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# Effect of the chain lengthening on transport properties of imidazolium-based ionic liquids

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## Abstract

The objective of this work is to study the effect of the lengthening of the linear alkyl chain of the imidazolium cation on some transport properties. We focused on hydrophobic ionic liquids based on bis(trifluoromethanesulfonyl)imide anion. Among the different properties, we measured at the viscosity and ionic conductivity of four different 1-alkyl-3-methylimidazolium ionic liquid in the temperature range between 293 to 333K. Thus, Electrochemical windows of these ionic liquids and the diffusion coefficient of ferrocenemethanol (FcMeOH) in the four ionic liquids were studied using cyclic voltammetry at 298K. The FcMeOH diffusion coefficient was found to be higher in shorter alkyl chain ionic liquids.

**Keywords:** ionic liquid; imidazolium; diffusion coefficient; ferrocenemethanol

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## 1. Introduction

In the past several years, room temperature ionic liquids (RTILs) have attracted a fast-growing research interest as innovating solvents. This growth is explained in particular by the need of developing respectful processes of the environment [1]. The understanding of the relationship between the molecular structure and the physicochemical properties is a basic need in chemistry in aim to create specific task materials with desirable properties. RTILs, composed entirely of ions, have outstanding physicochemical properties that can be easily adjusted by changing the structure of the component ions [2, 3]. This class of salts, with a low melting point, has their specific characteristics, like negligible vapor pressure, high thermal stability, non-flammability, wide electrochemical window (even up to 4-6 V) [4, 5], enhanced solvent quality tunable nature and, above all, easy recycling procedures which make them potential substitutes of many traditional organic solvents. All those properties explain their potential application in the field of electrochemistry. However, in order to use these media, understand and predict their behaviors, the measurement of the physicochemical properties of ionic liquids such as density, viscosity and ionic conductivity are necessary. More and more data are presented in literature. For example, Tariq *et al.* [6-8] have studied several thermophysical properties, including density and viscosity of a family of 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ionic liquids in an extended temperature range. Vranes *et al.* [9] reported density, viscosity and ionic conductivity measurements of 1-butyl-3-methylimidazolium bis(trifluoro-methanesulfonyl)imide at temperatures from (293.15 to 353.15)K. Monti *et al.* [10] presented density, viscosity and conductivity measurements of 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide over a thermal window of 187 K to 423 K. Although, more and more data are present in the literature, it is still important to measure them accurately before any study since their purity and especially the water content can affect their values. In electrochemistry, ionic liquids are more used since they have, especially sufficient electric conductivity and large electrochemical window. Nevertheless, the majority of ionic liquids has a very high viscosity, which strongly influences one of the main steps of electrochemical processes, i.e., the matter transport by diffusion of soluble products.

The aim of this work was to study the effect of the length of the alkyl chain for a series of 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide on their electrochemical

behavior. For that, relevant physicochemical properties were studied, such as viscosity, density, conductivity of the neat ionic liquids according to the temperature in a range between 293 to 333K. Thus, the electrochemical windows of these RTILs and the diffusion coefficient of ferrocenemethanol (FcMeOH), taken as redox probe [11] were determined at 298K.

The RTILs studied in the present work have in common the anion bis(trifluoromethanesulfonyl) imide (TFSI<sup>-</sup>), which gives to RTILs their hydrophobicity, good electrochemical stability and high thermal stability [12]. In fact, imidazolium based ionic liquids, especially those based on hexafluorophosphate (PF<sub>6</sub><sup>-</sup>), tetrafluoroborate (BF<sub>4</sub><sup>-</sup>) and bis(trifluoromethanesulfonyl)imide (TFSI<sup>-</sup>) anions are commonly investigated for many years. However ionic liquids with PF<sub>6</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup> anions can be easily deteriorated by contact with water due to slow hydrolysis of BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> liberating HF [13]. For that reason, the use of imidazolium based ionic liquids with more hydrophobic anions such as TFSI<sup>-</sup> is preferable.

## 2. Experimental

### - Chemicals

The source and the purities of all the chemicals used are listed in Table 1. The four imidazolium salts were synthesized according to standard methods [14]. They were prepared by anion exchange from the corresponding bromide salts of 1-alkyl-3-methylimidazolium cations with different n-alkyl (2, 4, 8 and 10) substituents. 1-alkyl-3-methylimidazolium bromide was prepared from a quaternization reaction of 1-methylimidazole with a slight excess of the corresponding alkyl bromide in ethyl acetate at 77°C under reflux with stirring for 24 hours. The reaction was stopped when two phases were formed. The top phase, containing unreacted starting material in ethyl acetate, was decanted and discarded. The bottom phase, in which the 1-alkyl-3-methylimidazolium bromide was contained, was washed three times with ethyl acetate in order to remove any unreacted reagents. Then, residual ethyl acetate was removed by heating at 70°C under vacuum overnight. The bromide salt was obtained as a colorless hygroscopic solid. A solution of LiTFSI in water was then added to an aqueous solution of the bromide salt at room temperature and rapidly stirred for four days. Two phases were formed. The top phase, containing lithium bromide (LiBr) in water, was removed and discarded. The bottom phase, with the given 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, was washed with small volumes of distilled water until no precipitation of AgBr occurred in the aqueous phase on addition of molar AgNO<sub>3</sub> solution. Traces of volatile solvents were removed by rotary

evaporator and water by freeze-drying (Operon Dry Freezer -90°C) just before any experiment. Structures of the resulting salts were confirmed by <sup>1</sup>H NMR spectroscopy and mass spectrometry. The residual water in the four freshly prepared and freeze-dried RTILs was titrated using a Karl – Fisher coulometer (C20, Mettler Toledo). The four RTILs based on bis(trifluoromethanesulfonyl)imide (TFSI) anion, 1-ethyl-3-methylimidazolium (EMIMTFSI), 1-butyl-3-methylimidazolium (BMIMTFSI), 1-octyl-3-methylimidazolium (OMIMTFSI) and 1-decyl-3-methylimidazolium (DMIMTFSI) contained less than 50 ppm of water. After drying, the RTILs were stored in a Ar-filled glovebox until use. To avoid water uptake or atmospheric moisture, the protective Ar atmosphere was maintained during all steps of measurement protocols for density, viscosity and ionic conductivity by using syringe techniques.

Table 1- Materials description

Chemical name	Source	Purification method	Mass fraction purity	Analysis method
<b>1-methylimidazole<sup>a</sup></b>	Alfa Aesar	-	0.99	-
<b>1-bromoethane<sup>a</sup></b>	Alfa Aesar	-	0.98	-
<b>1-bromobutane<sup>a</sup></b>	Alfa Aesar	-	0.98	-
<b>1-bromooctane<sup>a</sup></b>	Alfa Aesar	-	0.98	-
<b>1-bromodecane<sup>a</sup></b>	Alfa Aesar	-	0.98	-
<b>Ethyl acetate<sup>a</sup></b>	Merck	-	0.995	-
<b>dichloromethane<sup>a</sup></b>	SDS	-	0.998	-
<b>Ferrocenemethanol<sup>a</sup></b>	Acros Organics	-	0.97	-
<b>LiTFSI<sup>a</sup></b>	Solvionic	-	0.99	-
<b>EMIMTFSI<sup>b</sup></b>	own synthesis	Water-washing, Freeze-drying	≥ 0.99	Karl-Fisher, <sup>1</sup> H NMR, MS <sup>c</sup>
<b>BMIMTFSI<sup>b</sup></b>	own synthesis	Water-washing, Freeze-drying	≥ 0.99	Karl-Fisher, <sup>1</sup> H NMR, MS <sup>c</sup>
<b>OMIMTFSI<sup>b</sup></b>	own synthesis	Water-washing, Freeze-drying	≥ 0.99	Karl-Fisher, <sup>1</sup> H NMR, MS <sup>c</sup>
<b>DMIMTFSI<sup>b</sup></b>	own synthesis	Water-washing, Freeze-drying	≥ 0.99	Karl-Fisher, <sup>1</sup> H NMR, MS <sup>c</sup>

<sup>a</sup> used as received

<sup>b</sup> from Karl-Fisher analysis, the water content in each IL was about 50 ppm

<sup>c</sup> Mass Spectroscopy

## **- Techniques**

### **Density measurements**

Density was measured with an Anton Paar vibrating tube densimeter, model DMA 5000, operating at atmospheric pressure and in the temperature range between 293 to 333 K. The internal calibration of the instrument was confirmed by measuring the density of bi-distilled water. All reported density data were corrected for the viscosity effect using the internal calibration of the densimeter. During the measurement the liquid was transferred to a syringe and injected into the densimeter.

As the density is extremely sensitive to temperature, the latter was controlled it within ( $\pm 10^{-3}$  K) by means of a Peltier module. The reproducibility of density value was  $\pm 5 \cdot 10^{-6}$  g.cm<sup>-3</sup>.

### **Viscosity measurements**

The viscosities were measured using an Anton Paar rolling-ball viscosimeter Lovis 2000M/ME that is based on the concept of a falling ball inside a capillary of known diameter. The apparatus can be operated in a wide range of temperatures and angles. The temperature of the capillary is controlled by a Peltier device within a precision of  $\pm 10^{-3}$  K. Two measuring system sets were used: the first one equipped with a capillary tube of diameter 1.8 mm was used to obtain viscosities up to 70 mPa.s<sup>-1</sup>, and the second one with a diameter of 2.5 mm for higher viscosities.

### **Ionic conductivity measurements**

Ionic conductivity was measured using a CDM 230 Conductivity Meter from MeterLab<sup>TM</sup>, Radiometer analytical. The conductivity cell was a Radiometer Analytical CDC741T-6 with temperature sensor (2-pole Pt sensor,  $K=1.0$  cm<sup>-1</sup>, glass body). Temperature and data acquisitions were made by a personal computer connected to the conductivity meter. The experimental cell was calibrated with standard 0.1 mol.L<sup>-1</sup> KCl solution, and the resulting cell constant was 1.0358 cm<sup>-1</sup>. The temperature of the samples was controlled using cryothermostat polystat with thermal stability of  $\pm 0.03$  K. The sample was allowed to spend about 20 min at constant temperature before performing any single measurement.

### **Electrochemical window measurements**

Linear sweep voltammetry was performed using a GAMRY Reference 600+ Potentiostat/Galvanostat/ZRA. An electrochemical cell was designed to use a small quantity (8 mL) with three electrodes. The reference electrode was based on the Ag/Ag<sup>+</sup> couple, consisting on a silver wire immersed into a AgNO<sub>3</sub> saturated solution in the considered RTIL. The counter

electrode was a platinum gauze (1 cm<sup>2</sup>). The working electrodes used to determine the stability potential range of the RTILs was a gold electrode (diameter 200 μm). The working electrode was grinded with SiC paper, rinsed with bi-distilled water and dried with a pure nitrogen stream. The scan rate was 5 mV.s<sup>-1</sup>.

The use of microelectrodes has unique benefits, since they allow the use of tiny volumes of RTILs, so conserving rare and valuable materials.

### **Electrochemical measurements**

In the aim to explore the electrochemical properties of a range of RTILs using cyclic voltammetry, the ferrocenemethanol (FcMeOH) was chosen as a redox probe. FcMeOH can be easily dissolved in aqueous electrolytes [15, 16] and has been used as a redox mediator to probe surface properties in RTILs [17]. It is soluble at millimolar level in a large range of RTILs which allows us to explore its electrochemical behavior in RTILs environments.

Cyclic voltammetry was used to study the mass transport properties of the RTILs by using gold microelectrode.

All electrochemical measurements have been realized in a glove box.

### **3. Results and discussion**

Although the density and the viscosity of the studied RTILs were widely described in the literature [6-8], these parameters have been measured since they are needed for the determination of transport magnitudes. In general, the literature data are well comparable with our data. The temperature dependence of the density ( $\rho$ ) of the four studied RTILs, in the temperature range from 293 to 333 K, is presented in figure 1(a) and table S1. A linear dependence on temperature is observed for all of them. Two main effects are observed in this representation. First, in the studied range of temperature, the density slope depends very little on the cationic chain length. Then, the density decreases at given temperature as the alkyl chain length increased. In fact, as the length of the cationic alkyl chain increases, RTILs present difficulties for packing and intermolecular hydrogen bonds associated with size increase [6]. The average distance between ions increases when the alkyl chain length increases, so that makes the formation of hydrogen bonds difficult. The increased repulsions arising from the greater size of the hydrocarbon chains prevents the ions from approaching at distances lower than the hydrogen bonding RTILs with shorter alkyl chain are expected to be more hydrogen bonded and so, denser.

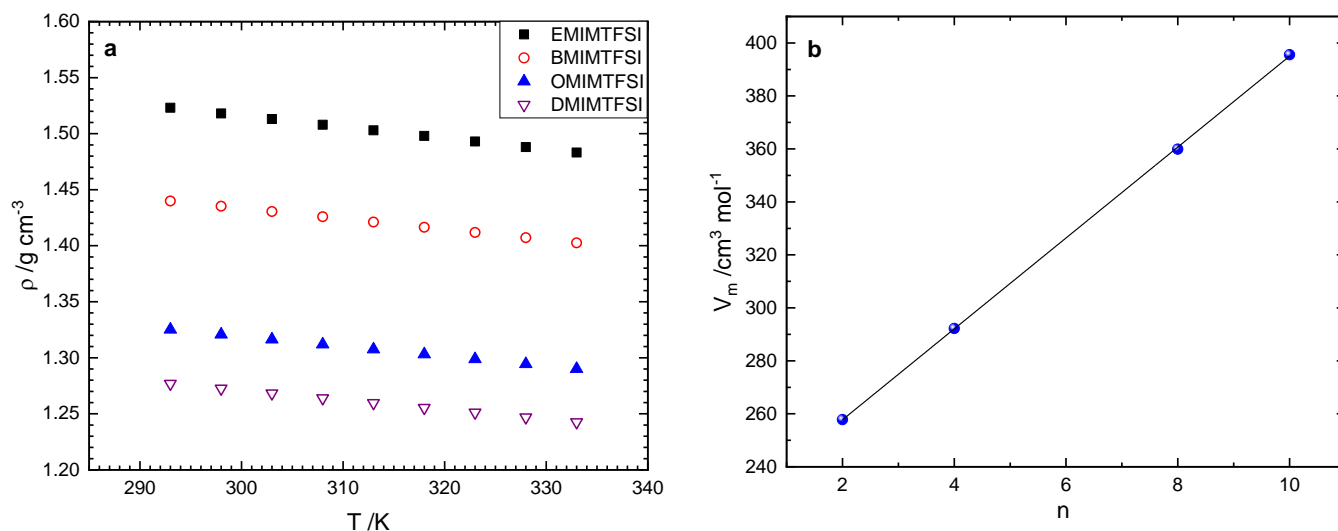


Figure 1- (a) Temperature dependence of the density of studied RTILs. (b) Molar volume of the four ILs as a function of the number of carbons in the alkyl side-chain of the 1-alkyl-3-methylimidazolium cation at 298K.

$$V_m = a + b \times n \quad (\text{Eq. 1})$$

From the density measurements, the molar volume ( $V_m$ ) of each RTIL was calculated. By plotting  $V_m$  according to the carbon number ( $n$ ) of the alkyl chain of the cation, a straight line (figure 1(b)) was obtained which can be described by:

Where  $a$  and  $b$  are temperature dependent fitting parameters. In figure 1(b), the molar volume of the four RTILs were plotted in function of the carbon number of alkyl chain at 298K. In such conditions, the fitting parameters of Eq.1 are  $a = 223.4 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$  and  $b = 17.2 \pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$ . The latter would correspond to the molar volume of a methylene ( $\text{CH}_2$ ) unit. This value is in good agreement with those described in the literature for the lengthening alkyl chain in the anion side [18] or the cation side [19]. The y-intercept  $a$  should stand for the molar volume of the ionic pair [methylimidazolium][TFSI].

Molar volume is a function of molar mass and density; the latter decreases linearly with increasing temperature. However, molar mass is not affected by the temperature, the molar volume increases linearly with increasing temperature. But, molar mass increases more sharply than density, so the molar volume also increases with increasing temperature.

The thermal expansion coefficient ( $\alpha$ ) can be calculated using conventional thermodynamics as:



$$\alpha = \frac{1}{V_m} \frac{\partial V_m}{\partial T} \quad (\text{Eq. 2})$$

Where  $V_m$  is the molar volume of the sample and  $T$  the temperature.

As is shown in Table 2, when the alkyl chain length increases, the thermal expansion coefficient slightly increases. This can be due to lower hydrogen bonding degree for RTILs with longer chain. It is observed that as expected for all studied RTILs  $\alpha$  is less than  $6.9 \cdot 10^{-4} \text{ K}^{-1}$  [7, 20]. The deviations between our density values and those reported by other authors can be caused by the presence of some impurities (water or halide) in the samples but also related to experimental problems of temperature control [21]. In our case, the water content was very low and the absence of halide was controlled.

Table 2- thermal expansion coefficient of the four RTILs

RTIL	$\alpha (10^{-4} \text{ K}^{-1})$
EMIMTFSI	$6.577 \pm 0.003$
BMIMTFSI	$6.660 \pm 0.003$
OMIMTFSI	$6.725 \pm 0.005$
DMIMTFSI	$6.812 \pm 0.005$

Dynamic viscosity of RTILs is much higher than those of water ( $\eta(\text{H}_2\text{O}) = 0.89 \text{ mPa.s}$  at 298 K). Typically, the values are about 30-50 mPa.s, but in some cases, they can be much higher, even several hundreds of mPa.s. This high viscosity, characteristic for RTILs, causes some difficulties with their handling.

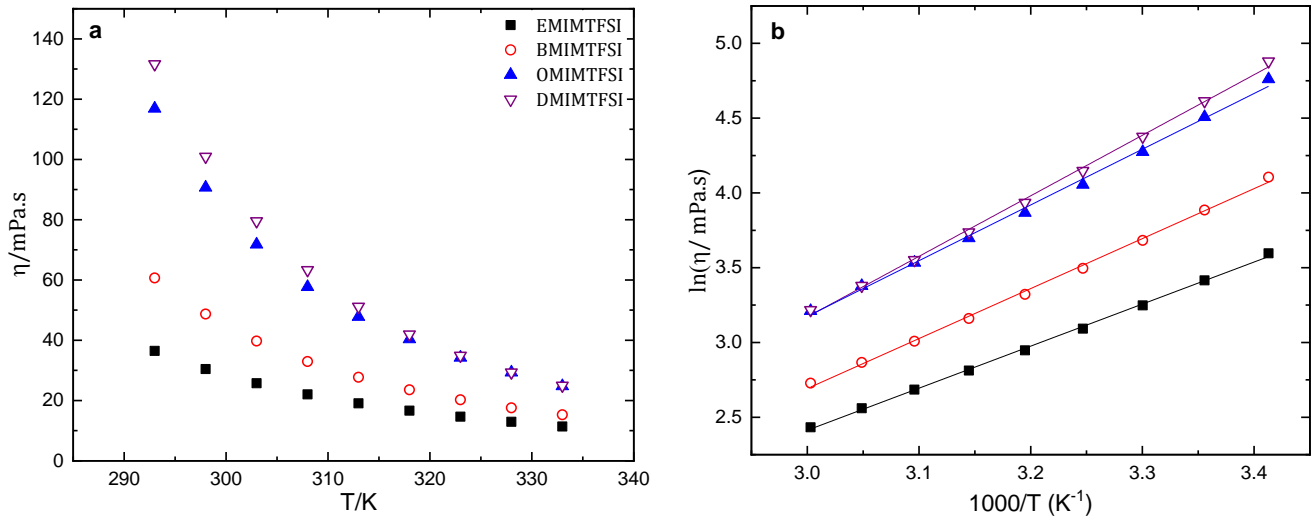


Figure 2- (a)Viscosity temperature dependence for pure RTILs. (b) Arrhenius plot of the studied RTILs.

Figure 2 (a) presents the variation of the dynamic viscosity ( $\eta$ ) of the four RTILs as function of temperature (values are gathered in table S2). We observe that the viscosity of these RTILs increases with the increasing alkyl chain length, an effect correlated to strengthened Van der Waals forces. It is clear that the viscosity increases though not linearly, with the lengthening of the cationic chain. Bonhôte *et al.* [22] explained that the increase in viscosity is caused by the augmentation of Van der Waals interactions between the cationic alkyl chains in a homologous series. Tokuda *et al.* [23] proposed the use of the term “ionicity” to explain this behavior. Ionicity is the proportion of ions that contributes to the ionic conductivity from the overall diffusing species. In fact, these authors showed a direct relationship between ionicity and viscosity. An increase of the cationic chain length decreases the ionicity and this is because Van der Waals interactions between the alkyl side-chains of the cation increases. In 2007, Triolo *et al.* [24] have shown that imidazolium-based ionic liquids with alkyl chain length higher than 6 carbons exhibit the formation of nanodomains permeated by charged/polar network. For short chains, the formation of nanodomains is not possible as the non-polar part is not large enough. But, some RTILs can be more or less organized and kind of nanostructuration can rise. In such case, even for short alkyl chain the viscosity increases [25]. The formation of such nano-segregated domains can also contribute to enhanced viscosity.

In the literature, various theoretical models and empirical expressions have been found to represent the viscosity temperature dependence of liquids [26, 27]. Okoturo *et al.* [28] presented a systematic study of viscosity of ILs and showed that the temperature variation of ILs viscosity follows Arrhenius equation or Vogel-Tamman-Fulcher (VTF) relation. However, the latter equation describes the temperature dependence of RTILs viscosity for glass forming liquids not too far above glass transition temperature. The variation of transport extents (such as viscosity or conductivity) with the temperature can be derived in an approximate way from the rate theory approach of Eyring, in which the liquids are assumed to have a quasi-crystalline structure [29]. Thus, molecules can move and occupy free volume sites in the lattice creating a liquid layer flow. The molecules contained in the liquid need to leave out a potential energy barrier in order to flow. The height of this barrier corresponds to the activation energy of the flow. This magnitude is independent of the temperature but depends on the nature of the liquid. However,

external forces acting on the liquid influence the energy. The temperature dependence of the viscosity based on the rate theory by Arrhenius equation [29-32] is:

$$\ln(\eta) = \ln(\eta^\infty) + \frac{E_\eta}{RT} \quad (\text{Eq. 3})$$

Where  $\eta^\infty$  is the viscosity at infinite temperature,  $E_\eta$  is the activation energy of viscous flow and  $R$  is the universal gas constant. Although glass forming liquids such as RTILs are not expected to follow Arrhenius' behavior, the narrow temperature range studied leads to linear adjustment of Eq. 3 as shown on Figure 2(b).

Table 3 gathers the activation energies and the viscosities at infinite temperature as function of the alkyl chain length. The activation energy,  $E_\eta$ , increases and  $\eta^\infty$  decreases when the alkyl chain lengthens.  $E_\eta$  is the energy barrier that must be overcome by the ions to move in the RTIL. The larger is  $E_\eta$ , the harder it is for the ions to move in the liquid, this might be due to the ionic size or stronger interactions in the RTIL (and hence leading to a more ordered medium). At infinite temperature, interactions contributing to the viscosity at room temperature in RTILs are no longer effective and the value of  $\eta^\infty$  is purely governed by geometric structure of the RTIL ions. Therefore, it may be representative of a structural contribution of the ions to the viscosity [28, 33]. Indeed, at high temperature, interactions that contribute to viscosity such as Van der Waals interaction force between long alkyl chains, H-bonding of anions, and molar weight of the component ions) are no longer effective. The viscosity is governed by the geometric structure of the ions. So, the structural contribution of the ions rules the viscosity at high temperature and the impact of the alkyl chain is then negligible. The increase of the viscosity with the alkyl chain length can be related to solvophobic interactions between alkyl groups cause nanoscale heterogeneities, so they are enhanced as the number of carbon atoms in the molecular architecture of the ions is increased, but electrostatic and H-bonding, also play important roles in the nanostructuring of the bulk mixture [34]. The existence of persistent nanostructure is known to provoke a decrease of the mobility of the ions in the RTIL [35]. Since the viscosities of the studied RTILs are essentially governed by the Van der Waals interactions and H-bonding, an increased alkyl chain length and the presence of bulkier side chains reduce the rotational freedom of molecules. That is the main cause of the rise of activation energy while the cationic alkyl chain length increases.

Table 3- Fitting parameters of experimental viscosity and conductivity of the studied RTILs to Arrhenius equations

RTILs	$E_\eta$ (kJ.mol <sup>-1</sup> )	$\eta^\infty$ (mPa.s)	$E_\sigma$ (kJ.mol <sup>-1</sup> )	$\sigma^\infty$ (mS.cm <sup>-1</sup> )
<b>EMIMTFSI</b>	23.4±0.3	2.43	20.8±0.2	25.3
<b>BMIMTFSI</b>	27.8±0.5	0.65	26.9±0.2	194.8
<b>OMIMTFSI</b>	31.0±0.6	0.33	29.2±0.3	135.9
<b>DMIMTFSI</b>	33.6±0.5	0.13	30.6±0.3	161.1

In the same way as for viscosity, the temperature dependence of the ionic conductivity ( $\sigma$ ) of pure ionic liquids in the temperature range from 293 to 333K is presented in figure 3(a) and table S3. As we can see, for a given temperature, the conductivity decreases as the alkyl chain lengthens.

In fact, viscosity plays important role in the RTILs conductivity. Indeed, the diffusion coefficient of an ion,  $D_i$ , is linked to the viscosity by the Stokes-Einstein equation (Eq.4) defined for a model spherical species  $i$  of an effective radius  $r_i$  as follow:

$$D_i = \frac{k_B T}{6\pi r_i \eta} \quad (\text{Eq. 4})$$

in which  $k_B$  is the Boltzmann constant,  $\eta$  is the viscosity and  $T$  the absolute temperature.

The conductivity of an ion  $i$ ,  $\sigma_i$ , can be expressed from the Nernst-Einstein equation as:

$$\sigma_i = \frac{c_i z_i^2 \mathcal{F}^2 D_i}{RT} \quad (\text{Eq. 5})$$

Where  $z_i$  stands for the valence of the charge carrier,  $c_i$  is the molar concentration and  $\mathcal{F}$  the Faraday constant.

By combining these two relations, we can write

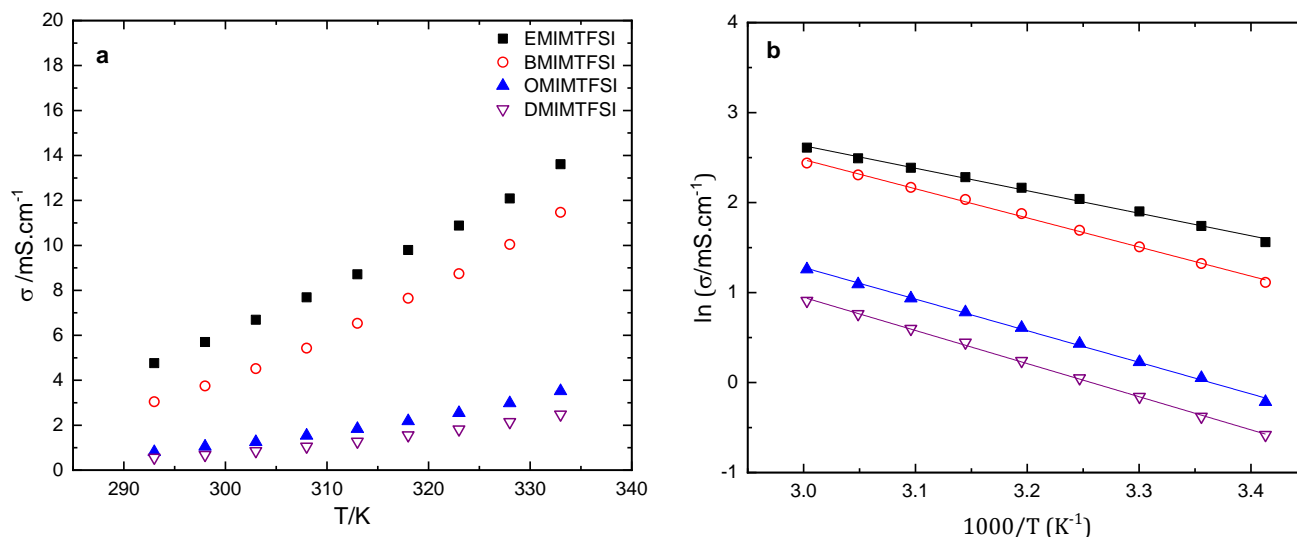
$$\sigma_i = \frac{c_i z_i^2 \mathcal{F}^2}{6\pi N_A r_i \eta} \quad (\text{Eq. 6})$$

with  $N_A$  the Avogadro number. The latter relation links the conductivity of an ion  $i$  to the viscosity of the medium. From this last equation it would be possible to calculate the radius of the cation of the studied RTIL knowing the radius of the TFSI<sup>-</sup> anion ( $r_{\text{TFSI}^-} = 3.65 \text{ \AA}$ ) [5], but Eq. 6 supposes that all the ions are spherical, this assumption cannot be reasonably adopted for all the 1-alkyl-3-methylimidazolium selected in this study Then, the values of diffusion coefficient determined from Einstein-Stockes or the conductivity from the Nernst-Einstein relation are marred by a high uncertainty. However, the conductivity of the RTIL is given by the sum of the

anion and cation conductivities and is inversely proportional to the viscosity  $\eta$ . And then, as for the viscosity, the temperature dependence of  $\sigma$  must obey to Arrhenius law:

$$\ln(\sigma) = \ln(\sigma^\infty) - \frac{E_\sigma}{RT} \quad (\text{Eq. 7})$$

Where  $\sigma^\infty$  is a constant corresponding to the conductivity at infinite temperature,  $E_\sigma$  is the activation energy of the conductivity. This Arrhenius equation for the conductivity is plotted on Figure 3(b) for all studied RTILs. The parameters of this relation are gathered in Table 3.



**Figure 3-** (a)Conductivity temperature dependence; (b) Arrhenius plot of studied RTILs

As both activation energies,  $E_\eta$  and  $E_\sigma$ , are not equal (but very close), the Walden equation  $\Lambda\eta=\text{cte}$  [36] is not fully followed, the mechanism of ionic conduction in these RTILs cannot be considered completely ionic. In fact, ionic solutions with large and weak coordinating ions in solvents with nonspecific ion-ion solvent interactions obey the Walden rule, as for KCl aqueous solution, for example. So, in RTILs, ion mobility and electrical conductivity are caused only by ion migration. That makes deviations from Walden rule due to ionic association and other correlations which influence conductivity.

The electrochemical stability of the four RTIL has been determined by linear sweep voltammetry (LSV) at 298 K with a gold microelectrode (diameter of about 200  $\mu\text{m}$ ). The voltammograms obtained with a scan rate of 5  $\text{mV}\cdot\text{s}^{-1}$  are presented in figure 4. The electrochemical windows of the four ILs do not show significant differences and are about 4.5 to 5 V. Therefore, the electrochemical window does not depend on the alkyl chain length.

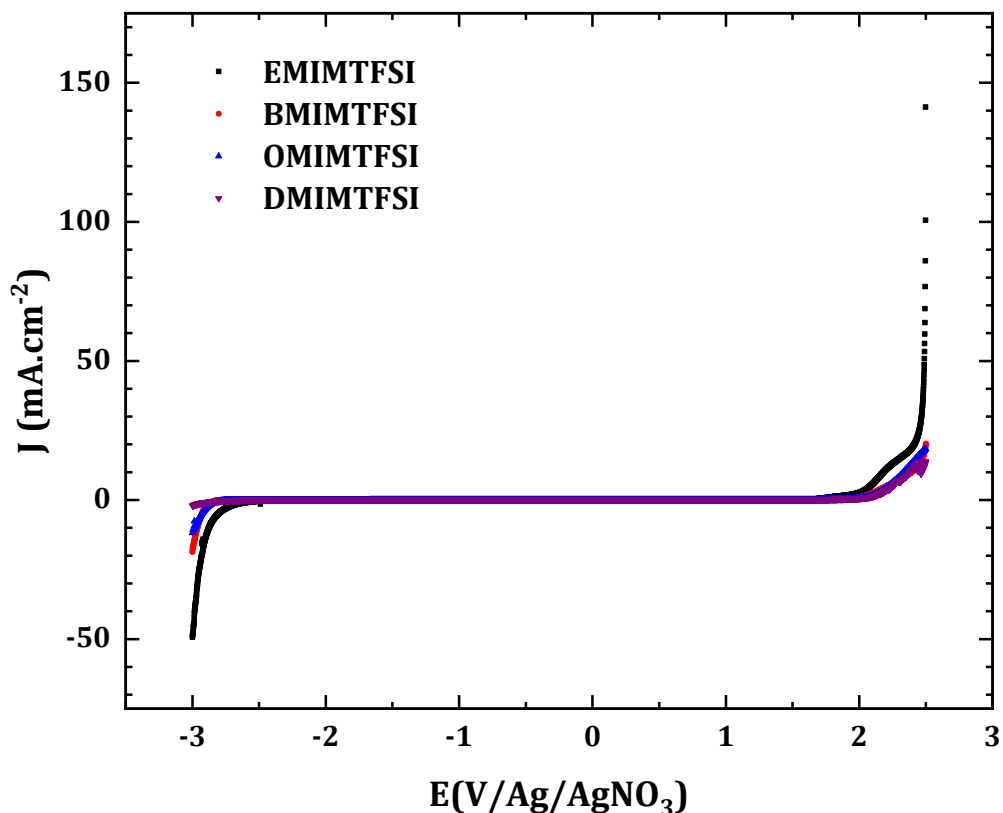


Figure 4- Linear sweep voltammeteries on gold electrode for the four RTILs at 5 mV.s<sup>-1</sup> at 298K

Characterized by their intrinsic conductivity, RTILs provide very attractive electrochemical media, as no supporting electrolyte is required. But their high viscosity has a significant consequence when studying voltammetric behavior.

In order to characterize this the electrochemical behavior of ferrocenemethanol (FcMeOH) were investigated in the four RTILs. Cyclic voltammograms of FcMeOH in these media show a reversible behavior that is controlled by diffusion. Figure 5(a) displays cyclic voltammograms obtained for FcMeOH in DMIMTFSI at a range of scan rate between to 10 and 2000 mV.s<sup>-1</sup> at 298K using a gold microelectrode.

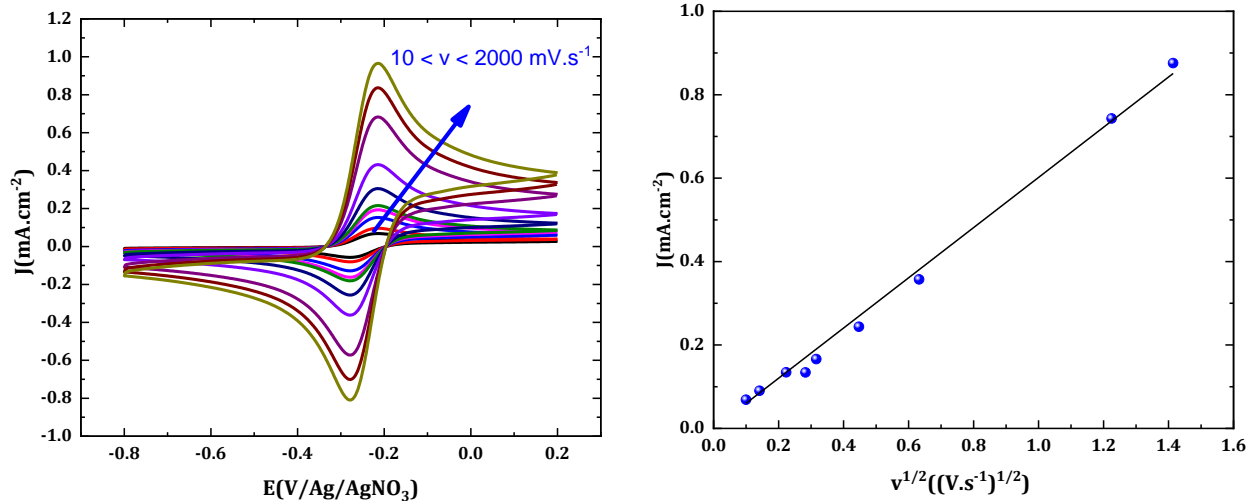


Figure 5- (a) Cyclic voltammograms of FcMeOH in DMIMTFSI at 298K for various scan rates (10 to 2000 mV·s<sup>-1</sup>) on a gold electrode (200µm diameter); (b) Plot of the anodic peak current vs. the square root of scan rate

In each case, a well-defined oxidation peak and its corresponding reduction peak were observed. For each scan rate, the ratio of the anodic peak current density,  $J_{p,a}$ , to the cathodic peak current density,  $J_{p,c}$ , was close to 1. In addition,  $J_{p,a}$  is proportional to the square root of the scan rate as shown in figure 5(b), leading to prove that the mass transfer of FcMeOH on the electrode surface was diffusion-controlled. Similar results were observed for the three other RTILs. Indeed, the expected classical behavior of a microelectrode (the sigmoid) was not observed. The obtained voltammograms resemble to those obtained in the case of a macroelectrode [37]. This is due to the viscosity of the medium. To obtain classical steady-state voltammograms, smaller diameter microelectrodes must be used. The separation between the anodic peak potential and the cathodic peak potential,  $\Delta E_p$ , was about 59 mV, even for the higher scan rates investigated in this study. The diffusion coefficient,  $D$ , has been determined from the cyclic voltammograms of FcMeOH in each of the RTILs, and after using the equation of Randles-Sevcik (for microelectrodes):

$$J_p = 2.99 \times 10^5 \times \alpha^{\frac{1}{2}} \times C_0 \times D^{\frac{1}{2}} \times v^{\frac{1}{2}} \quad (\text{Eq. 8})$$

where  $J_p$  is peak current density (in A cm<sup>-2</sup>),  $D$  is the diffusion coefficient (in cm<sup>2</sup> s<sup>-1</sup>),  $C_0$  is the FcMeOH concentration in the solution (in mol cm<sup>-3</sup>),  $v$  is the scan rate (in V s<sup>-1</sup>) and  $\alpha = \frac{nF}{RT}$  at 298K.

$D_{\text{FcMeOH}}$  decreases when cationic alkyl chain length of the RTIL increases (Table 4). This is mainly due to the increase of the viscosity with the lengthening of the alkyl chain. This viscosity increase makes the mobility and, then, the diffusion of FcMeOH in the RTIL harder.

Table 4- Values of the diffusion coefficient of FcMeOH in each RTIL at 298K

RTIL	D. $10^{-7}$ ( $\text{cm}^2.\text{s}^{-1}$ )	$\eta$ (mPa.s)
<b>EMIMTFSI</b>	3.50±0.02	30.4±0.2
<b>BMIMTFSI</b>	2.80±0.01	48.7±0.1
<b>OMIMTFSI</b>	1.70±0.01	90.7±0.5
<b>DMIMTFSI</b>	0.40±0.01	100.9±0.3

The values of FcMeOH diffusion coefficients in the RTILs are comparable to those reported by Lovelock et al.[38]. The slight difference could be attributed to the RTIL water content.

## Conclusion

In the present paper, a systematic study of the effect of the cationic chain lengthening on several physicochemical and transport properties of the 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide family with 2, 4, 8 and 10 carbons in the alkyl chain have been realized in a temperature range between 293 and 333K. Density, viscosity and conductivity were measured and the temperature dependence of viscosity and conductivity were studied in the Arrhenius framework obtaining effective activation energies. At 298K, the electrochemical stability on gold microelectrode does not significantly depend on the alkyl chain length. The effect of the RTILs viscosity on the mass transfer dynamics within each RTIL was studied using ferrocenemethanol as a redox probe. The length of the alkyl chain of the cation affects the viscosity of RTILS and strongly influences one of the principle steps of electrochemical processes, mass transport by diffusion of soluble products.

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