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Role of propylene carbonate chirality on physicochemical properties of the corresponding ion conductors

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ABSTRACT

The properties of the lithium triflate-propylene carbonate of various enantiomeric purity solid and liquid systems were investigated. Properties of the solutions were studied by means of vibrational spectroscopy (supported by X-ray data for sodium triflate as a base of the analysis of the spectra of the lithium triflate-propylene carbonate electrolytes) and impedance spectroscopy (conductivity). Thermal properties of the obtained electrolytes were studied by means of DSC. The main impact was put on ability of the system to the crystallization. These studies show that in the systems of higher enantiomeric purity and lower salt concentration, crystallization of the solvent is more pronounced (higher enthalpy of melting is observed). The use of enantiomerically pure solvents leads to the conductivity enhancement up to 15%. As the crystallinity of the system is higher for enantiomerically-pure systems, the conductivity increase may be ascribed to the organization of the electrolyte.

1. Introduction

Propylene carbonate (PC) is a polar and aprotic solvent of high relative permittivity ($\varepsilon = 64{,}9$ at 20 °C) and relatively good cation coordination properties. Hence, it is concerned as one of the most important solvents being ingredient of electrolytes dedicated to lithium batteries [1–3]. PC was also studied in solid and gel polymer electrolytes as potential plasticizer of poly (ethylene oxide) [4,5] and polyacrylonitrile [6]. Moreover, this compound can be used also in polymer chemistry in synthesis of the polycarbonate diols used in the packaging applications [7], as a biodegradable drug carrier [8], in the solvent-free coatings, as a dispersions stabilizers as well as in the synthesis of thermoplastic and elastomeric polyurethanes [9]. Also several blends and composites of poly(propylene carbonate) were elaborated [10,11]. Such a wide range of applications occurs from the fact that PC is one of the cheapest aprotic solvents of high polarity. This in turn is due to easiness of PC synthesis from carbon dioxide and propylene oxide. Another advantage of PC is its high boiling point (∼240 °C) [12,13] and low (- ∼−50 °C)[1] [14–17] temperature of melting in comparison to other organic carbonates. It is worth to remark that such "liquidity range" of other organic is significantly more narrow. For instance, melting and boiling temperatures of the ethylene carbonate (EC) are ∼37 °C [18,19] and ∼248 °C [20,14–17], respectively. In case of dimethyl carbonate (DMC), these temperatures are equal ∼5 °C [21] and 90 °C [22,23].

This unusually broad "liquidity gap" comes from the fact that PC is in fact not the pure compound, but racemic mixture of two enantiomers (Scheme 1). Very similar properties exhibit other chiral cyclic carbonates. For example, racemic mixture of *(R,R)* and *(S,S)* 2,3-butylene carbonate as well as mixture of all its diastereoisomers is liquid at room temperature while pure *meso-(R,S)* diatereoisomer of this compound is solid (melting point 37 °C) [24–28]. Unfortunately, there is lack of detailed data on the melting point of 1,2-alkylene carbonates (e.g. 1,2-butylene carbonate, see e.g. Tokyo Chemical Industry catalogue) which are

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[1] There are some discrepancies in the melting point values of (racemic) PC in the literature. Some of the catalogues present it as higher than −50 °C (e.g. −49.2 °C [14]; −49 °C [15]). Several authors in their publications concerning PC do not disclose any phase change at about −50 ºC and below this temperature. The values in several articles is below −54 °C, e.g. melting point measured by Jones and Alkens [16] equals −54.53 °C, in publication of J. L. Allen et.al. [17], the onset temperature is about−56.8 °C.

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racemic mixture of the enantiomers. However, electrochemical studies on the electrolytes based on the 1,2-butylene carbonate suggest that they are liquid at a wide range of temperatures [29–31]. Therefore, we can say that there is a correlation between the chirality and tendency of the system to crystallize, at least for cyclic carbonates.

This makes formation of the crystal structure much more complicated in comparison to other carbonates like EC or DMC. The fact of the chirality, however, is often omitted when physicochemical properties of PC-containing systems are discussed. The majority of these studies are conducted on racemic mixture of PC.

In this article, we present data for PC-lithium trifluoromethanesulfonate (lithium triflate, LiTf) electrolytes. The main impact in this study is put on the role of enantiomeric purity of the PC on the properties of the system. The most important research in which chirality of the PC was taken into consideration was conducted by Trulove et al. [32], however, it was limited to systems of very high salt concentration and with the single enantiomer. We decided to study also systems containing two enantiomers but with excess of one of them. Moreover, we decided to concentrate on the electrolytes of the salt concentration typical for electrolytes used in the lithium batteries.

2. Experimental

2.1. Materials used

Enantiomerically pure *(R)*- and *(S)*-propylene carbonate (4-methyl-1,3-dioxolan-2-one, Tokyo Chemical Industry) was used as received. The humidity content, measured by means of Karl–Fischer titration, was below 0.1% (1000 ppm). The solutions of the compositions of various content of the enantiomers were obtained by mixing the enantiomerically pure solvents in order to omit problem of the different water content in the samples. LiTf (Aldrich, 99.995%) was dried for 100 hours at the 100 °C under high vacuum (10^{-6} torr) Scheme 1.

2.2. Impedance spectroscopy

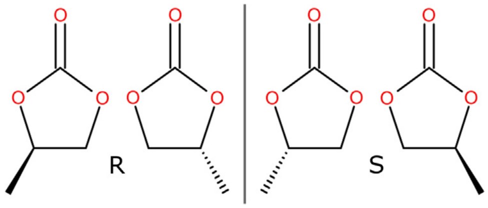
The ionic conductivity was determined by the means of impedance spectroscopy. Stainless-steel blocking electrodes were used. The data were registered on VMP3 multi-channel potentiostat equipped with impedance modules. The 1 Hz–500 kHz frequency range was applied. The cell was immersed in a HAAKE DC 50 cryostat to control the measurement temperature. A Bernard Boukamp EQ software [33] was used for analysis of the obtained impedance data. The relative error of the measurement was lower than 2%.

2.3. DSC

The thermal properties of the samples were studied by the means of differential scanning calorimetry technique (DSC). The experimental data were registered on TA Q200 differential scanning calorimeter. The samples were heated at a rate of 10° min^{-1}. An empty aluminum pan was used as the reference.

2.4. FTIR spectroscopy

Infrared absorption spectra were recorded on a computer interfaced Perkin-Elmer 2000 FTIR system with a wavenumber resolution of 2 cm^{-1}. FTIR studies were performed in the −120 to 40 °C temperature range. Spectra were recorded for the samples in a form of a thin film sandwiched between two NaCl plates. Cells filled with electrolytes were placed in the FTIR temperature-controlled unit; the accuracy of the temperature was estimated to be ±1 °C. The cell was placed in a vacuum isolated holder, cooled with liquid nitrogen and then slowly heated and stabilized for 10 min at each particular temperature.



Scheme 1. *(R)* and *(S)*- propylene carbonate. The pairs on each side of the mirror are identical.

2.5. Raman spectroscopy

Raman spectra were recorded on Nicolet Almega dispersive Raman spectrometer with use of 532 nm excitation line and 2400 lines high resolution gratings. The exposure time was set to 30 s. Samples were placed in the sealed quartz cuvettes in an inert gas atmosphere.

2.6. Crystal structure determination of [(S)-PC]$_1$(NaTf)$_2$ and [(R)-PC]$_1$(NaTf)$_2$.

Selected single crystal was mounted in inert oil and transferred to the cold gas stream of the diffractometer. Diffraction data were measured at 120.0(2) K with graphite monochromated MoKα radiation (λ = 0.71073) on an Oxford Diffraction κ-CCD Gemini A Ultra diffractometer. Cell refinement and data collection as well as data reduction and analysis were performed with the $\text{CRYSALIS}^{\text{PRO}}$ software [34]. The structure was solved by direct methods using the SHELXS-97 structure solution program and refined by full-matrix least-squares against F^2 with SHELXL-2014 [35] and OLEX2 [36] programs. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure model at geometrically idealized coordinates and refined as riding atoms. These data have also been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC1030761–CCDC1030762. They can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for $[(R)\text{-PC}]_1(\text{NaTf})_2$: $C_6H_6F_6Na_2O_9S_2$, M = 446.21, monoclinic, *a* = 5.7804(4) Å, *b* = 12.2394(8) Å, *c* = 11.0705(10) Å, β = 104.011(7)°, *V* = 759.93(10) $Å^3$, *T* = 120.0(2) K, space group $P2_1$,

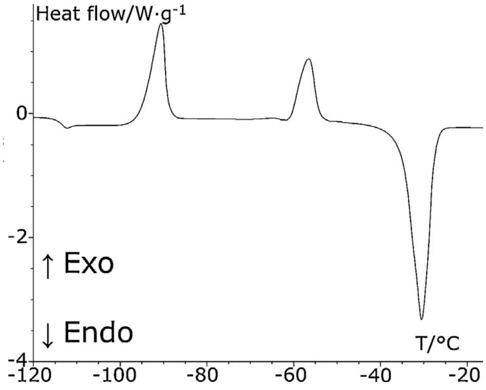


Fig. 1. DSC thermogram of *(S)* PC. The possible phase changes: glass transition (second-order transition, −115C°), formation of the crystalline **II** phase (first-order transition, −95C°), formation of the amorphous **III** phase (second-order transition, −65C°), formation of the crystalline **IV** phase (first-order transition, −60C°), melting (first-order transition, −35C°).