

Joninių skysčių Pyr14TFSI ir Pyr12O1TFSI statinės dielektrinės skvarbos tyrimai

Static Dielectric Permittivity of Pyr14TFSI and Pyr12O1TFSI Ionic Liquids

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Ionic liquids (IL) have received significant research focus due to their unique set of properties that has allowed them to be used in numerous applications. [1], [2] To name a few, ILs have been used as media for organic synthesis, bioscience, chemical sensing, green chemistry including recycling of rare earth/heavy metals and in variety of different electrochemical and electromechanical applications such as electrodeposition of metals and semiconductors, biofuel cells, electromechanical actuators, lithium-ion and other battery applications, dye-sensitized solar cells, supercapacitors, etc. ILs, which are salts that are in a liquid state below room below 100°C (and in many cases at room temperature), have good thermal and chemical stability, low melting point, negligible volatility (and thus low flammability), high ionic conductivity, polarity, miscibility with many compounds and moderate viscosity. In addition to the many attractive properties of ILs, one interesting aspect of ILs is the dipolar dynamics. However, this investigation of the dipolar dynamics is not an easy task because of their inherent high ionic conductivity, which makes data extraction in the lower frequency region ($f < 1$ GHz) particularly challenging [3].

This work presents the dielectric spectroscopy of two ILs, N-butyl-N-methyl-pyrrolidinium bis-(trifluoromethanesulfonyl)imide (Pyr₁₄TFSI) and N-(methoxyethyl)-N-methylpyrrolidinium bis-(trifluoromethanesulfonyl)imide (Pyr_{12O1}TFSI). These two ILs have been extensively studied as candidates to replace organic electrolytes in Li-ion batteries, primarily due to the enhanced safety offered by them. Conventional methods to analyze dielectric spectra of these ILs failed to give unambiguous results because of contact blocking phenomenon (or Maxwell-Wagner polarization), which obscures the static dielectric permittivity (ϵ_{DC}) at low frequencies. An approach similar to the one described in [4] is presented here. It requires a recalculation of the dielectric spectra to give the specific resistance spectra, which allows parameters of dipolar dynamics, as well as static dielectric permittivity, of the ILs to be extracted. Using this approach, the aim of this work was to characterize the dipolar dynamics of these two materials – Pyr₁₄TFSI and Pyr_{12O1}TFSI – and compare them to the dynamics of other known ILs.

The dielectric permittivity of Pyr₁₄TFSI and Pyr_{12O1}TFSI ILs was measured in the frequency range of 40 MHz to 20 GHz and temperature range from 298 K

(room temperature) to 370 K. The measurements were performed during the heating cycle with 0.75 K/min temperature variation rate. The sample cell was a circular waveguide, which has a transition to a coaxial probe. The reflectance measurements were made using a vector network analyzer Agilent E8363B. The dielectric permittivity data was extracted from the reflectance according to a full-wave model of the waveguide configuration used for measurements. The temperature measurements were performed with a T-type thermocouple connected to a multimeter Keithley Integra 2700. This equipment and specific data analysis allowed to obtain temperature dependence of static dielectric permittivity of Pyr₁₄TFSI and Pyr_{12O1}TFSI ILs (figure 1)

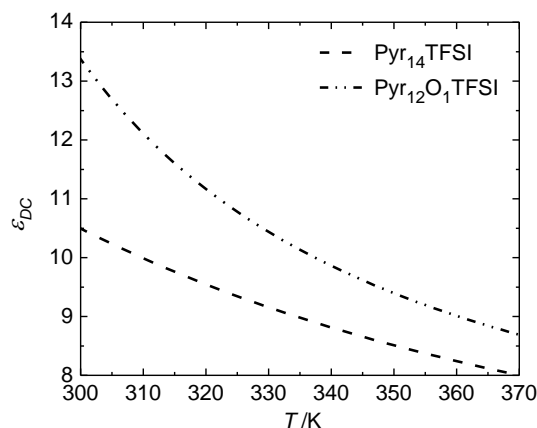


Fig. 1 Temperature dependence of ϵ_{DC} of the Pyr₁₄TFSI (black) and Pyr_{12O1}TFSI (red) ionic liquids.

Key words: ionic liquid, dielectric spectroscopy, liquid phase.

References

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