The study of dielectric properties of some ionic liquids based on imidazolium by dielectric spectroscopy and data mining.

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Abstract

Ionic liquids (ILs) are liquid salts of differentiating to all molten salts with temperature below 100 °C (arbitrarily set with reference to the boiling point of water), but a large number of them are liquids at room temperature. The properties of ionic liquids such as their wide field of electro activity, their high conductivity, and high thermal stability have made them new prime candidates in searching for a new energy systems (photovoltaic cell, battery, solar concentrator ...). The present work objective is to study the physicochemical properties of some ionic liquids based on imidazolium ([BMIM] [BF₄]-, [BMIM] [PF₆]-, [HMIM] [Br], [BMIM] [Br]) and more particularly the dielectric properties. We performed measurements by dielectric spectroscopy to see the influence of the size of the anion and the length of the alkyl chain of the cation on the conductivity of ionic liquids at different temperatures. We made also theoretical study by using data mining techniques such as the analytical method principal components (PCA), that help us to study the relationships between variables (σ RT (S / m), Tg (K), lnσ∞ (S / m), B, T0 (K), m) and their relation with ionic liquids structure.

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1. Introduction

Ionic liquids have been in recent years the subject of growing research activities because of their interesting physical properties, high electrical conductivity and very low vapour pressure and their potential as designer solvents for catalytic and chemical applications. By definition, ionic liquids are organic salts with a melting temperature below 100 °C. The polarity, dielectric constant, electrochemical window, and electrical conductivity are important physical properties that determine whether an ionic liquid is suitable for a given application.

Due to the large number of possible cation-anion combinations, it is of great interest to understand how the properties of newly synthesized ILs can be predicted from the structure of the molecule, in order to choose suitable candidates for a given application.1

From the applied point of view, there are many proposed applications for ILs in the field of green chemistry. Among them we can name those of replacement of organic solvents, charge transport in energy generators, batteries and electrolytic medium in aluminium electrodeposition processes2,3. In fact important advances have been achieved recently in the application of ionic liquids to Li batteries4, as electrolyte in electrochemical processes and devices5, and even in solar power applications6.

To develop these proposed applications with the most adequate IL it is first necessary to know the value of their physical magnitudes, and their behaviour with temperature. Experimental data of the different physical magnitudes are also necessary to develop a theoretical model to explain and to predict them in the different ionic liquids (which does not exist nowadays up to our knowledge), and to extend the molecular dynamic simulations reported until now7,8.

Experimental data or databases are traditionally viewed as “static” documents that are used in a “search and retrieval” mode. These static data can be transformed by informatics and data mining tools into a dynamic dataset for analysis of the properties of the materials and for making predictions.

2. Experimental

2.1. Materials and Methods

To make our experimental conductivity measurements, we used an LCR meter (L for inductance, C for capacitance and R for resistance). The functional role of an LCR bridge is based on measuring the electrical impedance Z of the compound under test. The electrical impedance is defined as the opposition that presents a compound or a circuit against the flux of an alternating electric current for a given frequency. This impedance is a complex quantity, the real part corresponds to the resistor R and the imaginary part to the reactance X that is written as:

\[ Z = Z' + iZ'' = R + iX \]  

The ionic conductivity measurements were taken using a conductivity cell with coaxial cylindrical copper electrodes manufactured locally; in this case, the cell constant was calculated by:

\[ k = \frac{1}{2\pi h} \ln \frac{R_1}{R_2} \]  

h, R1, R2 respectively represent the height of the electrodes (cm), rayons of the two electrodes from small to large (cm) and constant k of the cell (cm⁻¹).

The dielectric measurements were performed on pellets processed by applying uniaxial pressure on powder. Dielectric spectra were recorded by using BDS-4000 Novocontrol spectrometer, which was coupled with the quarto system to ensure the temperature variation from -80 to 20°C for the frequency range (10⁻² to 10⁶Hz). For conductivity data analysis, the complex conductivity is defined as:

\[ \sigma^* = \sigma' + i\sigma'' = \varepsilon_0 \omega \varepsilon'' + i\varepsilon_0 \omega \varepsilon' \]  

Where \( \varepsilon_0 \) and \( \omega \) refer to the permittivity of free space and angular frequency (\( \omega = 2\pi f \)), respectively.
2.2. Results and Discussion

2.2.1. Conductivity:

The conductivity value (σ) has been determined from the electrolyte resistance (Rₑ) drawn from the diagram impedance by the following relationship:

\[
\sigma = \frac{k}{R_e}
\]

(4)

In this paper we present experimental data on the temperature dependence of the electrical conductivity σ, in four different imidazolium based ionic liquids \([\text{C}_n\text{MIM}]^+\text{[Br]}^-\] with \(C_n\) representing butyl and hexyl chains, to study the dependence of σ with the cation length. Moreover, to study the influence of the anion size in the electrical conductivity, we measured three different \([\text{BMIM}]^+\text{[X]}^-\] with X being, from smaller to bigger sizes, \(\text{Br}^-, \text{BF}_4^-, \text{PF}_6^-\). The influence of the anion size on the electrical conductivity was also studied.

According to the Nyquist diagram and by applying equation (4), conductivity (σ) and the resistance of the electrolyte (Rₑ) of the two ionic liquids are mentioned in the following table (Table 1).

Table 1. The values of (Rₑ) electrolyte resistance, (V) volume, (σ) conductivity of LIs of \([\text{BMIM}]^+\text{[Br]}^-\), \([\text{BMIM}]^+\text{[BF}_4^-\), \([\text{BMIM}]^+\text{[PF}_6^-\) and \([\text{HMIM}]^+\text{[Br]}^-\).

<table>
<thead>
<tr>
<th>LI</th>
<th>[BMIM]^+[Br]</th>
<th>[HMIM]^+[Br]</th>
<th>[BMIM]^+[BF4^-]</th>
<th>[BMIM]^+[PF6^-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rₑ (Ω)</td>
<td>6.49</td>
<td>28.55</td>
<td>30.58</td>
<td>30.18</td>
</tr>
<tr>
<td>V(ml)</td>
<td>1.2</td>
<td>2</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>σ(mS.cm⁻¹)</td>
<td>3.75</td>
<td>0.5</td>
<td>1.9</td>
<td>0.96</td>
</tr>
</tbody>
</table>

If we analyse the table (1), we observe, as expected, when the length of the cation \([\text{C}_n\text{MIM}]^+\) increases the electrical conductivity of the liquid decreases. The long alkyl chains make the movement of cations difficult and thus LIs with longer chains contribute weakly in the electrical conductivity.

Discussing the influence of anion size on the electrical conductivity, we observe in the table that when size of the anion increases (\(\text{Br}^<\text{BF}_4^<\text{PF}_6^-\)) electrical conductivity decreases, because of the external electrical charge density that decreases with the increasing of the anion size.

From a theoretical point of view, a detailed knowledge of the molecular interactions responsible of the ionic character of ionic liquids is to be known. In particular, although it is clear that the large size of the cation is the primary cause of their liquid state, the exact influence of the size in the transport properties is not known.

2.2.2. Dipolar relaxations:

Physically, the dielectric modulus corresponding to the relaxation of the electric current in the material become constant when the electric displacement, so the electric modulus presents the real process of the dielectric relaxation, which is expressed by the relation

\[
M^* = \frac{1}{\varepsilon'(\omega)} = M' + iM''
\]

(5)

The imaginary part \(M''(\omega)\) of the complex spectra of dielectric modulus in frequency was determined.

Secondary relaxation processes were observed in this liquid at high frequencies and low temperatures. These are the β relaxations which are modelled by the empirical function Havriliak-Negami.

\[
M^* = M_\infty + \frac{\Delta M}{1 + (i\omega\tau_{HN})^\beta}
\]

(6)

τHN is the relaxation time Havriliak-Negami and β, γ are the parameters of the complex dielectric function and the module M.

The temperature evolution of the relaxation time is adequately fitted using the phenomenological Vogel-Fulcher-
Tammann (VFT) model.

The relaxation time is defined by the equation:
\[
\tau = \tau_0 \exp \left( \frac{D}{T - T_0} \right)
\]

Equation is commonly adopted to describe the relaxation dynamics of glass formers. In this equation, \( \tau_0 \) is the high temperature limit of the fast relaxation and \( T_0 \) represents the temperature at which the average value of the relaxation time diverges. The coefficient \( D \) can be regarded as a measure of the system fragility. The lower its value is, the larger the departure from Arrhenius behaviour.\(^9\)

So we conclude that the conductivity of the ionic liquids often presents a classical linear of Arrhenius behaviour above ambient temperature. However, when the temperature of these ionic liquids approach their glass transition temperature \( T_g \), the conductivity displays a significant negative deviation from linear behaviour.

\[
\sigma = A^{-1/2} \exp \left( -B \left( T - T_g \right) \right)
\]

When \( A, B, \) and \( T_g \) are adjusted parameters. Comparing the Arrhenius equation with the VFT equation (8), we can observe that the second is equal to the first if \( T_g = 0 \). Thus, we can connect the fitting parameters the VFT-type equation with the physical parameters of the Arrhenius equation: \( A = B = \sigma \infty \) and \( E_a / k_B \).

Equation (9) is the modified version of the Vogel-Tamman-Fulcher (VFT) equation (9)\(^10\):

\[
\sigma = \sigma \infty^{-1/2} \exp \left[ -E_a / k_B \left( T - T_g \right) \right]
\]

3. Theoretical Study.

Application of the principal component analysis method.

The objective of this part is to search the correlations between the parameters of the VFT equation (m: fragility, \( T_g \): glass transition temperature, \( \ln \sigma \infty \): logarithm of the conductivity to \( \infty \), \( B \): constant, \( T_\infty \): the temperature at which the conductivity \( (\sigma) \) tends to zero, \( \sigma \infty \): conductivity at room temperature) on the one hand and the length of the cation and the size anion of the other hand using the Principal component analysis technique (PCA).

Principal components analysis (PCA), which is a descriptive technique permitting to study the relationships between variables and identify the dependence of the structure among the observations to obtain a description or representation, in a projection data on different axes, called principal axes.

Table 2. Table of data used in the principal component analysis\(^1\).

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>( \sigma \infty ) (S/m)</th>
<th>( T_g ) (K)</th>
<th>( \ln \sigma \infty ) (S/m)</th>
<th>B</th>
<th>( T_\infty ) (K)</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_3 mim, BF_4</td>
<td>0,159</td>
<td>175,1</td>
<td>7,86</td>
<td>1284</td>
<td>139,7</td>
<td>78</td>
</tr>
<tr>
<td>C_4 mim, BF_4</td>
<td>0,364</td>
<td>177,9</td>
<td>6,89</td>
<td>1160</td>
<td>146,8</td>
<td>93</td>
</tr>
<tr>
<td>C_5 mim, BF_4</td>
<td>0,163</td>
<td>182,8</td>
<td>6,69</td>
<td>1240</td>
<td>147,1</td>
<td>78</td>
</tr>
<tr>
<td>C_6 mim, BF_4</td>
<td>0,118</td>
<td>187,6</td>
<td>6,37</td>
<td>1238</td>
<td>148,5</td>
<td>66</td>
</tr>
<tr>
<td>C_7 mim, BF_4</td>
<td>0,067</td>
<td>186,1</td>
<td>6,03</td>
<td>1291</td>
<td>146,1</td>
<td>68</td>
</tr>
<tr>
<td>C_8 mim, BF_4</td>
<td>0,059</td>
<td>189,7</td>
<td>6,1</td>
<td>1295</td>
<td>148,3</td>
<td>62</td>
</tr>
<tr>
<td>C_9 mim, BF_4</td>
<td>0,042</td>
<td>190,5</td>
<td>5,8</td>
<td>1324</td>
<td>145,9</td>
<td>55</td>
</tr>
<tr>
<td>C_6 mim, Br</td>
<td>0,0074</td>
<td>187,8</td>
<td>7,47</td>
<td>1668</td>
<td>158,4</td>
<td>158</td>
</tr>
<tr>
<td>C_6 mim, Tf_2 N</td>
<td>0,17</td>
<td>187,1</td>
<td>5,59</td>
<td>1057</td>
<td>148,3</td>
<td>57</td>
</tr>
<tr>
<td>C_6 mim, FAP</td>
<td>0,096</td>
<td>184,7</td>
<td>3,86</td>
<td>965</td>
<td>152,2</td>
<td>73</td>
</tr>
</tbody>
</table>

(For simplification we have omitted the charges + and – and the brackets in the representation of ionic liquids)
The first analysis is to examine differences between the 10 different ionic liquids. The observations of the graph (plot scores) of this analysis is given in fig.1. For this analysis, the sign of each principal component has no significance. The principal axis PC1 of variance for the data set, and the principal axis PC2 are the capture of the variance. No other principal axis (PC) is included because they do not provide significant information.

By observing the fig.1 it appears that the principal axis PC1 is strongly related to the variation in the size of the anion, when the value of the PC1 axis increases the size of the anion decreases (C₆mim, FAP; C₆mim, Br; C₆mim, Tf₂N; C₄mim, BF₄). The same observations for the PC2 axis that captures the change in size of the cations, when the value of the PC2 axis increases the size of the cations decreases (C₄mim BF₄, C₅mim BF₄; C₆mim BF₄; C₇mim, BF₄; C₈mim, BF₄; C₉mim, BF₄). The results can be classified into three clusters, and properties in each cluster are shown in the table 3.

### Table 3. the properties in each cluster.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>m, ln(σm, B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cluster 1</td>
<td>T₀, Tg</td>
</tr>
<tr>
<td>Cluster 2</td>
<td>σRT</td>
</tr>
</tbody>
</table>

The principal axes are the same for graph observations (plot scores) and the graph of the variables (plot loadings) so the information in these two graphs can be compared directly.

Clusters 1 and 3 contribute to the PC1 axes values of the scores plot; these are highly correlated because they have similar values in the same principal axes PC.

While the inverted values in the PC axes indicate inverted correlations. Therefore, the properties in the cluster 2 are inversely correlated with the properties in the cluster 3 (σRT, T₀, Tg). It seems that the ionic liquids Cₐmim BF₄ are glassy systems behaviour at the glass transition temperature (Tg) increases when the room temperature conductivity decreases because they are inversely related.

We also note that the fragility m is strongly correlated with B which describes the temperature dependence of the conductivity at a higher temperature (they belong to the same cluster).

From the cluster 3 and 2 we found out that the values of σRT decrease when length of the alkyl chain increases. As the conductivity is related to the electron mobility, it can be explained by the increase of the viscosity induced by the strong interactions of Van der Waals forces between the alkyl chains and the large cations.

On the other hand, the homologous series shows a relatively small decrease in fragility in terms of the growth of the length of the alkyl chain. The relationship between molecular parameters and fragility is not yet well understood. However, it is known that LI fragility is closely linked to the morphology of the cooperativeness and network
rearrangement. It depends heavily on local inter-ionic Coulomb forces. C₆mim, Br is an exception in this series. Its fragility is much larger than the fragility of ionic liquids with the fluorinated anions. This anomaly can be explained by the fact that the bromide ion is capable of forming strong hydrogen bonds with the hydrogen atoms of cation imidazolium. Inter ionic forces lead to the formation of hydrogen bonding and therefore greater fragility. The presence of this network also makes it more difficult for ions to travel through the sample, causing much lower conductivity. Fluorinated anions have a lower charge density, because the negative charge is distributed over a much larger volume. The interaction of these anions with the imidazolium cation is much weaker than the interaction between the bromide anion and the cation.

The cluster in Figure (1) shows that C₆ mim, FAP and C₆ mim, Tf₂N could be good candidates for high electrical conductivity at room temperature.

So we concluded that:

If we change the nature of the anion the most influencing parameter on the conductivity of the ionic liquid at room temperature is the fragility m.

If changing the length of the alkyl chain of the cation the most influencing parameter on the conductivity of the ionic liquid at room temperature is the glass transition temperature T_g.

4. Conclusion

We focused mainly on the study of physicochemical properties of ionic liquids based on imidazolium.
In this paper, we studied the influence of the size of the anions and cations on the dielectric properties of ionic liquids based on imidazolium at different temperatures.

The experimental work presented in this paper aimed to make physical measurements by dielectric spectroscopy. We observed that when the size of the anion increases the electrical conductivity increases also and the observed electrical conductivity decreases with increasing length of the alkyl chain of the cation CₙMIM. The conductivity as a function of the observed temperature is consistent with the behaviour of the vitreous compounds and it is explained by the Vogel-Fulcher-Tammann equation (VFT).

The objective of the theoretical study is to look for correlations between the parameters of the VFT equation and the length of the alkyl chain of the cation and the anion size by using data mining analysis in particular the PCA method.

The use of PCA shows that data can be used to determine some useful correlations, and then we use this knowledge to develop new materials.

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References