Journal of Molecular Liquids 269 (2018) 556–563

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Broadband dielectric spectroscopy of protic ethylammonium-based ionic liquids synthetized with different anions

Helen Mazzer [a,b], Lucio Cardozo-Filho [b], Paulo R.G. Fernandes [a,*]

[a] Departamento de Física, Laboratório de Fluidos Complexos, Universidade Estadual de Maringá, Avenida Colombo 5790, 87020-900 Maringá, Paraná, Brazil
[b] Departamento de Engenharia Química, Laboratório de Termodinâmica e Fluidos Supercríticos, Universidade Estadual de Maringá, Avenida Colombo 5790, 87020-900 Maringá, Paraná, Brazil

ARTICLE INFO

Article history:
Received 29 May 2018
Received in revised form 10 August 2018
Accepted 11 August 2018
Available online 13 August 2018

Keywords:
Protic ionic liquids
Electric impedance
Electric permittivity
Electric conductivity

ABSTRACT

In this work, we present the synthesis of the of 2 Hydroxy ethylammonium Lactate (HELa) and of 2 Hydroxy ethylammonium Citrate (HECi) protic ionic liquids and their electric characterization by broadband dielectric spectroscopy. The complex permittivity ε^* and electrical conductivity σ^* of HELa and HECi as a function of frequency and of temperature are obtained. The experimental results are discussed considering the type of anion in each ionic liquid. In the high frequency range (f > 1KHz), at room temperature (T ~25 °C), the HELa protic ionic liquid has been shown an electric conductivity higher than that formed by citrate anion.

1. Introduction

Environmental issues involving reduction of emission or control of environmental degradation are highlighted in the world. In this sense, alternatives to minimize waste production, the so-called "green chemistry", have been widely sought [1,2]. Among some investigated alternatives are special class of salts (organic/inorganic) called Ionic Liquids (IL). Due to their peculiar properties such as high thermal and chemical stabilities, low melting point (below 100 °C) and high solvability, these liquids are considered as substitutes for traditional chemical solvents [3]. In the last years, most investigations were focused in aprotic ionic liquids (AIL), but they are of high cost and high toxicity to water and soil. On the other hand, a new class of IL called protic ionic liquids (PIL) has been highlighting due to low cost and low complexity in their synthesis [4] and total biodegradability in the environment, being the decomposition products, nutrients in the medium usable by microorganisms and plants [5,6]. On this view, the industrial interest in protic ionic liquids is increasing [7] and the knowledge of its physical properties such as electric permittivity and electric conductivity of these materials are of fundamental importance.

In this work, we present the synthesis of the 2 Hydroxy ethylammonium Lactate (HELa) and 2 Hydroxy ethylammonium Citrate (HECi) protic ionic liquids (PILs) and their electrical characterization by means of Broadband Dielectric Spectroscopy (BDS) technique [8]. BDS is a powerful experimental technique that has also been applied to investigate the electrical properties of dielectric fluids such as water [9], ionic solutions [10,11], liquid crystal-doped hydrogel [12] and ionic liquids [13]. In BDS technique, the complex electric impedance $Z^*(\omega)$ of the investigated sample can be expressed in terms of their resistance $R(\omega)$ and their capacitance $C(\omega)$ as a function of the angular frequency $\omega = 2\pi f$ where f is the measuring frequency in Hz. From the experimental data of $R(\omega)$ and $C(\omega)$ it is possible to obtain the real and imaginary parts of the complex dielectric permittivity $\varepsilon^*(\omega)$ and of the complex electric conductivity $\sigma^*(\omega)$ of the material under investigation. The electrical permittivity and electrical conductivity are discussed considering the type of anion in each ionic liquid.

2. Fundamentals

The complex electric impedance is a frequency dependence function expressed as $Z^*(\omega) = Z'(\omega) + jZ''(\omega)$ where $Z'(\omega)$ and $Z''(\omega)$ are their respective real and imaginary parts, ω denotes the angular frequency and $j = \sqrt{-1}$. From the experimental values of $Z'(\omega)$ and $Z''(\omega)$ it is possible to obtain some complex dielectric quantities such as dielectric permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$ and electrical conductivity $\sigma^*(\omega) = \sigma'(\omega) + j\sigma''(\omega)$ of the sample under investigation. By taking a sample as a dielectric medium between two plates of a capacitor and it is submitted to an external AC voltage, the sample impedance can be regarded as a resistance $R(\omega)$ in parallel circuit with a capacitance $C(\omega)$. The

* Corresponding author.
E-mail address: pricardo@dfi.uem.br (P.R.G. Fernandes).

https://doi.org/10.1016/j.molliq.2018.08.076
0167-7322/

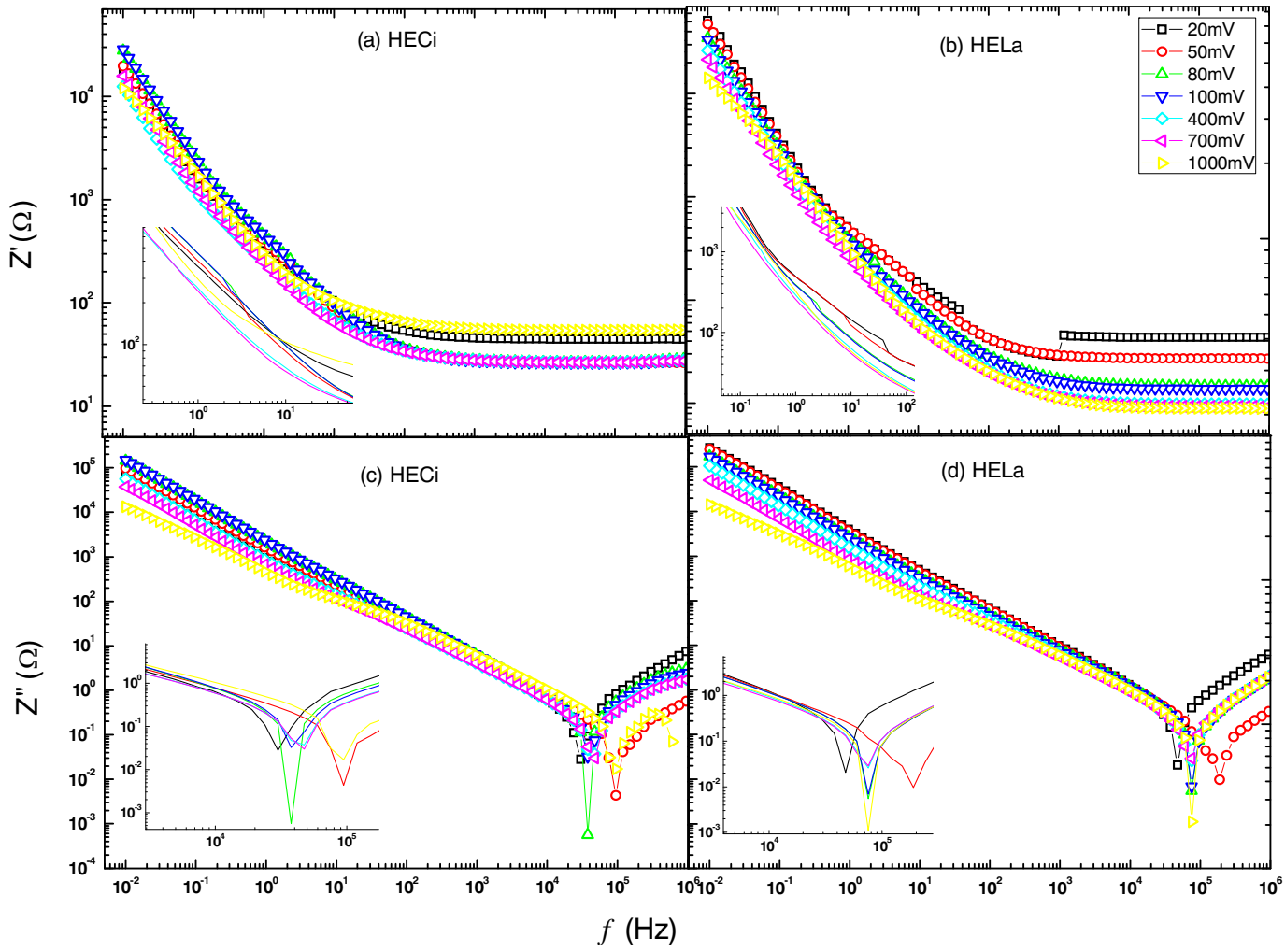

Fig. 1. Log-Log plot of real (up) and imaginary (below) parts of the frequency-dependent complex impedance of synthetized 2 Hydroxy ethylammonium Citrate ((a) and (c)) and 2 Hydroxy ethylammonium Lactate ((b) and (d)) ionic liquids for different external voltages (20 mV–1 V) at T ~25 °C. The continuum lines are only a guide of eyes.

real ($\varepsilon'(\omega)$) and imaginary ($\varepsilon''(\omega)$) parts of $\varepsilon^*(\omega)$ are related to R(ω) and C(ω) by means of the Eqs. (1) and (2) [14].

$$\varepsilon'(\omega) = \frac{dC(\omega)}{\varepsilon_0 A} \tag{1}$$

$$\varepsilon''(\omega) = \frac{d}{\varepsilon_0 A \omega R(\omega)} \tag{2}$$

In Eqs. (1) and (2), d is the thickness of the sample, A is the area of the capacitor plates, $\omega = 2\pi f$ being f the frequency in Hz and $\varepsilon_0 = 8.85418 \times 10^{-12}$F/m is the permittivity of free space. For small electric field strength, the dielectric displacement can be expressed by $\vec{D}(\omega) = \varepsilon^*(\omega)\varepsilon_0 \vec{E}(\omega)$. In such manner, the real and imaginary of $\sigma^*(\omega) = j\omega\varepsilon_0\varepsilon^*(\omega)$ [8,15] can be related to experimental parameters by the following expressions:

$$\sigma'(\omega) = \varepsilon_0 \omega \varepsilon''(\omega) = \frac{d}{AR(\omega)} \tag{3}$$

and

$$\sigma''(\omega) = \varepsilon_0 \omega \varepsilon'(\omega) = \frac{d\omega C(\omega)}{A}. \tag{4}$$

3. Materials and methods

The monoethanolamine and acid citric are from Sigma Aldrich (purity better than 99%) and lactic acid is from Merck (better than 99%). The synthesis of protic ionic liquids of 2 hydroxy ethylammonium lactate (HELa) and 2 hydroxy ethylammonium citrate (HECi) is based on Bronsted tritation between acids and bases [4,16]. The ionic fluids were stored at constant temperature (~300K) and in the presence of silica in order to guarantee a low moisture. The reactor used to prepare the protic ionic fluids has an agitation control and the sample is placed into an ice bath to avoid the heating due to exothermic reaction and partial degradation of the synthesis products. The amine is completely deposited in the reactor and the acid (limiting agent) should be added slowly (dropwise) under mechanical stirring for at least 24 h at 299 K. After this step, the purification process is made. In the purification process, the ionic liquid is heated up to 323 K and fixed in this temperature for 12 h in order to remove all unreacted compounds and to eliminate the water. The HELa ionic liquid synthetized in this work has similar physicochemical properties of the literature [16,18]. However, for 2 hydroxy ethylammonium citrate (HECi) few data are found in the literature [17].

By using a Solartron frequency response analyzer (1260A Model) the real $Z'(\omega)$ and imaginary $Z''(\omega)$ parts of complex impedance $Z^*(\omega)$ were measured from 10.0 mHz to 1 MHz. At first, the stainless-steel