



Thermal Properties, Conductivity, and Spin-lattice Relaxation of Gel Electrolyte Based on Low Molecular Weight Gelator and Solution of High Temperature Ionic Liquid



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ARTICLE INFO

Article history:

Received 28 January 2015

Accepted 3 March 2015

Available online 5 March 2015

Keywords:

high temperature ionic liquid

low molecular weight gelator

gel electrolytes

thermal properties

enhanced ionic conductivity

spin-lattice relaxation

ABSTRACT

Gel electrolyte based on low molecular weight organic gelator methyl-4,6-O-(*p*-nitrobenzylidene)- α -D-glucopyranoside was formed by the self-assembly phenomena in aqueous solution of high temperature ionic liquid tetramethylammonium bromide. The solidification process was based on sol-gel technique with controlled gelation temperature. When the temperature was below the characteristic gel-sol phase transition temperature, T_{gs} , the gel electrolyte was solid-like. The gel electrolytes showed enhanced ionic conductivity to those of the pure electrolyte in liquid state in whole temperature range below T_{gs} . The thermal stability, ionic conductivity and molecular dynamics investigated as a function of temperature and concentration of the gelator, together with the gel microstructure were performed to get some insight in to the origin of the enhanced conductivity properties. Intermolecular interaction between ion complexes and gelator aggregates was implicated by the data obtained and suggested as the origin of the conductivity enhancement effect.

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1. Introduction

The electrolytes and ionic liquids acting as ionic conductors, together with electrodes acting as electric conductors, form a circuit in electrochemical cells and thus are the important elements of batteries, supercapacitors and fuel cells in a variety of electrical devices. However, such systems based on liquid electrolytes show many undesirable properties such as the possibility of leakage, evaporation, and corrosion. On the other hand, the solid-state electrolytes are characterized by no leak, non-volatility, mechanical strength and processing flexibility but unfortunately, also by low conductivity caused by their immobile matrix and because of that, their use has been limited. Therefore, gel electrolytes has been invented to combine high conductivity of liquid electrolytes with the advantages of solid electrolytes.

Depending on the nature of gelator, gel electrolytes can be classified into polymer gel electrolytes [1–14] and low molecular weight gel electrolytes [15–28]. The former are in most of the cases the chemical gels formed as a result of polymerization reactions and chemical bonding. The latter ones are always physical gels formed by the self-assembly of low molecular weight gelators

(LMWGs) in liquid media (solution of electrolytes or ionic liquids) through the intermolecular interactions such as hydrogen bonding, π - π stacking, van der Waals and electrostatic interactions, coordination, or charge transfer. As a result of such interactions a three dimensional network of LMWGs aggregates is formed which adsorbs (incorporates) solvent into its structure [15–28]. The low molecular weight gel electrolytes are thermoreversible. Therefore, they melt above the gel-to-sol phase transition temperature of the gel and can be reformed upon cooling. This feature is an advantage over polymer gel electrolytes and makes the fabrication of the real electrochemical devices easier, less time and costs consuming. Moreover, it allows also to create gel electrolyte inside the device, thus improving contacts between the cell elements. Unlike the polymer gel electrolytes, low molecular weight gel electrolytes can be formed with a small weight percent of gelator and it has been found that ionic conductivities of gels are similar to those of the pure electrolyte [15–28].

In recent years, the gel electrolytes based on the low molecular weight gelators have attracted considerable attention owing to their potential applications in electrochemical devices. Although many LMWGs have been demonstrated to form gels in organic solvents [29,30], much less attention has been paid to appropriate gelators for ionic liquids or electrolytes [15–17]. Based on our experience in the studies of low molecular weight gels [31–37] we selected one of the sugar base gelators: methyl-4,6-O-(*p*-

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nitrobenzylidene)- α -D-glucopyranoside [38–40]. Its proven gelation abilities to gelatinize organic solvent [32–34] but also water [35] prompted us to make use of this gelator for preparation of low molecular weight gel electrolytes.

In this paper, we report on the studies of a low molecular weight gel electrolyte formed by self-assembly of methyl-4,6-O-(*p*-nitrobenzylidene)- α -D-glucopyranoside (**1**) in the tetramethylammonium bromide (TMABr) aqueous solution. A gel electrolyte was prepared with gelator (**1**) and 500 mM TMABr aqueous solution. The sol-gel technique was used to obtain gel samples at 0.5%, 1.0%, 1.5% and 2.0% weight concentration of gelator. The preparation of the gel electrolyte and its characterization, including determination of the ion conductivity, thermal properties, molecular interactions and gel microstructure are presented in this work.

2. Experimental

2.1. Materials

The LMWG methyl-4,6-O-(*p*-nitrobenzylidene)- α -D-glucopyranoside was synthesized according to the method described elsewhere [40]. The presence of the nitro group in the *p*-position induces a strong ability to gelatinize different non-polar and polar solvents. Reports on such bifunctional gelators are limited in literature [40,41], but they give the opportunity to create new system based on aqueous and non-aqueous electrolyte solutions for preparation of physical gel electrolytes. In the previously published paper [32–35] we have studied the thermal properties and aggregation mechanisms responsible for the gelation in molecular gels made of gelator **1** with organic solvents and water. It was found by the FT-IR spectroscopy that the hydrogen bonding interactions between gelator molecules are mainly responsible for the aggregation. As in the present work, the aqueous solution of tetramethylammonium bromide (TMABr) was used to prepare the gel electrolyte with **1**, we postulate that also in this case the hydrogen bonding will play the main role in the gelation process. TMABr was obtained commercially from the Sigma-Aldrich and was used without further modification. Fig. 1 presents its chemical structure together with the most possible conformation of the gelator molecule obtained by quantum chemistry methods [32] and the chemical structure of TMABr.

2.2. Preparation of the gel electrolytes

The gelator **1** and 500 mM TMABr aqueous solution taken in appropriate weight proportions were heated in flame sealed glass tube until the gelator was completely dissolved. After cooling down to room temperature, the physical gel phase was obtained. To verify the gel phase, the bottom-up test was performed to check for no flow. After gelation, the sample was fully transparent and stable in time. The concentrations of 0.5%, 1.0%, 1.5% and 2.0% weight of the gelator to the weight of water used to prepare the electrolyte for studied gel, were chosen for the investigation.

2.3. Determination of the gel-sol phase transition temperature (T_{gs})

The gel-sol phase transition temperature (T_{gs}) of the low molecular weight gel electrolytes was determined by air bath method and visual inspection of the samples in specially designed experimental setup used in the studies of physical gel systems and described previously [34]. The phase transition temperature was determined on heating the sample to the temperature at which the system starts to flow and was measured to the accuracy of ± 0.5 K.

2.4. Electrical conductivity measurements

The electric conductivity was characterized using the digital conductivity meter S230 SevenExcellence from Mettler-Toledo (Schwerzenbach, Switzerland) with InLab 710 four electrode conductivity cell. The sample was loaded in a closed glass tube with conductivity cell placed in. The cell constant was calibrated using 1.413 μ S/cm standard. All measurements were performed in thermostatic water bath at a certain temperature maintained by a Haake circulating thermostat to the accuracy of 0.1 K. The conductivity measurements were carried out for the gel samples containing 0.5%, 1.0%, 1.5% and 2.0% weight of gelator **1**. The uncertainty in the measurement of conductivity was estimated to be 0.1%. The temperature dependence of the conductivity of aqueous electrolyte solution and low molecular weight gel was measured from 293 K to 363 K in 2 K steps.

2.5. The field cycling NMR relaxometry method (FC NMR relaxometry)

The spin-lattice relaxation times T_1 of protons (^1H) of aqueous 500 mM TMABr electrolyte solution and gel electrolyte made with **1** were measured on SpinMaster 2000 field cycling (FC) relaxometer from Stelar Company (Meda, Italy), which covers the proton frequencies from 0.01 to 40 MHz. The measurements were performed as a function of magnetic field B_0 expressed as proton Larmor frequency. The plot of the relaxation rate R_1 ($R_1 = 1/T_1$) vs Larmor frequency is called the nuclear magnetic resonance dispersion (NMRD). The technical details of the FC NMR relaxometry method are reported elsewhere [42–44]. The magnetization measured in the gel phase comes only from the electrolyte protons because the contribution of the gelator aggregates protons, which form a rigid matrix in the gel with strong restricted motion, is undetectable under the applied NMR measuring conditions. As the sensing nucleus in the experiment was ^1H , we get the

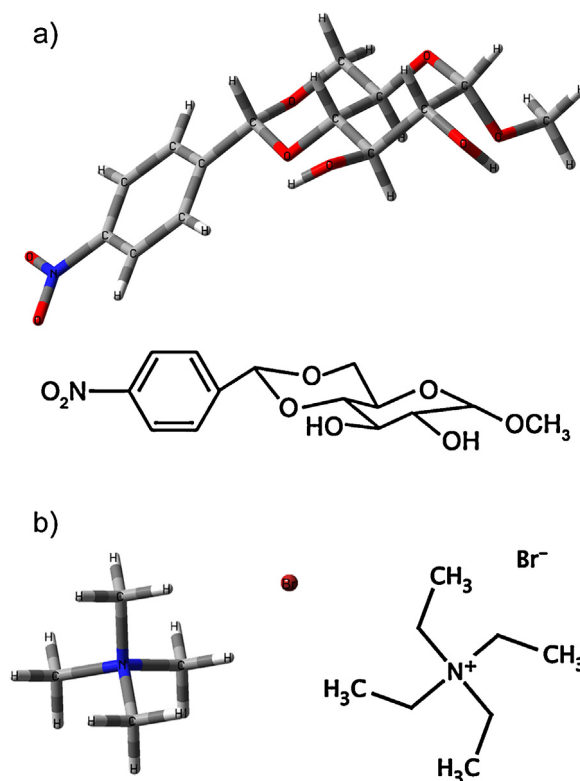


Fig. 1. Optimized geometry for methyl-4,6-O-(*p*-nitrobenzylidene)- α -D-glucopyranoside (a) and tetramethylammonium bromide (b).

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