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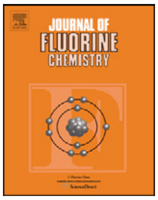

Generation and stability of superoxide ion in tris(pentafluoroethyl)trifluorophosphate anion-based ionic liquids

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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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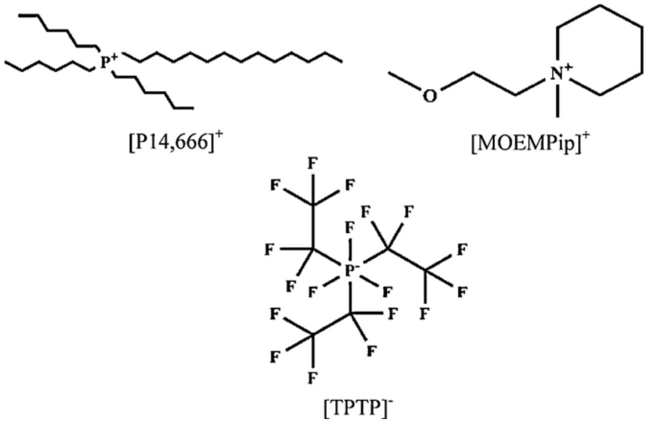

Scheme 1. Structure of ions comprising the studied ILs.

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].

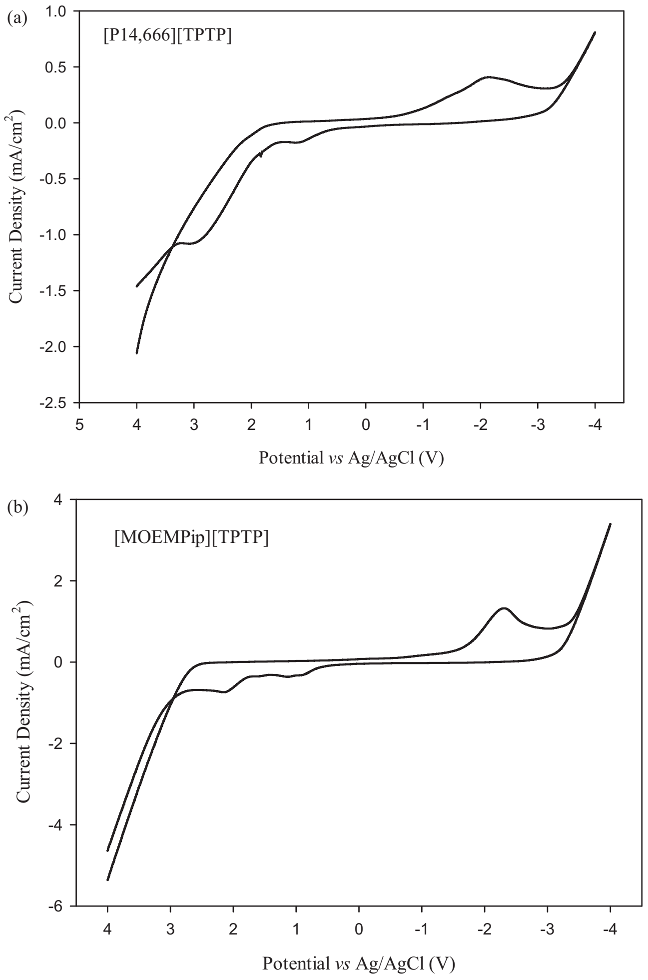

Fig. 1. Electrochemical windows of (a) [P14,666][TPTP] and (b) [MOEMPip][TPTP] at 25 °C using GC macro-electrode, sweep rate 100 mV/s.

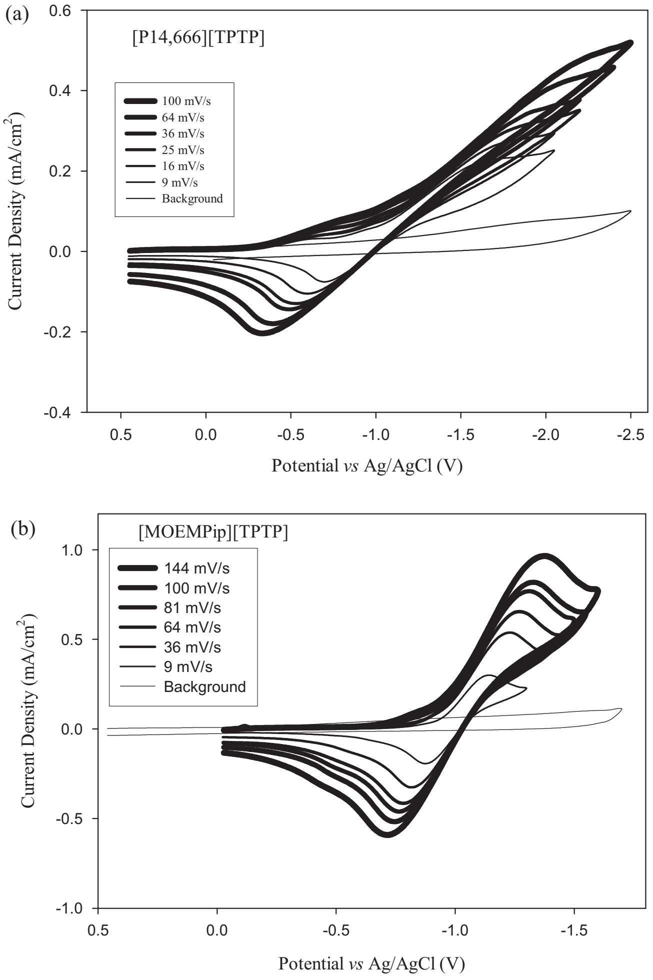

Fig. 2. CVs in (a) [P14,666][TPTP] and (b) [MOEMPip][TPTP] after sparging with oxygen and nitrogen (background) at GC macro-electrode for different sweep rates at 25 °C.

3. Results and discussion

3.1. Electrochemical window

In general, it was found that the tested ILs have wide potential ranges, as can be seen in Fig. 1, and this is consistent with other reported EWs of ILs [43–48]. Table 2 shows that $[P14,666]^+$ has wider reductive window than $[MOEMPip]^+$. This is in agreement with Rogers et al. as they mentioned that ILs containing this phosphonium cation gave the largest EWs, especially when coupled with $[TPTP]^-$ or $[TFSI]^-$ [49]. It is also worth mentioning that some small peaks, humps or plateaus, were observed in the CVs of screened EWs, and since their currents are below the limit of cut-off current density, 0.5 mA/cm^2, they were neglected. The presence of these peaks could be attributed to the slight increase of currents associated with the double layer charging and/or other processes [48] or to the presence of impurities in ILs. It was found that both ILs have almost the same anodic limit which can be ascribed to the common anion since breakdown towards the anodic direction is presumed to be due to the oxidation of the anionic component of the IL [49]. Furthermore, oxidative value of $[TPTP]^-$ was found to be close to the value reported by O'mahony et al., where it was 2 V for 1-hexyl-3-methylimidazolium tris(perfluoroethyl)trifluorophosphate [30]. The reductive limits of $[P14,666]^+$ and $[MOEMPip]^+$ are in a good agreement with values reported by Hayyan et al. [36,50].

Table 2
The EW of ILs at cut-off current density of 0.5 mA/cm^2.

IL	$E_{C.L.}$	$E_{A.L.}$	EW
[P14,666][TPTP]	−3.64	2.17	5.81
[MOEMPip][TPTP]	−1.75	2.12	3.87

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

Fig. 2 depicts both the forward reduction peak and the backward oxidation peak in ILs after sparging with O_2 or N_2. The presence of the backward peak confirms that the generated $O_2^{\bullet -}$ is stable within the time limits of the experiments. The negligible background CV in the presence of N_2 indicates that these ILs are electrochemically stable within this range of potential. The potential of $O_2^{\bullet -}$ generation was ≈ -1 V. Similar results were obtained in ILs previously reported in the literature [18,19,22,36,37,51–54].

From the analysis of the CVs at various sweep rates, it was found that the net separation value between the cathodic peak E^c_p and half peak potential $E^c_{p/2}$, $|E^c_p - E^c_{p/2}|$, was not 56.5 mV, Table 3. Moreover, the difference between the reduction and oxidation peaks changes with sweep rate. This indicates that the electrochemical generation of $O_2^{\bullet -}$ in the studied ILs is not reversible. The peak currents and peak potentials are proportional to the square root and the log of the sweep rate, respectively. This is consistent

Table 3
The net values of $|E_p^c - E_{p/2}^c|$ for sweep rate 9–144 mV/s at 25, 35, and 45 °C using GC macro-electrode.

Sweep rate (mV/s)	$\lvert E_p^c - E_{p/2}^c \rvert$ (mV)					
	[P14,666][TPTP]			[MOEMPip][TPTP]		
	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
144	890	636.5	595.3	372.4	207.4	226.3
100	854.8	559.8	554.5	287.1	194.9	191.9
81	758.6	520.8	468.8	246.2	173.8	194.5
64	785.1	480	439.2	191.7	170.9	179.4
63	726.5	475	413.8	147.9	153.8	161.8
9	500.8	395.7	388.7	34.6	127.7	132.6

with the electrochemistry of a kinetically irreversible soluble redox couple [35]. This is in agreement with the results reported for other ILs [36,37,55,56]. It should be noted that strong (bond forming) ion-paring or protonation leads to electrochemical irreversibility [57–59].

Sawyer discussed the variation in the peak-separation values ΔE_p for the CV, and he interpreted that in terms of heterogeneous electron-transfer kinetics, and deduced that the most reasonable explanation was uncompensated resistance and surface reactions, especially for the metal electrodes [16]. The separation between the oxidative and reductive peaks also depends largely upon the electrode substrate, and a broadening of voltammetry on Pt compared to Au and GC in the order Pt > Au > GC had been reported, suggesting possibly coupled chemical reaction or product adsorption on Pt [24,60].

In the voltammetry of O_2 in $[P14,666]^+$, a forward wave similar to that in $[MOEMPip]^+$ based IL can be observed, however, the oxidation peaks are broader and further removed from the initial reductive wave, suggesting that $O_2^{\bullet-}$ might react with the quaternary phosphonium cation as it is the proton source in the ILs. Based on this, an alternative mechanism was proposed by Evans et al., involving R-proton abstraction from [P14,666] by $O_2^{\bullet-}$. One possible fate for the protonated form of $O_2^{\bullet-}$ is to undergo disproportionation to give H_2O_2 and regenerate O_2. The presence of the weakly acidic [P14,666] renders superoxide unstable in these solvents with respect to the formation of a perhydroxyl radical and phosphorus ylide and, through follow up homogeneous reactions, the partial regeneration of O_2 [25,50,54].

Fig. 3 shows that the reduction peak currents of CVs are increasing with increase in temperature. This can be attributed to the decrease of viscosity of IL, and thus the increase in diffusion coefficients of O_2 despite the slight decrease of solubility of O_2. This is in agreement with other results reported previously [22].

The linear relationship between the reduction peak currents and the square root of sweep rates, Fig. 4, indicates that the electrochemical reaction is diffusion controlled. This is in agreement with O'Toole et al. and Zhang et al. [58,60], and consistent with the electrochemistry of kinetically irreversible soluble redox couple [35,37].

It is also worth noticing that some CVs have, in addition to redox peaks of $O_2/O_2^{\bullet-}$ couple, small pre-cathodic peaks after O_2 sparging, Fig. 3. However, their characterization was not possible. Evans et al. observed small pre-wave just prior to the onset of O_2 reduction. They attributed this to the presence of an unknown trace impurity in IL, which could not be removed by any amount of purging with argon or exposure to vacuum conditions [54]. However, in this work the screened CV background after sparging N_2 prior to the reduction of O_2 confirms that there are no observed small peaks close to −1 V, and subsequently no impurities might affect the electrochemical reduction of O_2. Another possible reason was heterogeneous reactions on the electrode. Nevertheless, perhaps the impurities were not electrochemically active but they reacted with O_2 to produce electrochemically active compounds. Yet, another possible reason for the presence of the observed small cathodic peaks can be attributed to the adsorption of ILs cations on the surface of the GC working electrode. This is in agreement with Islam et al. who observed similar small peaks in their conducted work and concluded that this was due to the adsorption of the cation of the IL of the surface of the working electrode [61–63].

3.3. Calculation of the diffusion coefficient and solubility of O_2

The numerical values of the diffusion coefficient and solubility of O_2 at different temperatures are listed in Table 4.

It can be observed in Table 4 that the diffusion coefficients and CA steady state currents are increasing with increasing temperature while the solubility of O_2 is decreasing; this is in agreement with Katayama et al. [52]. However, it was found that the solubility in [P14,666][TPTP] did not have any significant trend. This behavior also was reported by Huang et al. as they found that the solubility of O_2 was essentially independent of temperature [22].

As illustrated in Table 4, the values of the diffusion coefficient of O_2 increase with the increase in temperature. According to the Stokes–Einstein relationship, Eq. (1); this can be attributed to the

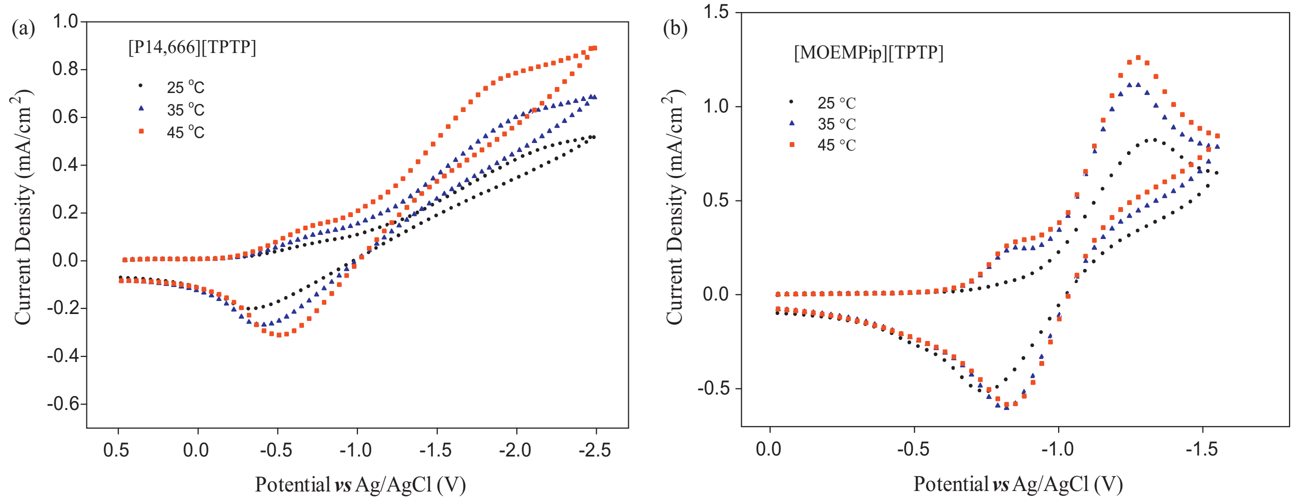

Fig. 3. CVs in (a) [P14,666][TPTP] and (b) [MOEMPip][TPTP] after sparging O_2 as a function of temperature at GC macro-electrode, sweep rate 100 mV/s.

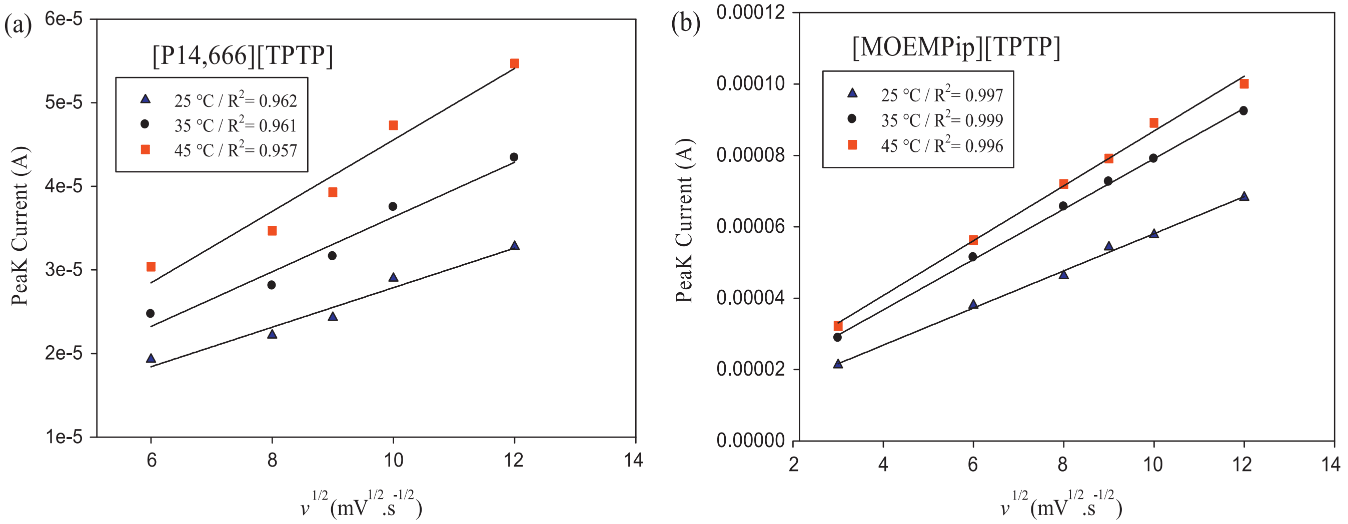

Fig. 4. Reduction currents peaks vs. square root of sweep rates in (a) [P14,666][TPTP] and (b) [MOEMPip][TPTP].

Table 4
Diffusion coefficient (Do) × 10^{10} (m^2/s), solubility of O_2 (C) (mM) and CA steady state current (nA) at 25, 35 and 45 °C.

Temp.	25	35	45
[P14,666][TPTP]			
Do	9.5	12.5	13.1
C	8.0	7.9	9.1
CA current	16.2	20.8	25.0
[MOEMPip][TPTP]			
Do	2.1	2.7	2.9
C	17.6	16.1	9.6
CA current	4.20	6.40	7.20

decrease in viscosity, and this is in agreement with Hayyan et al. and Huang et al. [22,36].

$$D = \frac{K_B T}{c \pi \eta r_s} \tag{1}$$

where K_B is Boltzmann constant (1.38×10^{-23} $m^2\ kg\ s^{-2}\ K^{-1}$), T is the temperature in K, c is a constant and r is the hydrodynamic radius of the diffusing species, assuming the molecule is spherical [22,64]. However, Tokuda et al. noted that slopes of the straight lines for ionic diffusivity in the ILs were not identical; although Eq. (1) was applicable for them. The Stokes law is based on the assumption of a rigid solute sphere diffusing in a continuum of solvent, and in the case of a large solute in a small solvent, the factor, c, can attain the value of 6. However, if the ratio of the solute size to solvent is increased, especially for highly viscous media, the correlation breaks down, and the value of c in Eq. (1) is reduced. Therefore, the factor c may help to understand the microscopic ion dynamics in the ILs [65].

The values of diffusion coefficient of O_2 in [P14,666][TPTP] were in agreement with values reported by Evans et al. Furthermore, the solubility of O_2 in [P14,666][TPTP] was almost the same, i.e. 7.9 mM at 35 °C [54].

Although the mechanism for O_2 reduction was reported to be the same in ILs and conventional solvents, the different behavior in ILs suggests that the kinetics of diffusion for O_2 and $O_2^{\bullet-}$ are sensitive to the choice of the IL medium [25,54,66–68].

The fast diffusion of O_2 can be explained by the weak interaction between O_2 and the IL because there is no Coulombic interaction between the organic ions and neutral O_2. Additionally, the diffusion of O_2 does not seem to be affected by the apparent viscosity of IL, probably because O_2 is small enough to move through the interstices between the bulky organic ions [52]. However, significant differences have been reported for the two species involved, i.e. O_2 and $O_2^{\bullet-}$, in terms of reversibility and diffusion coefficients [69].

The presence of solute such as O_2 in an IL can modify the mass transport properties. The reason that N_2 does not cause a

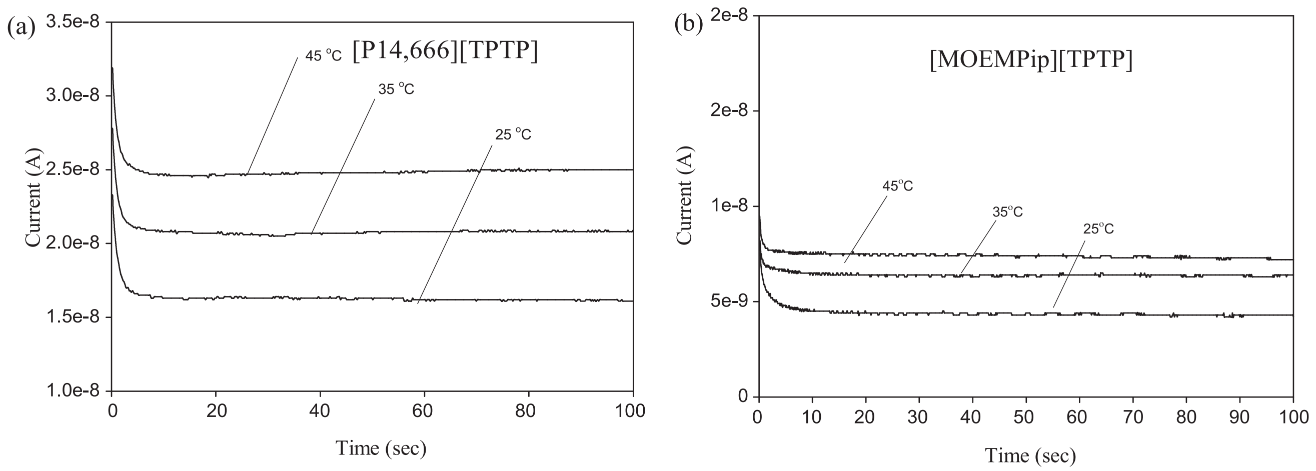

Fig. 5. CAs for O_2 reduction at CF ultramicro-electrode in (a) [P14,666][TPTP] and (b) [MOEMPip][TPTP] saturated with oxygen at 25, 35 and 45 °C.

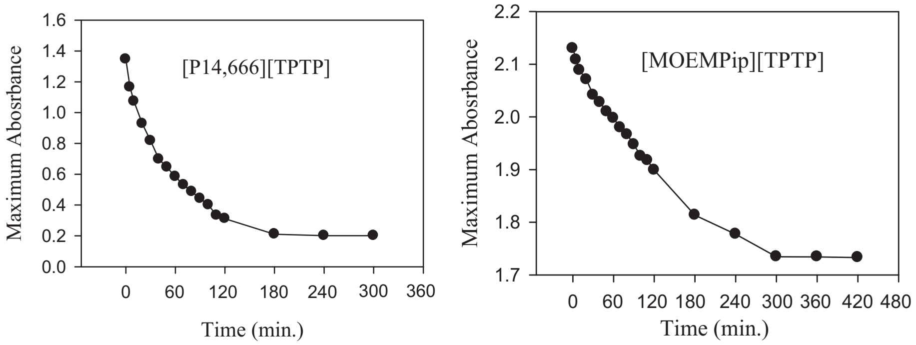

Fig. 6. The change of superoxide absorbance peak with time.

Table 5
Rate constant, total consumption percentage and rate of $O_2^{\bullet-}$ in ILs.

IL	Rate constant × 10^5 (s^{-1})	Total consumption % of $O_2^{\bullet-}$ after 120 min	Consumption rate of $O_2^{\bullet-}$ × 10^3 (mM/min)
[MOEMPip][TPTP]	1.5	10.85	2.438
[P14,666][TPTP]	19.1	76.85	10.903

measurable change in the diffusion coefficient value is probably due to its low solubility in the IL [70,71]. Nevertheless, in principle, N_2 could also alter the mass transport properties [39].

It has been reported in several studies that the diffusion coefficients of oxidized and reduced forms of a redox couple can be very different in ILs while in molecular solvents the differences are small [39,54].

Fig. 5 shows that the steady state current of CAs increases with temperature increase, as stated in Table 4. Again, this is due to the reduction of the viscosity of the ILs with increasing temperature and consequently the increase in the diffusivity of O_2. Table 4 shows that $[P14,666]^+$ based IL has higher diffusion coefficient, CA steady state current than the corresponding $[MOEMPip]^+$ based IL, while the solubility of O_2 is higher in $[MOEMPip]^+$ than in $[P14,666]^+$.

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

Fig. 6 shows the effect of time on the maximum absorbance of the ILs. A slight decrease in the absorbance peak of $O_2^{\bullet-}$ with time can be seen in [MOEMPip][TPTP]. In contrast, the consumption rate of $O_2^{\bullet-}$ in [P14,666][TPTP] is high. However, the absorbance peak of $O_2^{\bullet-}$ tends to be more stable after the first 180 min of measurements.

Table 5 shows the rate constant of reaction, total consumption and consumption rate of $O_2^{\bullet-}$ in the studied ILs. The rate constants were calculated based on the assumption of pseudo 1st order reaction between the cation of the ILs and $O_2^{\bullet-}$. The rate constant of $O_2^{\bullet-}$ in [MOEMPip][TPTP] and [P14,666][TPTP] were estimated to be 1.5×10^{-5} s^{-1} and 19.1×10^{-5} s^{-1}, respectively. These values are similar in terms of the order of magnitude to that reported by AlNashef et al. and Hayyan et al. [25,71]. However, it was found that the $O_2^{\bullet-}$ rate constant in [MOEMPip][TPTP] is less than that reported earlier by our group in [MOPMPip][TFSI] [25] where it was 4.8×10^{-5} s^{-1}, confirming that $O_2^{\bullet-}$ is more stable in [TPTP] based ILs.

The total consumption of $O_2^{\bullet-}$ in ILs was calculated by comparing the initial concentration of $O_2^{\bullet-}$ with the concentration along 2 h of measurement [25]. Results showed that only 10.85% of the initial $O_2^{\bullet-}$ in [MOEMPip][TPTP] was consumed after 2 h of reaction time. On the other hand, it was found that 76.85% of generated $O_2^{\bullet-}$ was consumed in [P14,666][TFSI], confirming that it is not an appropriate medium for the generation of a stable $O_2^{\bullet-}$. The consumption rate of $O_2^{\bullet-}$ was calculated by dividing the concentration of $O_2^{\bullet-}$ being consumed over the time period of the measurement. The consumption rate of $O_2^{\bullet-}$ in [MOEMPip][TPTP] is 2.438×10^{-3} mM/min which is less than, by almost the half value, that reported in [MOPMPip][TFSI], as stated in Table 5.

4. Conclusion

$O_2^{\bullet-}$ was generated electrochemically using cyclic voltammetry (CV) and chronoamperometry (CA) techniques from O_2 dissolved in [MOEMPip][TPTP] and [P14,666][TPTP]. Furthermore, $O_2^{\bullet-}$ was generated chemically by the addition of KO_2 to the studied ILs. UV/Vis spectrophotometer was used for testing the long term stability of generated $O_2^{\bullet-}$. The diffusion coefficients and solubility of O_2 were determined. It was found that diffusion coefficient of O_2 in $[P14,666]^+$ based IL is higher than in $[MOEMPip]^+$ based IL while the solubility of O_2 is higher in $[MOEMPip]^+$ than in $[P14,666]^+$. The long term stability of $O_2^{\bullet-}$ tests showed that $O_2^{\bullet-}$ in [MOEMPip][TPTP] is stable while in [P14,666][TPTP] is unstable.

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