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## Generation of Superoxide Ion in Trihexyl (Tetradecyl) Phosphonium bis (Trifluoromethylsulfonyl) imide Room Temperature Ionic Liquid

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**Abstract:** Superoxide ion has been generated in room temperature ionic liquid trihexyl (tetradecyl) phosphonium bis (trifluoromethylsulfonyl)imide, [P14,666][N(Tf)<sub>2</sub>]. Cyclic voltammetry and chronoamperometry techniques were used for the electrochemical generation of O<sub>2</sub><sup>•-</sup>, while chemical generation was done by adding KO<sub>2</sub> to dimethylsulphoxide (DMSO). The long term stability of O<sub>2</sub><sup>•-</sup> was investigated using UV/Vis spectrophotometer. It was found that the quaternary phosphonium cation, [P14,666]<sup>+</sup> is a reasonably stable cation in the presence of O<sub>2</sub><sup>•-</sup> which indicates the possible use of these ILs for further useful applications.

**Key words:** Superoxide ion, phosphonium, stability, ionic liquids

### INTRODUCTION

Ionic liquids (ILs) have been accepted as a new green chemical revolution which gained attention of the academia as well as the chemical industries (Welton, 1999). They have unique properties such as high electrical conductivity, wide temperature range of the liquid state, thermal stability and low volatility (Wassersheid and Welton, 2003; Murase *et al.*, 2001). Moreover, because of their intrinsic conductivity and wide electrochemical windows, they have been utilized in a wide range of electrochemical applications (Hultgren *et al.*, 2002; Saheb *et al.*, 2006; Buzzeo *et al.*, 2004a).

Recently, ILs have become popular alternative mediums for the reduction of oxygen into superoxide ion (O<sub>2</sub><sup>•-</sup>) (Carter *et al.*, 1991; AlNashef *et al.*, 2001, 2002; Buzzeo *et al.*, 2003; Katayama *et al.*, 2004; Evans *et al.*, 2004). AlNashef *et al.* (2001) were the first to report the evidence of the electrochemical generation of a stable O<sub>2</sub><sup>•-</sup> in the ionic liquid, [BMIM][PF<sub>6</sub>]. Many ILs have been investigated after that depending on their structure (cation and anion) such as hexafluorophosphate, chloroaluminate trifluoromethylsulfonyl and tetrafluoroborate, combining with alkylated imidazolium or ammonium cations (Katayama *et al.*, 2004; Evans *et al.*, 2004; Buzzeo *et al.*, 2004b; Zhang *et al.*, 2004; Islam *et al.*, 2009). Evans *et al.* (2004) investigated the electrochemical reduction of O<sub>2</sub> in two phosphonium based ILs, namely tris(n-hexyl) tetradecyl phosphonium bis

(trifluoromethylsulfonyl)-imide and tris(n-hexyl) tetradecylphosphonium, trifluoro tris (pentafluoroethyl) phosphate. They found that in cyclic voltammetry the oxidation peaks are broader and further removed from the initial reductive wave. The measured diffusion coefficients for O<sub>2</sub> in the two ILs were higher than those reported in other ILs. However, Evans *et al.* (2004) indicated that the generated superoxide ion reacted with the cation of the phosphonium-based RTIL.

In order to investigate the strange behaviour of the superoxide ion in phosphonium based ILs, in this work; we studied the electrochemical and chemical generation of the superoxide ion in trihexyl (tetradecyl) phosphonium bis (trifluoromethylsulfonyl) imide, IL. The stability of the superoxide ion was studied using UV-vis spectrophotometer. The effect of temperature on the variation of O<sub>2</sub> diffusivity and solubility was also studied.

### MATERIALS AND METHODS

Figure 1 shows the structures of the cation and anion of the IL trihexyl (tetradecyl) phosphonium bis (trifluoromethylsulfonyl) imide, [P14,666][N(Tf)<sub>2</sub>], (for synthesis, MERCK) which was selected for this study. Its molecular weight is 764.02 g mol<sup>-1</sup> and the chemical formula is (C<sub>34</sub>H<sub>68</sub>F<sub>6</sub>NO<sub>4</sub>PS<sub>2</sub>).

**Electrochemical generation:** Cyclic voltammetry (CV) tests were performed in [P14,666][N(Tf)<sub>2</sub>]. The IL was dried overnight in a vacuum oven at 50°C. The

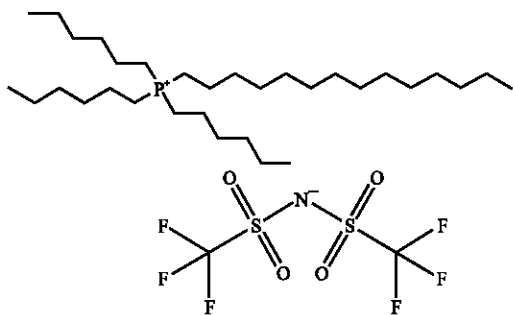


Fig. 1: The structure of [P14, 666] [N(Tf)<sub>2</sub>]

electrochemistry was performed using potentiostat/galvanostat controlled by computer and data acquisition software. CVs can be conducted in a one compartment cell since the time of the experiment is relatively small to affect the ILs.

Glassy carbon macro-electrode (3 mm diam) was used as working electrode for cyclic voltammetry while glassy carbon ultramicro-electrode (11 μm diam) was used for chronoamperometry and platinum electrode was used as a counter electrode, while Ag/AgCl electrode was used as a reference electrode. All experiments were performed in a dry glove box under either an argon or helium atmosphere. Prior to superoxide ion generation, a nitrogen sparge was used before obtaining a background voltammogram. Oxygen was then bubbled through the system for 30 min to allow sufficient solubilization. Between consecutive CV runs, O<sub>2</sub> was bubbled briefly to refresh the system with oxygen and to remove any concentration gradients. Nitrogen or oxygen sparging was discontinued during the CV data acquisition. Chronoamperometry measurements were conducted inside a Faraday cage to avoid any interference.

**Chemical generation:** Dimethyl sulfoxide, DMSO (Fisher, 99.98%) was dried overnight in a vacuum oven. The chemical generation of O<sub>2</sub><sup>•-</sup> was performed by dissolving potassium superoxide (KO<sub>2</sub>) (Sigma Aldrich, 99.9%) in DMSO while stirring with a magnetic stirrer. Subsequently, a certain amount of RTIL was added to the generated O<sub>2</sub><sup>•-</sup> in DMSO to investigate the stability of O<sub>2</sub><sup>•-</sup> with time. A computer-controlled UV-Visible spectrophotometer (Perkin-Elmer) was used to measure the absorption spectra of O<sub>2</sub><sup>•-</sup> every 10 min until reaching 2 h of reaction time. The reference solution of spectral measurements was DMSO or DMSO solution containing an appropriate amount of ionic liquid.

## RESULTS AND DISCUSSION

The electrochemical window shown in Fig. 2 has a wide potential range which indicates the feasibility of

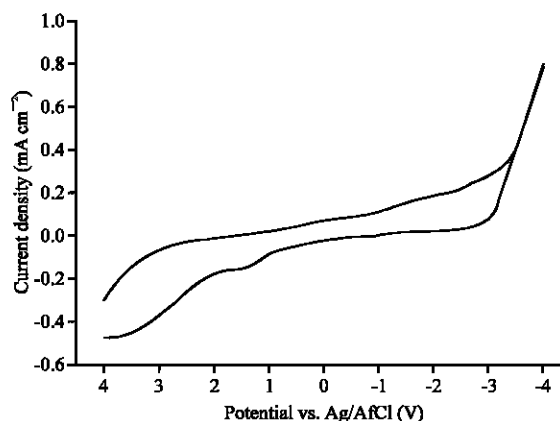


Fig. 2: Electrochemical window of [P14, 666] [N(Tf)<sub>2</sub>]

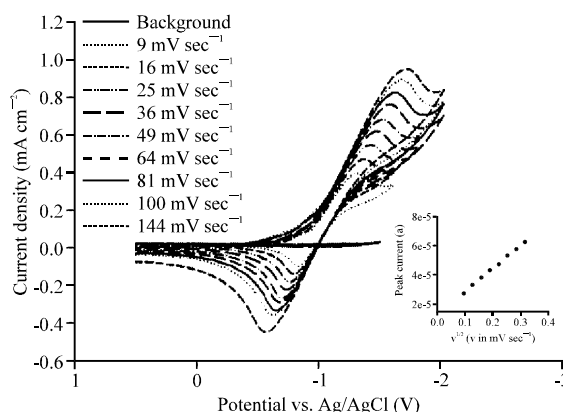


Fig. 3: CVs for various scan rates (mV sec<sup>-1</sup>) with oxygen and nitrogen (background) in [P14, 666] [N(Tf)<sub>2</sub>] at 45°C. Inset shows the plot of peak current vs. square root of sweep rate at 45°C

using this RTIL for many electrochemical applications. One of these applications is the electrochemical generation of O<sub>2</sub><sup>•-</sup>, due to its stability at ±(-1) V at which generation of O<sub>2</sub><sup>•-</sup> occurs by the reduction of O<sub>2</sub>. Figure 2 shows that the electrochemical window is about 6.9 V (3.29 V anodic to -3.61 V cathodic limits), this can be attributed to the existence of the quaternary phosphonium cation, [P14,666]<sup>+</sup> coupled to [N(Tf)<sub>2</sub>]<sup>-</sup> anion, since this type of RTIL has one of the widest electrochemical windows (Rogers *et al.*, 2009; Ignatev *et al.*, 2005).

Figure 3 shows the multi-scan rate cyclic voltammograms for the one-electron reduction of O<sub>2</sub> to O<sub>2</sub><sup>•-</sup>. Using a scan rate range of 9-144 mV sec<sup>-1</sup>, the reduction potential peaks range was -1.29 to -1.71 V while the oxidation peaks range varied from -0.83 to -0.44V. The presence of the backward peak (oxidation peak) confirms that the generated superoxide is stable within the time limits of the experiment. The change of the difference

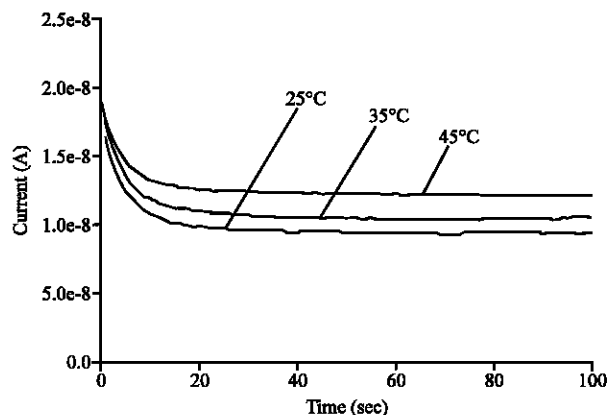


Fig. 4: CAs for O<sub>2</sub> reduction of a GC ultramicro electrode in [P14, 666] [N(Tf)<sub>2</sub>] saturated with oxygen at 25, 35 and 45°C

between the reduction and oxidation peaks with scan rate shows that the process is not reversible. The negligible background CV in the presence of nitrogen indicates that the RTIL is electrochemically stable in this range of potential. Furthermore, it can be noticed that the differences between the oxidation peaks and the reduction peaks are much higher than those reported for other types of RTILs; this is in agreement with Evans *et al.* (2004)

Figure 4 shows that the current of CA increased with increasing temperature. This can be attributed to the reduction of the viscosity of the RTIL with increasing temperature and consequently the increase of O<sub>2</sub> diffusivity.

**Calculations of diffusion coefficients:** Both cyclic voltammetry at macro-electrode and chronoamperometry at ultramicro-electrode techniques were used to determine the diffusion coefficients and solubility of oxygen in the studied RTIL. The following two equations were used:

$$i_p = (2.99 \times 10^5) \alpha^{0.5} A C_0 D_0^{0.5} \nu^{0.5} \quad (1)$$

$$i_{ss} = 4nFD_0 C_0 r_0 \quad (2)$$

In Eq. 1, which is used for the analysis of CV experiments,  $i_p$  is the cathodic peak current of CV in A;  $\alpha$  is charge transfer coefficient; A is the surface area of the macro working electrode in cm<sup>2</sup>,  $C_0$  is the bulk concentration of O<sub>2</sub> in mol mL<sup>-1</sup>,  $D_0$  is the diffusion coefficient of O<sub>2</sub> in cm<sup>2</sup> sec<sup>-1</sup>;  $\nu$  is the potential sweep rate in V/s, while in Eq. 2., which is used for CA experiments,  $i_{ss}$  is the steady-state current of CA in A, n the number of

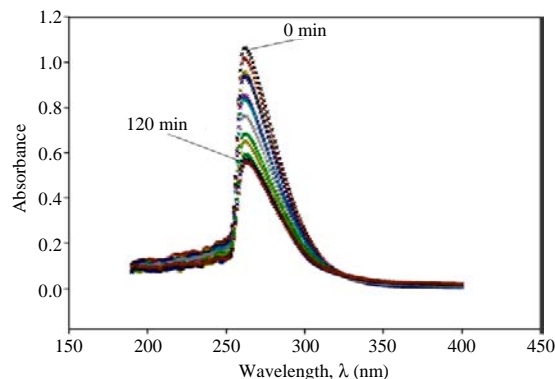


Fig. 5: UV-visible spectral changes with time (0, 10 and 20-120 min) for generated O<sub>2</sub><sup>•-</sup> in DMSO in the presence of [P14, 666] [N(Tf)<sub>2</sub>]

Table 1: The diffusion coefficients and solubility of O<sub>2</sub> in [P14,666][N(Tf)2] at 25, 35 and 45°C

Temp. (°C)	Diffusion coefficient (cm <sup>2</sup> sec <sup>-1</sup> )	Solubility of oxygen (mM)	Current (nA)
25	1.779×10 <sup>-6</sup>	26.168	9.881
35	7.052×10 <sup>-6</sup>	11.876	17.776
45	1.376×10 <sup>-5</sup>	8.430	24.621

electrons, F is Faraday's number and  $r_0$  is the radius of ultramicro- electrode. The numerical values of the diffusion coefficient and solubility of O<sub>2</sub> at different temperatures are listed in Table 1.

As can be seen in Table 1 the diffusion coefficients and CA steady state currents are increasing with increasing temperature, while the solubility of O<sub>2</sub> is decreasing. This is an expected behavior since the  $D_0$  is inversely proportional to the viscosity according to the Stokes-Einstein relationship; this is in agreement with Huang *et al.* (2009). The value of the diffusion coefficient of O<sub>2</sub> in the studied RTIL at 35°C is very close to that reported by Evans *et al.* (2004). However, the solubility of O<sub>2</sub> at the same temperature is twice that reported in the same reference.

However, Evans *et al.* (2004) interpreted that the presence of the weakly acidic [P14,666] renders O<sub>2</sub><sup>•-</sup> unstable with respect to the formation of a perhydroxyl radical and phosphorus yield and, through follow up homogeneous reactions, the partial regeneration of O<sub>2</sub>. Therefore, the long term stability of O<sub>2</sub><sup>•-</sup> was investigated in this research, since the electrochemical technique CV gives an indication for the short term stability.

Figure 5 shows the time course of the spectral changes with absorption bands of  $\lambda_{max}$  at 264 nm which are almost comparable to those previously reported for chemical generation of O<sub>2</sub><sup>•-</sup> (Islam *et al.*, 2009; Vasudevan and Wendt, 1995).

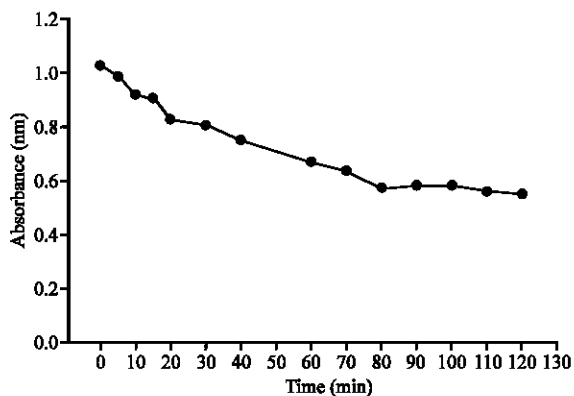


Fig. 6: The absorbencies of generated  $O_2^{\bullet-}$  Vs time (0,10,20-120 min.) in the presence of [P14, 666] [N(Tf)<sub>2</sub>]

Figure 6 shows the time evolution of the consumed  $O_2^{\bullet-}$ . It can be seen that  $O_2^{\bullet-}$  is decreasing regularly for 80 min, after that it becomes almost stable, thus the suggestion of Evans *et al.* (2004) can be implemented. These results prove the viability of using this ionic liquid for further applications involving oxidation reactions.

### CONCLUSION

Room temperature ionic liquid trihexyl (tetradecyl) phosphonium bis (trifluoromethylsulfonyl) imide, [P14,666][N(Tf)<sub>2</sub>] has been employed as medium for generation of  $O_2^{\bullet-}$ . It was found that this ionic liquid has a wide electrochemical window, which facilitates its use in many electrochemical applications. Superoxide ion was successfully generated in [P14,666][N(Tf)<sub>2</sub>] by the electrochemical reduction of oxygen. Cyclic voltammetry and chronoamperometry techniques were used for studying the electrochemical generation of  $O_2^{\bullet-}$ , while chemical generation was done by adding  $KO_2$  to DMSO. It was found that the diffusion coefficients are increasing with the increase of temperature, while the solubility of  $O_2$  is decreases. UV/Vis spectrophotometer was used to investigate the long term stability of  $O_2^{\bullet-}$ . It was confirmed that the quaternary phosphonium cation, [P14,666]<sup>+</sup> has the capacity to be a reasonably stable cation for the generation of  $O_2^{\bullet-}$ .

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