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Electrical Conductivity and Nyquist Plot of C_4C_1Im BF_4 at Room Temperature by Impedance Spectroscopy

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Abstract: Ionic liquids (ILs) represents a real alternative for electrochemical applications due to their remarkable characteristics, namely a very low vapour pressure, low flammability, high thermal stability, wide potential window and high ionic conductivity. In this work, Nyquist plot and impedance spectroscopy at room temperature is proposed as an alternative method to obtain the ionic conductivity for ionic liquids by using a RLC precision meter Agilent HP 4284A. For this propose, the IL 1-butyl-3-methylimidazolium tetrafluoroborate (C_4C_1Im BF_4) was selected and results were compared with the previously obtained from the conductimeter CRISON GLP31.

Keywords: ionic liquid; dielectric spectroscopy; electrolytes; impedance

1. Introduction

Ionic Liquids (ILs) are salts designed by a combination of an organic cation and an inorganic/organic anion with a melting point below 100 °C [1]. ILs with the melting point below room temperature are known as Room-Temperature Ionic Liquid (RTILs). Taking into account the big amount of possible anions and cations [2], the number of possible ILs becomes very big. Thus, Earle and Seddon [3] have estimated the number of RTILs near one billion of different possibilities, this is the reason why ILs are referred as tuneable liquids that can be chosen for each application.

One of the pioneers in the study of ionic liquids was P. Walden, who in 1910s synthetized and studied the first ionic liquid, ethylammonium nitrate, and over the time some interesting properties of this first IL have been reported and it is, even, under study nowadays. In the upcoming decades, the interesting for ILs will become significant with thousands of studies of properties, features, synthesis etc [4]. Currently, ILs can be considered as a referent in electrochemistry [5] and many other fields [6]. One of the most studied IL is C_4C_1Im BF_4, thermophysical, thermodynamics [7] and electrochemical properties like conductivity [8] among others are fully reported in literature.

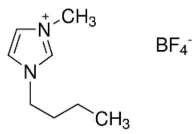
Furthermore, the most interesting properties to analyse in electrochemical applications is the ionic conductivity as indicate the numerous studies [3,4,8,11]. Then it is important to characterise deeply this property. In this work, impedance spectroscopy methodology is used to determine the ionic conductivity of the IL $C_4C_1Im\ BF_4$. Results obtained are compared with the obtained using a conductimeter.

2. Materials and Methods

Chemicals

The name, molecular weight, chemical structure, abbreviation, CAS number and provenance of the chemical compound used in this work can be found on Table 1. The sample was under vacuum sealed for 48 h.

Table 1. Chemicals.

Name	Molecular Weight ($g \cdot mol^{-1}$)	Structure	Abbreviation CAS number	Provenance
1-Butyl-3-methylimidazolium tetrafluoroborate	226.02		$C_4C_1Im\ BF_4$ 174501-65-6	ACROS ORGANICS

3. Experimental

3.1. -LCR Precision Meter

In order to obtain an impedance spectroscopy curve, a RLC precision meter HP 4284A from Agilent was used in the frequency range of 20 Hz to 1 MHz over 8610 selectable frequencies. The RLC presents 6 digits of resolution at any range, and a basic accuracy of 0.05%. 20 impedance parameters can be measured, and the measurement range depends on the selected parameter, i.e., G and B (admittance and conductance used in this work to obtain the dielectric spectroscopy) present a range from 0.01 nS to 99.9999 S, and Z′ and Z′′ (real and imaginary part of the impedance, or resistance and reactance respectively, used for the Nyquist plot determination) present a range from 0.01mΩ to 99.9999 Ω [12].

The sample was placed into a Swagelok sealed coin cell with two parallel plate electrodes of stainless steel with 1 mm thickness and 8 mm diameter.

3.2. Electrical Conductivity

The electrical conductivity obtained by impedance spectroscopy was compared with the value obtained by the GLP31 CRISON conductimeter, which presents a conductivity range from 0.01 μS/cm to 500 mS/cm. The accuracy of the conductimeter is ≤ 0.5% in conductivity measurement. The conductimeter was previously calibrated before the measurement with standard solutions at a 298 K. The probe is formed by two parallel electrodes of platinum which can take measurements in a temperature range from (243 to 323) K.

3.3. Temperature Stabilization

A calibrated Julabo F25 thermostat was used to control the temperature of the sample; the error in the temperature was lower than 0.1 K. These measurements need to be taken in an isothermal regime, so the time spent in every measurement was, at least 15 min.

4. Methodology

The admittance of a conductive sample can be defined as:

$$Y = \frac{1}{Z} = G + jB \tag{1}$$

where $\boldsymbol{Z}$ is the impedance, $\boldsymbol{G}$ the conductance, $\boldsymbol{B}$ the susceptance and $\boldsymbol{j}$ the imaginary number. The conductance and the susceptance can be related with the capacity of the sample ($\boldsymbol{C}$) and the dissipation factor ($\boldsymbol{D}$) by the following mathematic relations:

$$B = 2\pi f C \tag{2}$$

$$D = \frac{G}{|B|} \tag{3}$$

The complex dielectric constant is defined as:

$$\varepsilon = \varepsilon' + j\varepsilon'' \tag{4}$$

where $\boldsymbol{\varepsilon}'$ and $\boldsymbol{\varepsilon}''$ are the real and imaginary parts, respectively, of the dielectric constant. If the sample is placed in an electric capacitor, the real and the imaginary part of the sample can be obtained as:

$$\varepsilon' = \frac{C}{C_0} \tag{5}$$

$$\varepsilon'' = \frac{C \cdot D}{C_0} \tag{6}$$

where $\boldsymbol{C_0}$ is vacuum capacitance, defined as:

$$C_0 = \varepsilon_0 \frac{A}{h} \tag{7}$$

where $\boldsymbol{\varepsilon_0}$ is the vacuum dielectric constant, $\boldsymbol{A}$ the cross-sectional area of the capacitor and $\boldsymbol{h}$ the width of the sample. The conductive regime of the sample is given by the linear part of $\boldsymbol{\varepsilon}''$, this linear regime can be described by pure Ohmic conduction by the following model:

$$\varepsilon'' = \frac{\sigma}{\varepsilon_0 \omega} \tag{8}$$

where $\boldsymbol{\sigma}$ is the conductivity and $\boldsymbol{\omega}$ the angular frequency. For data analysis the region where the slope is −1.00 ± 0.02 on log $\boldsymbol{\varepsilon}''$ *vs* log $\boldsymbol{\omega}$ representation, was selected, and the conductivity can be obtained by two methods, a linear fitting of the parameters and by averaging of the conductivity of the every value in the conductive regime of the sample.

5. Results

Figure 1A shows the conductance ($\boldsymbol{G}$) and the susceptance ($\boldsymbol{B}$) obtained directly from RLC of the $C_4C_1Im\ BF_4$. By application of Equation (2) and (3), it is possible to obtain the capacitance ($\boldsymbol{C}$) and the dissipation factor ($\boldsymbol{D}$), which are presented in Figure 1B,C, respectively.

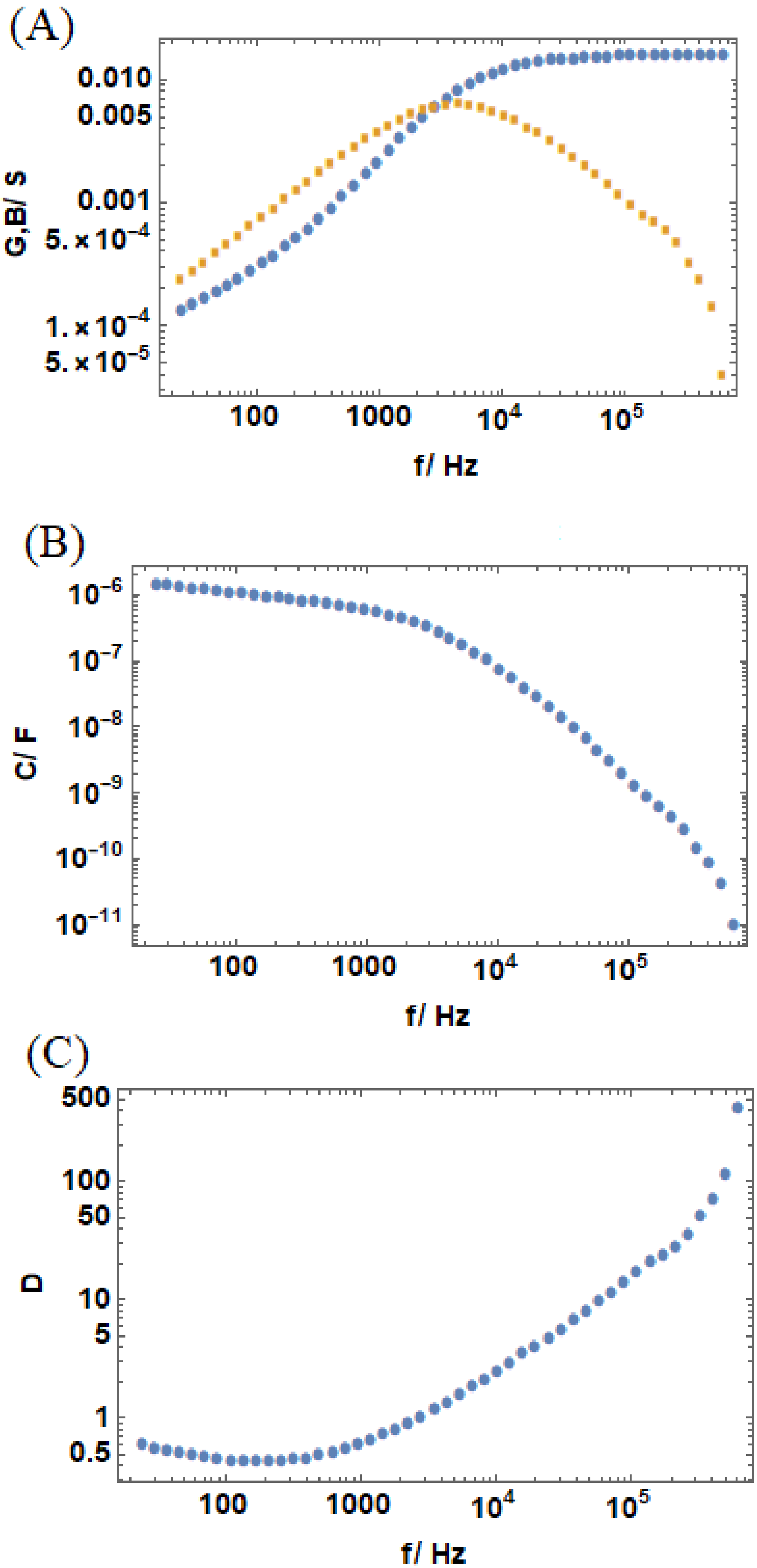


Figure 1. (**A**) Conductance (blue dots) and susceptance (orange square) of C_4C_1Im BF_4. (**B**) Capacitance of the sample. (**C**) Dissipation factor.

The complex dielectric constant (Figure 2A) can be obtained by application of Equation (5) and (6) and considering the vacuum capacitance (C_0) of the used coin cell. As it can be seen, the linear region of the imaginary part of the dielectric constant of this IL begins around 10^4 Hz. Figure 2B shows the logarithm of ε″ *vs* the logarithm of the angular frequency (**ω**), which corresponds to the conductive regime of this IL. This spectroscopic window fits well to the following linear equation.:

$$\ln \varepsilon'' = 24.031 - 0.983 * \ln \omega \quad (9)$$

From the fitting parameters, the conductivity of this IL can be obtained by application of Equation (8):

$$\sigma = 8.8542 * 10^{-12} * \mathrm{Exp}[24.031] = 0.242\ \mathrm{S/m} \quad (10)$$

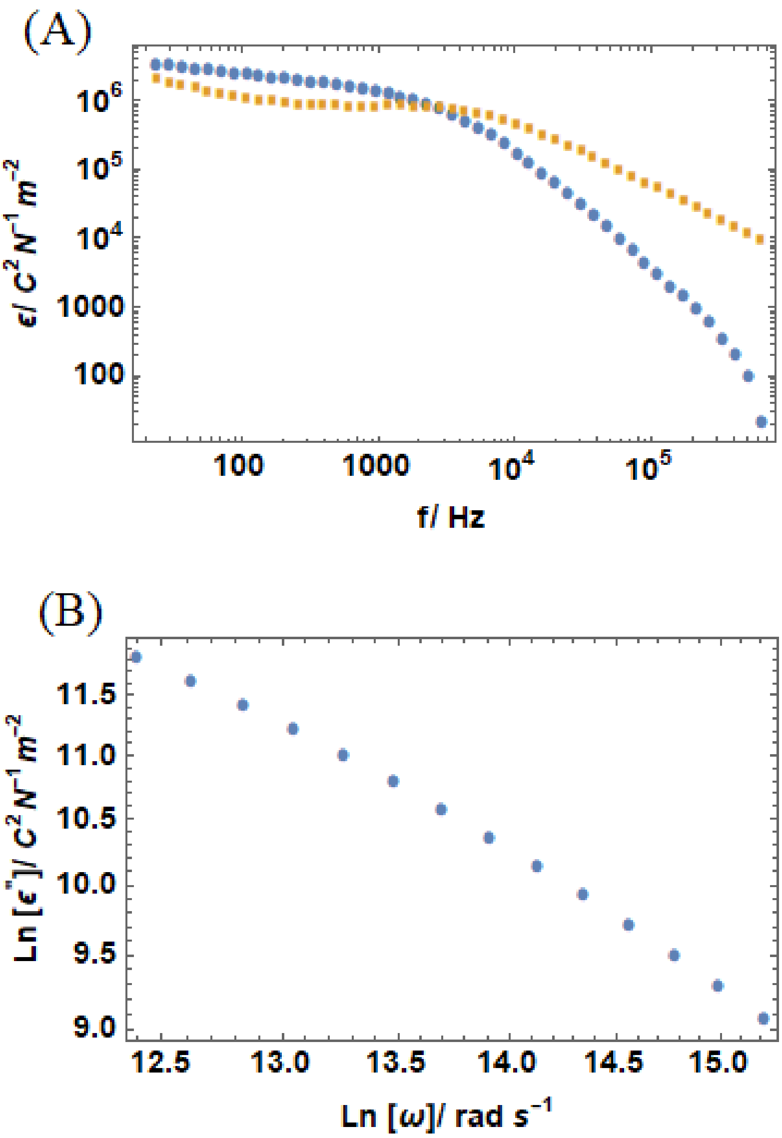


Figure 2. (**A**) Real part of complex dielectric constant (blue dots), and imaginary part of the complex dielectric constant (orange squares). (**B**) Linear region (conductive regime) of the imaginary part of the dielectric constant.

Furthermore, the conductivity can be obtained by averaging of the conductivity values in the conductive regime of IL. Figure 3 shows the conductivity *vs* frequency (obtained from Equation (8)), where it is clearly seen that the conductive regime begins around 10^4 Hz, as mentioned above. As previously pointed out, the average value of conductivity on conductive regime is 0.28 ± 0.09 S/m.

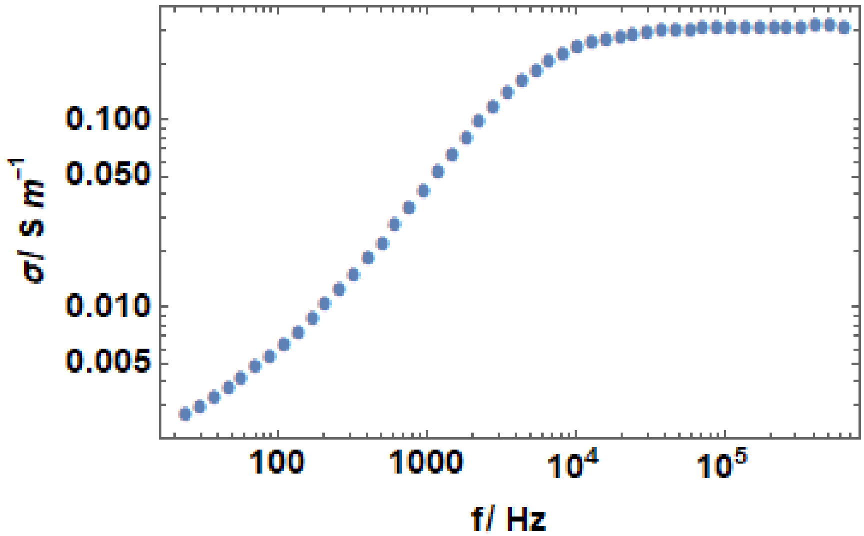


Figure 3. Conductivity vs frequency.

Figure 4 shows the Nyquist plot (Z′ *vs* Z″, this plot is a frequency response plot used to assess the stability of a system with feedback) of the $C_4C_1Im\ BF_4$ at room temperature. It can be clearly seen that the frequency range is not enough to observe the full semicircle of the dielectric relaxation. So, unfortunately, the spectroscopic frequency window carried in this system is not the suitable to study this phenomenon.

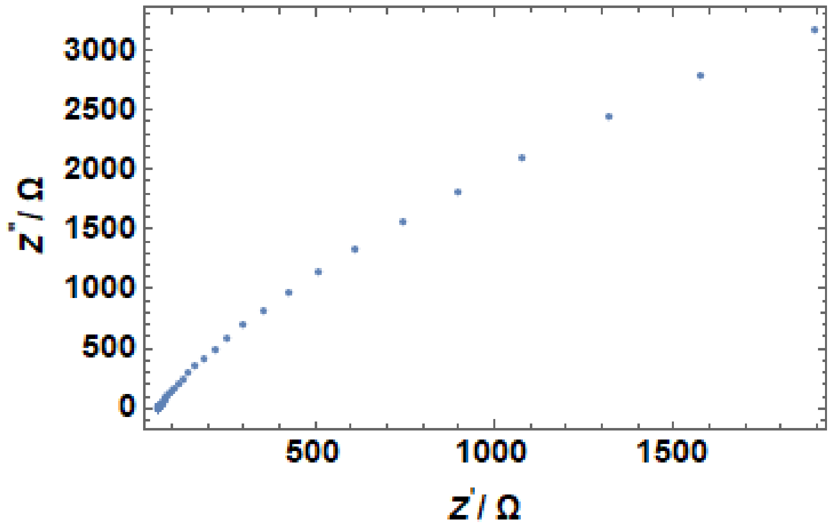


Figure 4. Nyquist plot of $C_4C_1Im\ BF_4$.

Finally, the conductivity at room temperature measured by GLP31 conductimeter is:

$$\sigma = 0.263 \pm 0.010\ \mathrm{S/m} \quad (11)$$

Obtained values from both apparatus are comparable and are in good concordance with the results of Harris et al. [13] and Rilo et al. [14] After this work, the main conclusion when comparing both techniques could be that conventional conductimeter give us quicker values although RLC provides more reliable results.

6. Conclusions

The identification of the conductive regime, and the conductivity calculation through a least square fitting, or by averaging of the conductivities in the mentioned regime, gives better results than the traditional conductimeter using a single frequency. Even more, the reproducibility of the impedance spectroscopic is higher than the conductimeters due to the higher amount of data to obtain the conductivity.

The difference between the conductivity measured by the GLP31 and the RLC could be since RLC takes an average value for the conductivity at different frequencies, while the GLP31 measures at just one.

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