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Generation and stability of superoxide ion in tris(pentafluoroethyl)trifluorophosphate anion-based ionic liquids

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ABSTRACT

Generation of the superoxide ion ($O_2^{\bullet-}$) in ionic liquids (ILs) media is one of the important areas which are currently being under investigation by several research groups worldwide. In this work, the superoxide ion was successfully generated and analyzed electrochemically using cyclic voltammetry (CV) and chronoamperometry (CA) techniques from O_2 dissolved in 1-(2-methoxyethyl)-1-methylpiperidinium tris(pentafluoroethyl)trifluorophosphate [MOEMPip][TPTP] and trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate [P14,666][TPTP]. Furthermore, $O_2^{\bullet-}$ was generated chemically by the addition of potassium superoxide to the studied ILs. UV/Vis spectrophotometer was used for testing the long term stability of the generated $O_2^{\bullet-}$. These results encourage more exploration on the use of these particular classes of ILs in various applications involving $O_2^{\bullet-}$. This study reports the first successful chemical generation of $O_2^{\bullet-}$ in tris(pentafluoroethyl)trifluorophosphate anion-based ILs which opens the way for further related studies.

1. Introduction

It is obvious that the electrochemical reduction of O_2 plays an important role in electrochemistry and electroanalysis, such as in fuel cells, biosensors and metal–air batteries [1–5]. In many aqueous and non-aqueous solvents, the reduction of O_2 is very intricate; hence reactions of protonation and disproportionation of intermediate species cannot be avoided [6–8]. Four oxidation states of O_2 are known: $[O_2]^n$ where n is the respective 0, +1, −1 and −2 for dioxygen, dioxygen cation, superoxide ion and peroxide dianion, symbolically expressed as O_2, $O_2^{\bullet+}$, $O_2^{\bullet-}$ and $O_2^{\bullet-2}$ [9].

$O_2^{\bullet-}$ is an anionic radical and it behaves either as an electron donor, an electron reducing agent, an oxidant, a base or as a nucleophile [10,11]. $O_2^{\bullet-}$ that is generated by the one electron reduction of O_2 is one of the most interesting species among reactive oxygen species (ROS) in biological processes [12,13]. It is an oxygen-centered radical with selective reactivity [14]. $O_2^{\bullet-}$ has been known since 1934, when Haber and Weiss proposed that $O_2^{\bullet-}$ can be formed in the decomposition of H_2O_2 and in the oxidation of ferrous ions by O_2 in aqueous solutions [15].

$O_2^{\bullet-}$ can be generated either chemically by solvation of KO_2 in aprotic solvents, or electrochemically via direct electrochemical reduction of O_2 in aprotic organic solvents, typically $E = -1.0$ V vs. SCE [16,17].

However, due to the limitations of using aprotic solvents in terms of high volatility, low boiling points and the negative ecological effects, no industrial implementations of the $O_2^{\bullet-}$ have been adopted. Therefore, the use of ILs is more preferable for $O_2^{\bullet-}$ generation.

Many studies have been carried out on ILs containing imidazolium, quaternary ammonium, quaternary phosphonium, piperidinium and pyrrolidinium cations [18–26]. It was found the stability of the generated $O_2^{\bullet-}$ depends strongly on the type of the cation in the IL structure.

Despite the fact that $O_2^{\bullet-}$ is regarded as a powerful nucleophile in aprotic solvents, it does not demonstrate such reactivity in H_2O, presumably due to its strong solvation as well as its rapid disproportionation and hydrolysis [27–29]. It was found that the anion of IL affects the level of water uptake and the hydrophobicity of the anions follows the sequence of $[TPTP]^- > [TFSI]^- > [HFP]^- > [BF_4]^- >$ halides [30]. Therefore, in this study, two tris(pentafluoroethyl)trifluorophosphate anion-based ILs were selected in order to investigate the generation of $O_2^{\bullet-}$ and its short and long term stability. The $[TPTP]^-$ is known as a hydrophobic anion and ILs with this anion are immiscible

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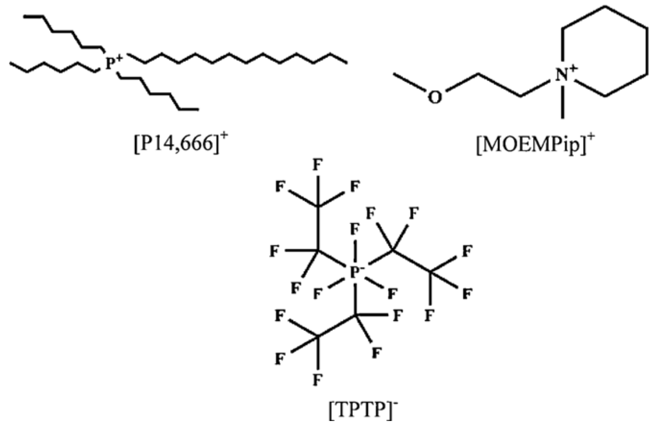

Scheme 1. Structure of ions comprising the studied ILs.

with water. It was reported that water uptake for [TPTP]$^-$ based ILs was much less than ILs containing other anions such as [TFSI]$^-$ and [HFP]$^-$ [31]. Recently, Huang et al. utilized [P14,666][TPTP] for making a micro-electrode array that had been used to form effective membrane-free amperometric gas sensors. They deduced that [P14,666][TPTP] was the most appropriate choice for use due to its hydrophobicity. This IL was found to readily form thin films on the hydrophobic surface of the micro-array, and due to its known low water uptake [30,32] these films were visually observed to be uniformly distributed on the surface of the array even after 72 h. For these reasons, as well as the IL's aprotic nature and wide electrochemical window (EW) [32,33] the reduction of O_2 to $O_2^{\bullet -}$ was clearly observed as steady-state waves for all IL thicknesses with the limiting current increasing as the IL layer thickness decreased. The layer of [P14,666][TPTP] acted as the diffusion layer, and the thinner the layer of IL the steeper the O_2 concentration gradient became, between electrode and gas phase [34].

2. Materials and methods

The ILs used in this work are 1-(2-methoxyethyl)-1-methylpiperidinium tris(pentafluoroethyl)trifluorophosphate and trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate. The ILs were supplied by Merck and were of synthesis grade. The studied ILs are in liquid form at room temperature. Scheme 1 shows the structures of the cations and anion that make up the ILs used in this study. The chemical formula and molecular weight of ILs are listed in Table 1. Dimethyl sulfoxide (DMSO) was purchased from Fisher with a purity of 99.98% and potassium superoxide (KO_2) from Sigma Aldrich with a purity of 99.9%.

2.1. Electrochemical generation of $O_2^{\bullet -}$ (short term stability)

CV tests were performed as the electrochemical analysis technique since this method is extremely powerful and is among the most widely practiced of all electrochemical methods [35]. The IL to be used was dried overnight in a vacuum oven at 50 °C. It should be noted that the ILs were acidic without pre-treatment, and the pH was 4–6. The pH of ILs was measured using pH strips from Merck. A very small quantity of KO_2 was added to the acidic IL until its pH became 7 [25,26,36]. AlNashef et al. reported that $O_2^{\bullet -}$ was not stable in some ILs because of the acidity of these ILs [37]. Therefore, small additions of KO_2 can neutralize the acidic ILs without affecting the electrochemistry in these ILs [25,26].

Table 1
Chemical formula and molecular weight of the investigated ILs.

IL	Formula	M. Wt. (g/mol)
[P14,666][TPTP]	$C_{38}H_{68}F_{18}P_2$	928.88
[MOEMPip][TPTP]	$C_{15}H_{20}F_{18}NOP$	603.27

The electrochemistry was performed using EG&G 263A potentiostat/galvanostat (PAR) controlled by computer and data acquisition software. CVs were conducted in a one compartment cell since the time of the experiment is relatively small to affect the ILs. The cell was a jacketed vessel (10 ml volume) with a Teflon cap including 4 holes for the three electrochemical electrodes and for the gas sparging tube.

Glassy carbon macro-electrode (BASi, 3 mm diam.) was used as working electrode for CV. Platinum electrode was used as a counter electrode. To avoid contaminating the target IL from water in the reference electrode, the content of the reference electrode was separated by glass frit, a filtering material. For this reason it was used in the Ag/AgCl electrode purchased from BASi [25,26]. The macro-electrodes were polished using alumina solution (BASi) and sonicated in distilled water for 10 min prior to each experiment. This was done to ensure that there are no impurities on the surface of the working electrode.

All experiments were performed in a dry glove box under either an argon or helium atmosphere. Prior to $O_2^{\bullet -}$ generation, a background voltammogram was obtained after removal of O_2. The O_2 removal was achieved by purging the IL with dry N_2. This particular method is quite effective and also simple to be employed. Previous studies reported that purging a solution with an inert gas can reduce the partial pressure of O_2 above the solution, and as a consequence the solubility of dissolved O_2 in the solution decreases according to Henry's law [38,39].

O_2 was then bubbled into the tested IL for at least 30 min to ensure that equilibrium was achieved [18,37,40,41]. In order to confirm that the tested IL is saturated with O_2, CVs at different time intervals were conducted and the final measurement was taken when the cathodic peak current of the CV is constant. Between consecutive CV runs, O_2 was bubbled briefly to refresh the system and to remove any concentration gradients. N_2 or O_2 sparging was discontinued during the CV runs. The CA measurements were conducted inside a Faraday cage to avoid any interference. The value of the steady state background current was deducted from the value obtained after sparging with O_2 to provide the net steady state current. The net value of the current was then used in the calculations [36].

2.2. Calculation of diffusion coefficient, solubility and charge transfer coefficient for O_2

In this study, both CV using macro-electrode and CA using ultramicro-electrode techniques were utilized to determine the diffusion coefficients and solubility of O_2 in the studied ILs. Detailed for calculations were reported in earlier publications [26,35–37].

2.3. Chemical generation of $O_2^{\bullet -}$ (long term stability)

DMSO was dried overnight in a vacuum oven. KO_2 was kept in a sealed vial filled with molecular sieves. The chemical generation of $O_2^{\bullet -}$ was performed by dissolving KO_2 in DMSO while stirring with a magnetic stirrer [12,42]. Subsequently, a certain amount of IL was added to the generated $O_2^{\bullet -}$ in DMSO to investigate the stability of $O_2^{\bullet -}$ with time. A computer-controlled UV/Vis spectrophotometer (PerkinElmer-Lambda 35) was used to measure the absorption spectra of $O_2^{\bullet -}$ every 10 min for 2 h. The reference solution of spectral measurements was DMSO or DMSO solution containing an appropriate amount of IL [25,26].