon-filled glovebox to avoid humidity uptake. 1 ± 0.05 mL of IL are measured by a micropipette equipped with a plastic tip and then weighted with a precision balance. This measurement procedure was repeated 5 times for each sample, in order to obtain the average density values at RT and leads to a precision of ± 10 %. However, this procedure could be only performed at RT. In order to estimate density values at other temperatures (which are

requisite for the determination of molar conductivities and dissociation degrees), we assumed that electrolyte density follows a linear variation, $\rho = b - aT$, as it is generally measured and used the a coefficient of pure BMImTFSI ($0.94 \text{ g.cm}^{-3}.\text{K}^{-1}$).⁴² Let's note that other tabulated values of the a coefficient for TFSI based ionic liquid are all lying in the range $1.0 \pm 0.6 \text{ g.cm}^{-3}.\text{K}^{-1}$.⁴³

II.3 Differential scanning calorimetry (DSC)

DSC measurements were carried out using a Mettler Toledo DSC1 STARe instrument and data were processed with STARe software. Heating/cooling rate are $10^\circ\text{C}/\text{min}$ in the range -150°C to 100°C and 5 minutes isotherms are used between the different sequence. Even if no variation was depicted with thermal history, the phase transition behavior temperature was determined for the second heating cycle. The rate of nitrogen flux around the DSC chamber was controlled at 150 mL.min^{-1} and 50 mL.min^{-1} inside the chamber. Liquid nitrogen was used to cool the samples.

II.4 Viscosity

Viscosity measurements were carried out with an ARES-G2 rheometer (TA Instruments), using a cone and plate geometry (diameter 40 mm, angle between cone and plate 1-2 degrees). In order to avoid humidity, the machine was covered by a plastic glovebag and filled with dried air. The temperature was controlled by a Peltier device from -10 to 90°C . The data were treated by TRIOS software.

II.5 Ionic conductivity

Ionic conductivity of electrolytes was measured by Electrochemical Impedance Spectroscopy (EIS) using an impedance meter Hewlett Packard 4192A and results were fitted by Zview software. Measurements were performed with a micro conductivity cell on a wide frequency range 10mHz to 1MHz between -10°C and 90°C . The samples were prepared in a glovebox and PTFE tap was used to ensure an anhydrous environment. The cell constant was determined from the conductance of a reference 0.1 M KCl solution.

II.6 Pulsed-field gradient nuclear magnetic resonance (PFG-NMR)

Self-diffusion coefficients were measured by PFG-NMR using a Bruker 400 Avance III HD spectrometer (frequencies are 400.13, 376.50 and 155.51 MHz for ^1H , ^{19}F and ^7Li , respectively) and a Bruker 300 Avance III spectrometer for ^{133}Cs PFG-NMR (frequency : 39.35 MHz), both equipped with 5mm diffusion probe and temperature regulation unit ($20 - 80^\circ\text{C}$, accuracy and stability $\pm 2^\circ\text{C}$). ILs were filled into small diameter tube ($d = 4 \text{ mm}$) in the glove box, then were flame sealed to prevent the humidity.

Stimulated echo sequence was used. The maximum magnitude of the pulsed field gradient for both spectrometer was 900 G.cm^{-1} , the diffusion delay Δ was adjusted between 50ms and 100ms, and the

gradient pulse length δ was set between 1ms and 5ms depending on the diffusion coefficient and the nature of the mobile species. At higher temperature, some measurements were also performed with $\Delta=200$ ms to confirm that no convection artifacts occur. The self-diffusion coefficients were determined from the classical Stejskal-Tanner equation⁴⁴:

$$\ln(I/I_0) = -DG^2\gamma^2\delta^2(\Delta-\delta/3)$$

where G is the magnitude of the two gradient pulses applied, γ is the gyromagnetic ratio of the nucleus under study and I and I_0 are the integrated intensities of the signal obtained respectively with and without gradient pulses. Here, we used 16 equally spaced gradient steps for each experiment. Data acquisition and treatment performed with Bruker Topspin software.

II.7 Infrared spectroscopy.

Fourier transform infrared (FTIR) analyses were carried out using an IR spectrometer Spectrum ONE (Perkin Elmer). The samples were analyzed in transmission in wavenumber range between 4000 and 400 cm^{-1} . The IR spectra were acquired with 16 accumulations and a resolution of 1 cm^{-1} . Ionic liquid electrolytes were placed in a liquid cell with ZnSe window and measurements were performed in N_2 atmosphere. Experimental data have been processed in using Origin software, and spectra are deconvoluted with gaussian shaped peaks to extract relative area of the different vibrations.

III. Results and discussion

In this study, several room temperature IL-based mixtures which could be potentially used as electrolytes in battery have been studied. One of the main objectives is to analyze and link the molecular level description with the limiting macroscopic properties such as ionic conductivity dependency on charge carrier nature and cation solvation. We were first interested by the solubility properties of the salts in the studied ionic liquid. Many works have been devoted to very various mixtures of MCl_x in BMIMCl mostly in the aim of obtaining less hydrolysable metal chlorides than those based chloroaluminate^{45,46,47,48}, but similar systematic data on MTFSI_x in BMIm TFSI are scarce, and obviously no general rules are observed.⁴⁹ The solubility limits (measured up to $f=1.0$) at 25°C for the different alkali/alkaline earth TFSI salts are presented in Figure 1 (and Table S2). A strong dependence on alkali/earth alkaline to the maximum miscibility was evidenced, with the possibility to reach high alkali concentration with Li^+ and Mg^{2+} , while Ca^{2+} is totally immiscible. For other alkali salt, the minimum of solubility is reached for the potassium ion ($f=0.2$). Let's note that the corresponding maximum concentrations are then above 0.9 mol.l^{-1} for Na^+ and 2 mol.l^{-1} for Li^+ and Mg^{2+} , which make these systems as potentially interesting electrolytes for post-lithium batteries. Similar variations of solubility between Li^+ and Na^+ cations in a series of ionic liquids were already

observed and investigated from a theoretical approach.⁵⁰ It evidenced the influence of cation polarizability (i.e. s^2 orbital energy) to the chemical bonding of alkali ions with the ionic liquid anions. However, compared to standard electrolytes (salt dissolved in a solvent), the concept of salt dissolution inside ionic liquid is somewhat different, and then could also influence the large variation of solubility for the different ions. As ionic liquid is already only made of ions, "dissolution" process of an alkali ion inside an ionic liquid may also be considered as a "simple" exchange between a BMIm^+ cation and an M^+ alkali ion (or two BMIm^+ in the case of M^{2+} alkaline-earth ions).⁵¹ If classical solubility is generally governed by ion polarity, polarizability and may be also expressed in other terms by Hard and Soft Acid and Bases principles⁵², the process to replace ions inside a condensed polar media may be also driven by entropic driving such as a subsequent change of coordination scheme from a large organic cation (BMIm) to the smaller alkali ions (number of neighbor, polarizability of ion or size and hardness of cation, favorable coordination scheme) which may lead to a substantial local reorganization of ionic liquid nanostructure.²⁹ As Li^+ is small, it should be surrounded by many TFSI^- anions while Cs^+ is much larger and more polarizable. Then, Cs^+ should have a volume and an electronic density more comparable to BMIm^+ and then help for its replacement and easier accommodation.^{53,54,55} The balance between these effects is probably less favorable for intermediate cations as it is highlighted from the lower attainable concentration. Similar situation has been observed in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonylimide where Li^+ is the most soluble and Cs^+ is not far behind, whereas Na^+ is twice less soluble.⁵⁶ Surprisingly, the two earth-alkali ions behave very differently, Mg^{2+} presenting a great solubility while Ca^{2+} is totally insoluble.

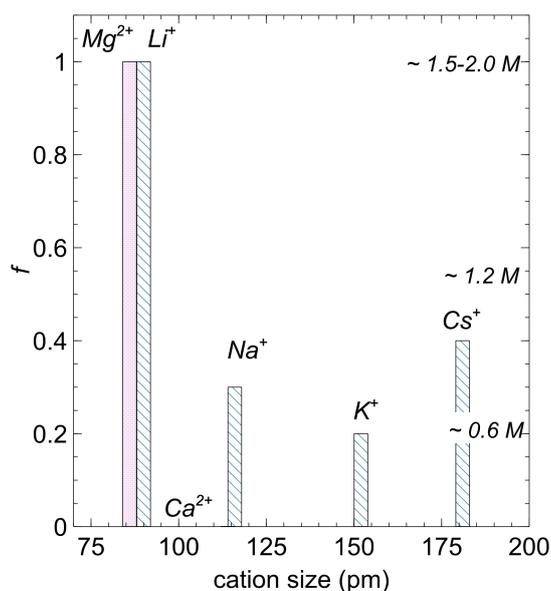
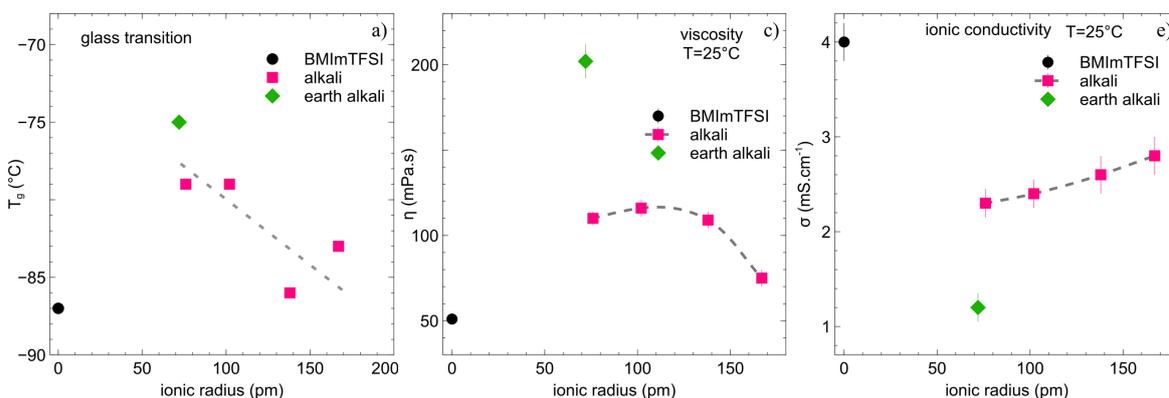


Figure 1: Solubility range, measured up to $f=1.0$ at 25°C of the various alkali/earth alkaline salts $M(\text{TFSI})_n$ in BMImTFSI ; $f=M/\text{BMIm}$. Annotations on the right side indicates the corresponding alkali molarity of the electrolyte.

DSC measurements have been performed for all electrolytes, which present only a glass transition (Figure S1). Figures 2 a) and b) (and Table S3) show the glass transition temperature (T_g) variation with cation size and concentration. A severe influence of cation replacement is measured even for the smallest f ratio, Fig. 2a). While neat BMImTFSI present a glass transition at -87°C , and a cold crystallization at -42°C followed by a melting point at -1°C , all $[\text{X}][\text{BMIm}][\text{TFSI}]$ electrolytes present only a glass transition at low temperature. Inhibition of crystallization in replacing a BMIm^+ cation by an alkali/alkaline earth ion was already depicted in the literature⁵⁷ and may be explained by the large size difference between the alkali/alkaline earth ion and IL cation which prevents efficient and regular packing inside the blend IL/XTFSI and lead to a more homogeneous fluid.⁵⁸ For a moderate alkali/earth alkali cation content ($f=0.2$), T_g increases when cation size decreases (Fig. 2a) and this should correspond to stronger reduction of the lattice energy for the more asymmetric systems (smaller ions) in reducing the packing of the ions.^{35,59} This is also confirmed by the measurements of electrolyte densities presented in table S3, which are larger when alkali/alkali earth is added to pure BMImTFSI, but rather independently to the nature of the salt itself. T_g also gradually increases with the increase of the salt concentration (Fig. 2b). This suggests a decrease of structural organization when replacing a large BMIm^+ cation to a smaller alkali cation in agreement with other studies.^{30,60} Stronger amplitude of this effect is measured with Mg^{2+} , this is probably related not only to the size of the cation but also because one cation replace two BMIm^+ , which induces inevitably a stronger structural disorder.



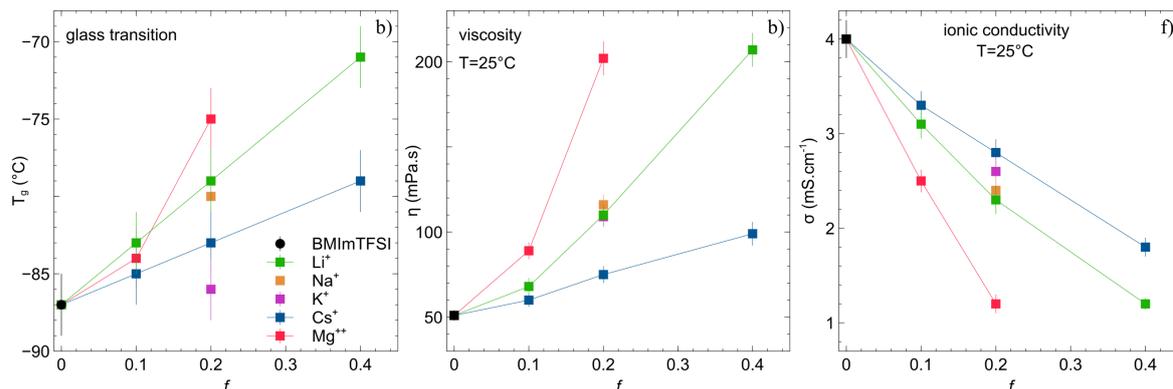


Figure 2 : Properties of [X][BMIm][TFSI] electrolytes a) and b) : glass transition temperature ; c) and d) : viscosity at 25°C ; e) and f) : ionic conductivity at 25°C. *upper section* : as a function of ionic radius for $f=0.2$ ii) *lower section* : as a function of the salt ratio f .

The variation of the viscosity η with the nature of alkali/earth alkaline salt inside the blends at 25°C is reported in Figure 2c for $f=0.2$ (and Table S3). The viscosity of the blend with alkali/earth alkaline salt is always higher than the pure ionic liquid, this variation being moderate for Cs⁺ cations ($\eta=75$ mPa.s), than for all other smaller alkali ($\eta\sim 110$ mPa.s for Li⁺, Na⁺ and K⁺) and even more pronounced for Mg²⁺ ($\eta=210$ mPa.s). Change of viscosity with cation concentration follows the same trends, figure 2d. Nevertheless, for similar molar ratio $f=0.2$, this effect is less pronounced for the biggest cation Cs⁺. As viscosity of molecular compounds arises from intermolecular/interionic cohesive forces, reinforcement of these effects by replacing a large BMIm⁺ cation by smaller ones may be related to a balance between size and ionicity of the coordinated cation and solvation shell reorganization leading also to change of nanoscale structural reorganization inside the blends as it was also depicted in other systems.^{27,28,46,61,62}

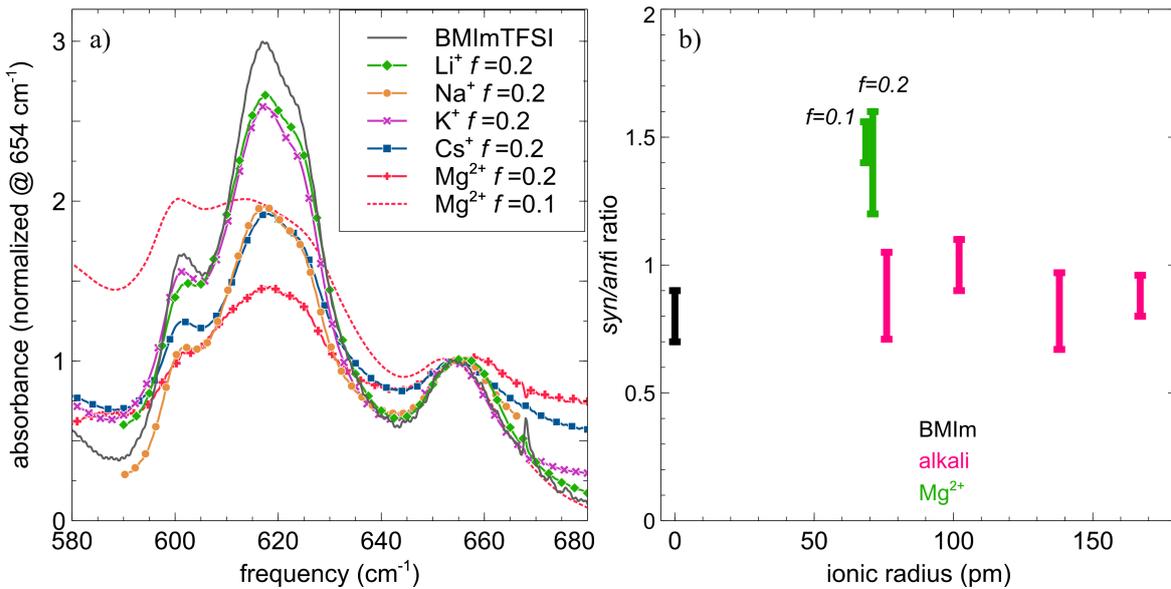
Figures 2 e) and f) present the ionic conductivity at 25°C of the studied electrolytes versus cation size and concentration. It evidences that ionic conductivity is reduced upon addition of alkali/earth alkaline salt and this decrease varies quasi-linearly with the f ratio for the different ions, figure 2 f). Such effect was already depicted in all systems obtained in mixing alkali salt to any ionic liquid and related to the change of local structuration inside the ionic liquid, and the consequent increase of viscosity.^{63,64} This effect appears to be more severe for Li⁺ and even Mg²⁺ than for Cs⁺ ions. As presented in figure 2 e), it seems that the ionic conductivity increases with the cation size. To better understand the results, the interactions of the cations in the electrolytes have been investigated by IR spectroscopy.

To get more information about the structure of charge carrier complexes in the electrolytes, a detailed vibrational spectroscopy study has been performed. We primarily analyzed the region

holding between 580 and 680 cm^{-1} , which corresponds to the specific signature of the conformation of the TFSI anion. It has a flexible structure and can exist in two inequivalent conformations e.g. cisoid (or *syn*) and transoid (or *anti*)⁶⁵, which are observed in the liquid or glassy state of the TFSI-based ILs. The ratio of these two conformations has strong influences on the IL physical properties.⁶⁶ Figure 3a presents IR spectra in this range: *syn*-TFSI being characterized by absorbance at 602 and 656 cm^{-1} (corresponding respectively to $\delta_{(\text{SO}_2)}$ and $\delta_{(\text{SNS})}$)^{67,68}, whereas the *anti* conformer is observed at 618 cm^{-1} in pure ionic liquid and also after addition of alkali ion, as it was already well documented in the literature.⁶⁹ The ratio between the two conformers is calculated from the following relationship:

$$r = \frac{I_{cis}}{I_{trans}} = \frac{I_{602} + I_{656}}{I_{618}} \quad (5)$$

where I_{cis} , I_{trans} , I_{602} , I_{656} and I_{618} are respectively the area of *syn* and *anti* conformers which are obtained from the intensity at 602, 656 and 618 cm^{-1} . The ratio r for all of electrolytes at 25°C are presented in Figure 2b.



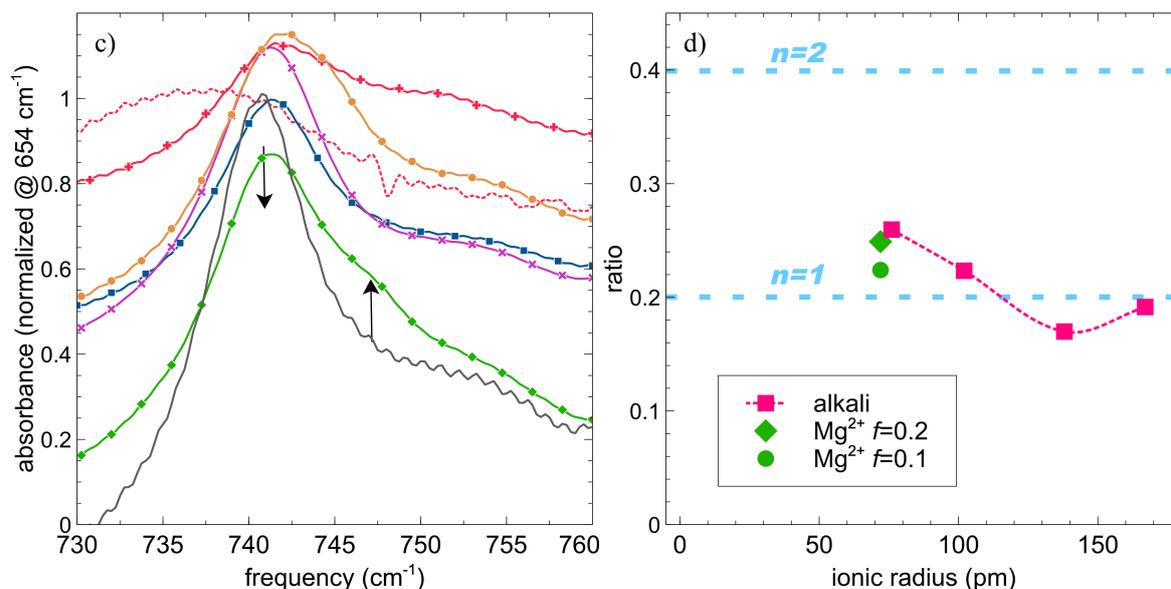


Figure 3: Infrared Spectroscopy of $[X][BMIm][TFSI]$ electrolytes at 25°C : i) TFSI⁻ *syn/anti* conformations (580cm⁻¹-680cm⁻¹ range a) spectra and b) ratio *syn/anti* (calc. from Eq. 5) ii) number of anion TFSI⁻ coordinated to cation (730-760 cm⁻¹) c) spectra and d) ratio = $I_{748}/(I_{748}+I_{740})$.

For neat BMImTFSI ionic liquid, the ratio of *syn/anti* conformers is nearly unity and addition of alkali salt do not change drastically this equilibrium, whatever is the amount of added salt. These results are in agreement with the literature,⁷⁰ where characteristic anionic clusters related to these conformations are already identified such as $[Li(TFSI)_2]^-$ dimers, larger $[Li_m(TFSI)_n]^{(n-m)-}$ aggregates or $[Na(TFSI)_3]^{2-}$, in which *syn* and *anti* conformers have similar populations.⁷¹ Similar *r* ratio are measured for other alkali ions (K and Cs), suggesting that close aggregation scheme may occur, while the ratio of *syn* population increases severely in blends of IL doped Mg(TFSI)₂. Furthermore, for this alkali earth cation, a strong dependence of *r* with *f* fraction is measured, and at *f* = 0.2, the quantity of *syn* conformer is nearly twice compared to the *anti*-TFSI. This behavior should be related to the formation of large and stable complex structures with the bi charged Mg²⁺. Similar data were obtained in other ionic liquids, with the simultaneous presence of Mg²⁺ ions as isolated solvated ions and in cluster, and an average of 3 to 4 TFSI anion surrounding an Mg²⁺.^{72,73} The presence of such large structures may be related to an increase of *T_g* in these blends, with the consequence of lower ionic conductivity.

Secondly, the region holding the strong 730-760 cm⁻¹ $\nu(SNS)$ band of the TFSI anion has been analyzed (Fig. 3c, 3d). This vibrational mode corresponds to expansion and concentration of the whole anion and can be linked to the TFSI⁻ solvation. From literature,⁶⁷ the band assigned to TFSI being coordinated to the cation in IL is located at 748cm⁻¹, whereas for the pure ionic liquid, the band associated to the anion TFSI⁻ is close to 740 cm⁻¹. To analyze the amount of TFSI being coordinated per cation, the total ratio $I_{748}/(I_{748}+I_{740})$ was used, where *I*₇₄₀ and *I*₇₄₈ are the areas of the bands located

at 740 cm^{-1} and 748 cm^{-1} , respectively. The variation of this ratio with the cation size is presented in Figure 3d. According to the method developed by Lassègues et al,⁶⁷ the solvation number of the cation can be determined for the different salt concentration. The values obtained for the different cations are therefore very close to 1. These results are a little different from those of the literature determined by Raman spectroscopy, which highlights values of $n=2$ for lithium.⁶⁷ If the effect of the nature of the spectroscopy can have an impact, one can also discuss the effect of the concentration. The studies carried out in the literature concern concentrations lower than 0.1. At higher concentrations, the complexation mechanism is probably modified. For alkaline cations, we observe a decrease of the ratio with the size of the cation to reach a solvation number below 1, which should contribute to an improvement of the ionic conductivity. This is in agreement with the results previously presented. The impact on the viscosity remains to be investigated. The behavior for magnesium is different and shows a stronger complexation, compared to that observed for alkali cations of the same size. This result was rather expected.

This first study allowed us to present the effect of the nature of several cations on key properties of electrolytes used in batteries. The nature of the cation and more particularly its size seems to have a large impact on these properties. For the rest of this study, we focused on the smallest and the largest alkaline cations (Li^+ , Cs^+) and the only earth alkaline cation (Mg^{2+}).

Figure 4a) presents the variation of viscosity with temperature ($1000/T$ abscissa scale) for Li^+ , Cs^+ and Mg^{2+} based electrolytes on a large range of temperature (-10°C to 90°C). Huge variations are measured, and all curves present rather similar curvature which indicates a free volume/VTF behavior with rather similar activation energies for all cations and concentrations (cf. Table S4). When these data are rescaled with T_g/T abscissa (Fig. 4b), viscosity for alkali ions are lying nearly on the same master curve as the pure BMImTFSI ionic liquid, rather independent of cations and their concentration, while those for Mg^{2+} are slightly shifted but still independent of the concentration. These curves are related to the fragility of the liquid^{74,75} which is then rather similar for the pure ionic liquid and electrolytes based on the two alkali and moderately smaller than those of mixture obtained with Mg^{2+} .

As depicted in the literature in other ionic liquid electrolytes,³⁷ such differences are related to some differences in the coordination scheme of monovalent vs. divalent cations as also observed from our IR data. It induces some structural perturbations, but then, surprisingly these effects are observed with similar magnitude whatever is the concentration of added salt.

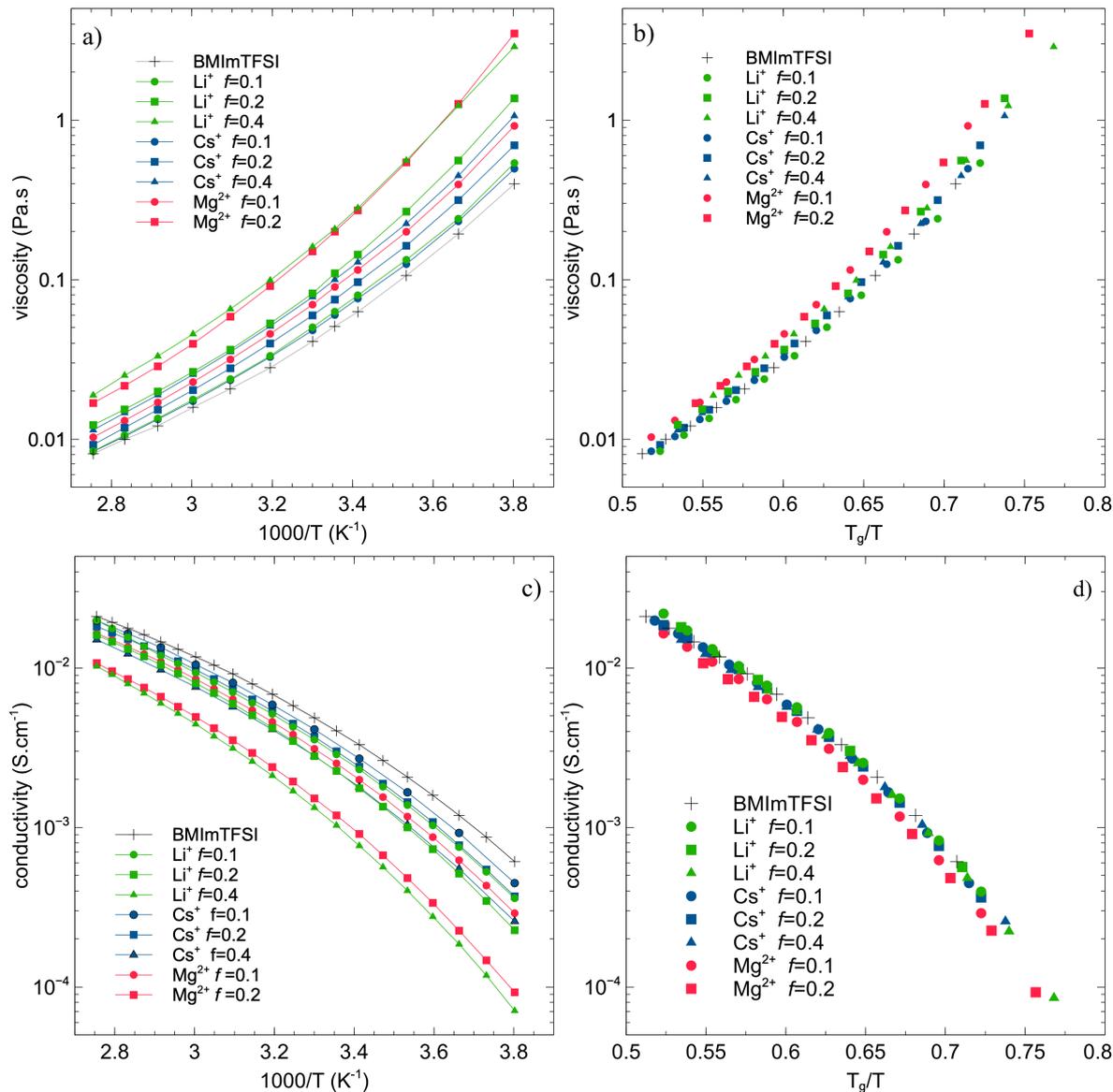


Figure 4 : Evolution of viscosity and ionic conductivity with temperature for [X][BMIm][TFSI] (X=Li⁺, Cs⁺, Mg²⁺) electrolytes ($f=0, 0.1, 0.2, 0.4$). a) and c) as a function of $1/T$, evidencing a free-volume behavior; b) and d) as a function of T_g/T evidencing similar fragility for the different electrolytes.

Figure 4c) presents the evolution of the ionic conductivities of these blends on large range of temperature. These plot present curved shapes evidencing that ionic mobility experience free volume like mechanisms in these blends, like it was already determined in other electrolytes based on ionic liquids.^{76,77,78} These data were fitted with a VTF model, and parameters are presented in Table S5. Activation energies of mixtures with alkali/earth alkaline salts are rather similar for all the mixtures with no clear dependence of the nature of ion or its concentration (and slightly higher than pure BMImTFSI). This similarity can be also evidenced from an Arrhenius plot of the conductivity σ as

a function of T_g/T (Fig. 4d), where curves of pure BMImTFSI, and all solutions with alkali ions are lying on an unique master curve (and independent to the salt ratio f), while the curves corresponding to solution of the divalent Mg^{2+} are slightly shifted to lower conductivity.

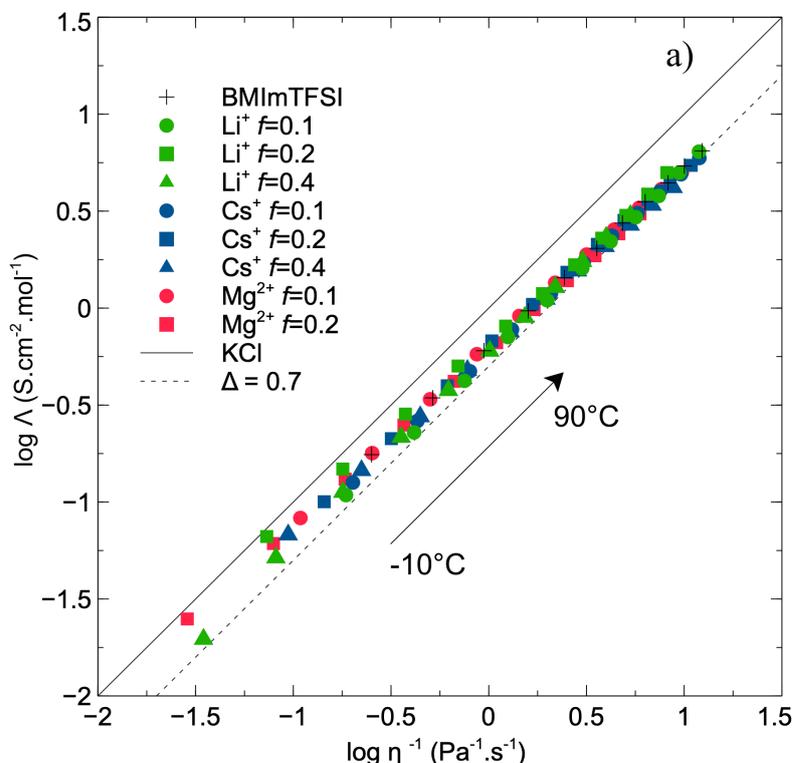


Figure 5 : Properties of $[X][BMIm][TFSI]$ electrolytes ($X=Li, Cs, Mg$): Walden plots combining viscosity and ionic conductivity in a large range of temperature. The line corresponds to the fully dissociated KCl 1M solution, while the dotted line corresponds to a deviation parameter Δ of 0.7 (refer to eq. 3)

Comparison of viscosity and ionic conductivity data allows to evidence the velocity cross-correlation of the ionic liquids⁷⁹ through Walden's approach establishing relationship between molar conductivity (Λ) vs. fluidity ($1/\eta$).⁷⁴ Figure 5 presents a Walden plot for neat BMImTFSI, as well as Li⁺ and Cs⁺ salts dissolved in BMImTFSI electrolytes at $f=0.1$ to 0.4 in a large range of temperature (-10°C to 90°C). Data for all these solvents are nearly lying on a same master curve indicating a very low influence of the added salt on macroscopic properties, as it was already evidenced above. As almost all neat ionic liquids⁸⁰, those curves are slightly below those of the ideal 1M KCl aqueous solution, which is fully dissociated. The fact that this deviation from the KCl line is small shows that our electrolytes can be considered as 'good ionic liquids'. This deviation slightly increases with temperature over the whole range of temperature explored here (-10°C to 90°C). This small evolution has

been observed for pure ionic liquids⁷⁹, and mixtures of ionic liquid with salt addition.^{81,82} The temperature dependence indicates that these solvents obey to a fractional Walden rule: $A\eta^\alpha = \text{constant}$ where A is the molar conductivity ($A = \sigma/M$, where σ is the ionic conductivity and M the molar concentration of the electrolyte), η is the viscosity and α is the slope of the curve in log-log plot. This last parameter is slightly smaller than 1 (between 0.87 and 0.96) and nearly independent from the nature of the added alkali/earth alkaline cation and its concentration. The gap with an ideal solution indicates that mobile ion relaxation modes are decoupled from those of the matrix⁸³, as it was also observed in superionic conductors, polymer electrolytes⁸⁴, molten lithium salts.⁸⁵ This also reflects that activation energies for viscosity and conductivity are slightly different, as it was also shown in other binary systems (e.g. 1-ethyl-3-methylimidazolium tetrafluoroborate/lithium tetrafluoroborate).⁸⁶

Further analysis requires to discriminate transport properties of each species. Such information is available from the selectivity of NMR which allows to measure specifically the behavior of BMIm⁺, Li⁺ or Cs⁺ cations and TFSI⁻ anions in measuring PFG-NMR for nuclei ¹H, ⁷Li, ¹³³Cs and ¹⁹F respectively. Figure 6a), Tables S3 and S4 exhibit the variation of individual self-diffusion coefficients of [X][BMIm][TFSI] (X=Li and Cs) electrolytes as a function of the alkali content f at 293K as well as a function of temperature (Fig S2). In pure BMImTFSI, self-diffusion of BMIm cation is higher than the TFSI anion, in agreement with results reported in the literature,⁴² as the anion is heavier/larger than the cation. Adding alkali ions, even in small amount, yields strong decrease of both BMIm and TFSI self-diffusion coefficients. Furthermore, the alkali cations self-diffusion coefficient are the smallest of the three species. This apparently surprising effect (alkali ionic radius is obviously much smaller than BMIm⁺ or TFSI⁻) has already been depicted in all electrolytes based on ionic liquid.^{29,36,63} This effect has been related to the complexation of the alkali cations with anions to make larger species, i.e. less mobile. This effect is less pronounced for Cs⁺ than Li⁺ cations, which indicate that Cs⁺ is less associated or more loosely than Li⁺ cation. The decrease of self-diffusion for the three kinds of ion when the alkali amount is increased, i.e. f ratio increase, is more pronounced with Li⁺ than Cs⁺. However, the largest decreased is observed for the TFSI in the [Li][BMIm][TFSI], thus supporting the idea of Li⁺ strong complexation. This is probably related to high ionic potential (z/r_{ion} , where z is the charge number and r_{ion} the ionic radius) of Li⁺ in comparison with Cs⁺. It can be noted that in inorganic molten salts, the ionic potential is also an important parameter to understand the ionic diffusion processes.⁸⁷ It is also the case for salts dissolved in water, where higher self-diffusion coefficients of Cs⁺ has also been documented.⁸⁸

To go further, the electrochemical ionic conductivity and self-diffusion coefficients can be compared. For this purpose, the Nernst-Einstein equation allows first to derive an ideal conductivity using the self-diffusion coefficients of each species:

$$\Lambda_{NMR} = \frac{e^2}{kT} (N_{alk} \times D_{alk} + N_{BMIm} \times D_{BMIm} + N_{TFSI} \times D_{TFSI}) \quad (2)$$

where N_i and D_i are respectively the molar ratio and the diffusion coefficient of species i ($i=BMIm^+$, TFSI, alkali⁺), D_i values being obtained by PFG-NMR. Second, the deviation to the Nernst-Einstein equation is given using the ratio Δ of the measured molar ionic conductivity by EIS (Λ) and the calculated one (Λ_{NMR}) corresponding to full dissociation:

$$\Delta = \Lambda / \Lambda_{NMR} \quad (3)$$

In fact, this ratio gives insight into the distinct diffusion coefficients (in contrast to the self-diffusion coefficient given by PFG NMR).⁸⁹ For neat BMImTFSI and as in almost all the ionic liquids, the deviation parameter Δ , is smaller than 1.²⁹ Figure 6b presents the evolution of Δ as a function of the composition of [X][BMIm][TFSI] electrolytes (X=Li⁺, Cs⁺, $f=0-0.4$). The value of Δ for pure BMImTFSI is 0.63, in good agreement with literature data⁹⁰ and is not much affected with the addition of XTFSI salt. Following the approaches of Kashyap et al.⁸⁹ and Harris et al.⁷⁹, it means that the term of velocity cross-correlation of unlike ions balances those of like ions in a greater manner than in the case of neat ionic liquids. It must be underlined that correlating the deviation ratio to a dissociation ratio in molten salts (in its widest definition) is a complete non-sense as already explained by Harris et al.⁷⁹

For batteries application, another crucial parameter is the fraction of charge which is transported by the desired ions, i.e. alkali ion in the frame of alkali batteries. This value, is called transport number and denoted as t_+^{alk} and is obtained from the individual self-diffusion coefficients, in using the following equation :

$$t_+^{alk} = \frac{N_{alk} \times D_{alk}}{N_{alk} \times D_{alk} + N_{BMIm} \times D_{BMIm} + N_{TFSI} \times D_{TFSI}} \quad (4)$$

Figure 6b reports also the variation of t_+^{alk} as a function of the electrolyte composition for both Li⁺ and Cs⁺ based systems. The values of t_+^{alk} are very small for the lower alkali ratio, as a consequence of the low mobility and the low content of alkali ion, and they increase linearly with the alkali content, as it was already depicted in other experimental and theoretical studies.^{32,57,91} However, for all compositions, t_+^{Cs} larger than t_+^{Li} show that under similar conditions, Cs⁺ is more mobile than Li⁺, in agreement with the Walden analysis. Modifications of transport numbers with the nature of dissolved cations were also already deduced from experimental and MD studies in different ionic liquid electrolytes and related to the dissolution mechanism and solvation shell and association of the cation.^{37,60}

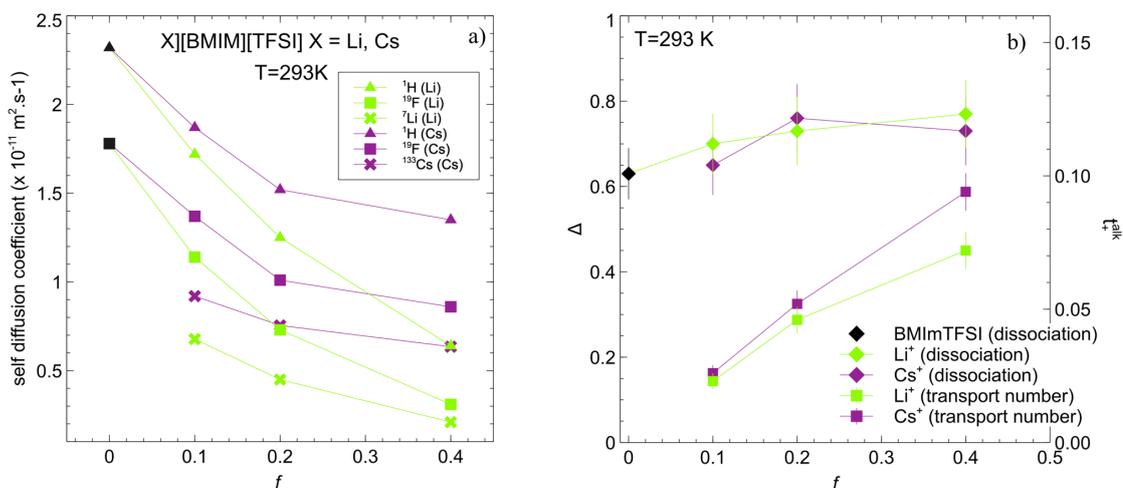


Figure 6 : Transport properties of [Li, Cs][BMIm][TFSI] electrolytes at 293K, as a function of salt concentration f , a) variation of self-diffusion coefficients for X, BMIm and TFSI for and b) deviation to Nernst-Einstein equation (Δ) and alkali transport numbers T_{alk}^+ .

Conclusion

Large quantities of alkali or earth alkaline salts (Li, Na, K, Cs, Mg) could be dissolved in the prototypical BMImTFSI ionic liquid, still keeping wide liquidus temperature range, starting below -70°C , as small amount of inorganic salt prevent crystallization that is observed in the neat ionic.

This study focuses on transport properties (viscosity, ionic conductivities and self-diffusion coefficients). When measured at given temperature, large differences are observed when changing the nature and/or the concentration of added inorganic salts. However, these differences may vanish if these physical quantities are scaled with the glass transition temperature, leading to two master curves with weak differences, one for all alkali ions and another one for Mg^{2+} electrolytes. Such behavior supports strong coupling between viscosity and ionic conductivity and also evidences that these electrolytes belong the class of "good ionic conductors". The addition of the inorganic salts induces a drop of the transport coefficients for all the species, the largest ionic potential, the largest drop. Nevertheless, the deviation ratio to the Nernst-Einstein equation decreases with the alkali concentration.

Finally, the transport number of Li^+ is slightly smaller as Cs^+ . This may be related to the difference in ionic size, and the lower charge surface of Cs^+ leading to less interactions with TFSI^- anions. Even small variations are observed with the charged Mg^{2+} , where one cation replaces two largest BMIm⁺ cations. These modification of transport properties may be also associated to some changes in the TFSI conformation as measured by infrared spectroscopy.

It is also well-known that strong structural organization at the nanoscale occurs in liquid electrolytes, and may be modified by exchanging part of the cations, with major implications on dynamical and electrochemical properties. These effects have already been deciphered in some Li⁺ based electrolytes, but never retrieved for Na⁺ or Mg²⁺ based electrolytes. They are key parameters for practical usefulness of such electrolytes for advanced batteries. However, these data are not yet attainable by experimental approach, and it should require some molecular dynamic approach which is already in progress to grab such information.

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