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INVESTIGATING THE LONG-TERM STABILITY AND KINETICS OF SUPEROXIDE ION IN DIMETHYL SULFOXIDE CONTAINING IONIC LIQUIDS AND THE APPLICATION OF THIOPHENE DESTRUCTION

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Abstract - The long-term stability of superoxide ion ($O_2^{\bullet-}$) with four ionic liquids (ILs), namely 1-(2-methoxyethyl)-1-methylpiperidinium tris(pentafluoroethyl)trifluorophosphate [MOEMPip][TPTP], 1-(3-methoxypropyl)-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide [MOPMPip][TFSI], N-ethyl-N,N-dimethyl-2-methoxyethylammonium bis(trifluoromethylsulfonyl)imide [N112,1O2][TFSI], and ethyl-dimethyl-propylammonium bis(trifluoromethylsulfonyl)imide [EDMPAmm][TFSI], was studied for up to 24 h using two-second intervals. This was achieved by chemical generation of $O_2^{\bullet-}$ by dissolution of potassium superoxide salt in dimethyl sulfoxide and the subsequent addition of the IL. The decrease in the concentration of $O_2^{\bullet-}$ after the introduction of the IL was monitored using a UV-vis spectrophotometer. The ammonium-based ILs were found to be more stable than piperidinium-based ILs. To the best of our knowledge, this was the first time that $O_2^{\bullet-}$ stability with ILs has been monitored continuously for up to 24 h. This should provide a better insight into the stability and kinetics of $O_2^{\bullet-}$ for industrial applications and its role in energy-storage devices. The most appropriate IL as a medium was [EDMPAmm][TFSI], and $O_2^{\bullet-}$ generated in this IL was used to destroy nearly 90% of thiophene.

Keywords: Reactive oxygen species; Kinetics; Deep eutectic solvents; Green solvents; Desulfurization; Potassium superoxide; Hazardous material.

INTRODUCTION

Superoxide ion has garnered interest mostly for its role in biological applications due to its involvement in diseases, such as Parkinson’s disease and cancer. Other sources of interest for $O_2^{\bullet-}$ are its role in fuel cells, batteries, and other electrochemical devices, as well as many other applications (Afanas'ev *et al.*, 1974; Yuan *et al.*, 2014). However, the main problem associated with implementing $O_2^{\bullet-}$ is the selection of a solvent in which $O_2^{\bullet-}$ is stable. It is well established that $O_2^{\bullet-}$ is a highly nucleophilic ion that initiates further reactions with any proton source that may be present in the medium (Tanner *et*

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*To whom correspondence should be addressed *al.*, 2014). This instability makes it impractical for industrial use. Furthermore, the instability of $O_2^{\bullet-}$ is a major issue for the performance of energy-storage devices, because $O_2^{\bullet-}$ cannot participate in the subsequent reduction reactions, thereby reducing the specific capacity of the device (Pozo-Gonzalo *et al.*, 2013). However, $O_2^{\bullet-}$ is stable in the absence of a proton source, as is the case in aprotic solvents, including dimethyl sulfoxide (DMSO), acetonitrile, and dimethylformamide (Sawyer and Valentine, 1981; Sawyer, 1991; Sawyer *et al.*, 1995; Hayyan *et al.*, 2016a). However, these solvents are hazardous due to their high volatility and negative ecological effects. Since 2001, $O_2^{\bullet-}$ has been shown to be stable in some ILs (AlNashef *et al.*, 2001), providing a potentially green alternative to volatile organic solvents due to their low volatility and potential to be benign if selected carefully.

Many studies have been dedicated to investigating the stability of $O_2^{\bullet-}$ in ILs and to identifying the products that result from the reaction of $O_2^{\bullet-}$ with some ILs (Hayyan *et al.*, 2012c; Hayyan *et al.*, 2012a; Pozo-Gonzalo *et al.*, 2013; Switzer *et al.*, 2013; Frith *et al.*, 2014).

The generation of $O_2^{\bullet-}$ in ILs and its short-term stability can be determined accurately by cyclic voltammetry (CV). However, to confidently confirm its long-term stability in ILs, the stability of $O_2^{\bullet-}$ must be monitored for a greater length of time, because the short timescale of voltammetry may not detect reactions that occur after the analysis has been completed. For example, imidazolium-based ILs produce $O_2^{\bullet-}$ that is stable in the short-term (AlNashef *et al.*, 2001; Islam *et al.*, 2009), but it was found later that the $O_2^{\bullet-}$ was stable only in the short-term, after which the cation reacted with $O_2^{\bullet-}$ (Islam *et al.*, 2009; Hayyan *et al.*, 2015a). Thus, it can reasonably be concluded that, from a practical perspective, the $O_2^{\bullet-}$ species is not stable in imidazolium-based ILs, although the reversible cyclic voltammetric redox reaction of the $O_2/O_2^{\bullet-}$ couple was observed (Islam *et al.*, 2009; Hayyan *et al.*, 2013a). Another example to illustrate the need to confirm cyclic voltammetry by other techniques is work that was published recently by Xiong *et al.* (2014). The authors reported that an additional reaction has more impact at a slower sweep rate since a longer voltammetric timescale allows the reaction to be detected. Furthermore, long-term monitoring of the $O_2^{\bullet-}$ concentration allows the reaction kinetics to be studied. Several studies have reported the long-term stability of $O_2^{\bullet-}$ with ILs (AlNashef *et al.*, 2010; Hayyan *et al.*, 2012d; Hayyan *et al.*, 2012f) and other electrolytes, such as glyme (Schwenke *et al.*, 2013). Recently, Schwenke *et al.* (2015) monitored $O_2^{\bullet-}$ with 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide for 18 h.

Increasingly stringent sulfur limits in fuels have driven intense research efforts to find a more efficient means of desulfurization to replace the conventional hydrodesulfurization method (Yahaya *et al.*, 2013; Ibrahim *et al.*, 2016). ILs have attracted attention due to their many desirable properties, such as low volatility, high conductivity, and their tuneability. Hence, they have been used to desulfurize fuels by various methods, including extraction (Ferreira *et al.*, 2014; Lu *et al.*, 2014) and oxidative desulfurization (Jiang *et al.*, 2014; Lü *et al.*, 2014). Recently, our group reported the possibility of using $O_2^{\bullet-}$ generated in ILs to destroy chlorinated hydrocarbons and sulfur compounds (Hayyan *et al.*, 2012f; Hayyan *et al.*, 2012e; Hayyan *et al.*, 2015b; Hayyan *et al.*, 2016b; AlNashef *et al.*, 2013). Therefore, it also was worthwhile to explore using $O_2^{\bullet-}$ to destroy sulfur compounds in one of the studied ILs.

In this work, we studied the stability of $O_2^{\bullet-}$ with four ILs for the long timespan of 24 h, using two-second intervals. The concentration of $O_2^{\bullet-}$ was monitored for up to 24 h by monitoring the concentration of $O_2^{\bullet-}$ in DMSO with the IL every 2 s, using the timedrive of a UV-vis spectrophotometer. Interestingly, $O_2^{\bullet-}$ generated in the ILs destroyed thiophene, which we used as a model sulfur compound.

EXPERIMENTAL SECTION

In this study, we used synthesis grade ILs provided by Merck (Table 1). Scheme 1 shows the chemical structure of the ILs used. DMSO (Fisher, 99.98%), potassium superoxide (KO_2) (Sigma Aldrich, 99.9%), acetonitrile (AcN) (UNICHROM, HPLC grade 99.9%), and thiophene (TH) (Merck) were used without any further purification.

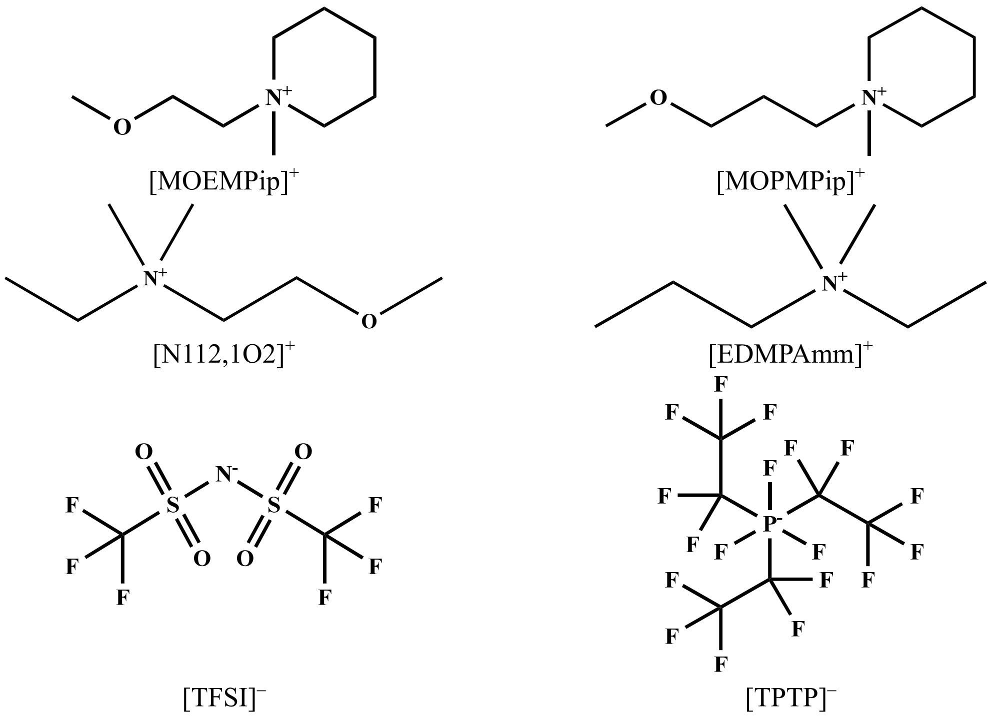
Electrochemical Generation of Superoxide Ion

CV tests were performed as the electrochemical analysis technique, since this method is extremely powerful and is among the most extensively practiced of all electrochemical methods. Protic impurities can have a dramatic effect on the stability of $O_2^{\bullet-}$ (AlNashef *et al.*, 2001; Evans *et al.*, 2004). Hence, the ILs were dried overnight at 50 °C under vacuum. It should be noted that some of the ILs used were acidic without pre-treatment, with pH values in the range of 4-6. AlNashef *et al*. (2001) reported that $O_2^{\bullet -}$ was unstable in some ILs due to their acidity and due to the reaction of $O_2^{\bullet -}$ with protons. Therefore, the pH of the ILs was measured using pH strips (Merck), and a very small quantity of KO_2 was added to the acidic ILs until their pH became neutral.

The electrochemistry experiment was performed using an EG&G 263A potentiostat/galvanostat (PAR) connected to a computer with data acquisition software. CVs were conducted in a one-compartment cell because the time required to affect the ILs was relatively short. The cell was a jacketed vessel (10-ml volume) with a Teflon cap with four holes for the three electrochemical electrodes and a gas sparging tube. A glassy carbon (GC) macroelectrode (BASi, 3-mm diameter) was used as working electrode for CV. A platinum electrode was used as a counter electrode, and an aqueous Ag/AgCl electrode (BASi) was used as the reference electrode. The macroelectrodes were polished using alumina solution (BASi) and sonicated in distilled water for 10 min before each experiment. This was done to ensure that there were no impurities on the surface of the working electrode.

Table 1: Formulae and molecular weights for ILs.

IL	Abbreviation	Formula	Molecular wt
1-(2-Methoxyethyl)-1-methylpiperidinium tris(pentafluoroethyl)trifluorophosphate	[MOEMPip][TPTP]	$C_{15}H_{20}F_{18}NOP$	603.27
1-(3-Methoxypropyl)-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide	[MOPMPip][TFSI]	$C_{12}H_{22}F_6N_2O_5S_2$	452.44
N-Ethyl-N,N-dimethyl-2-methoxyethylammonium bis(trifluoromethylsulfonyl)imide	[N112,1O2][TFSI]	$C_8H_{18}F_6N_2O_5S_2$	412.37
Ethyl-dimethyl-propylammonium bis(trifluoromethylsulfonyl)imide	[EDMPAmm][TFSI]	$C_9H_{18}F_6N_2O_4S_2$	396.37



$[MOEMPip]^+$ $[MOPMPip]^+$ $[N112,1O2]^+$ $[EDMPAmm]^+$ $[TFSI]^-$ $[TPTP]^-$

Scheme 1: Structures of ions comprising the ILs.

Due to the sensitivity of $O_2^{\bullet-}$ to water, all experiments were performed in a dry glove box, with tight humidity control of less than 1 ppm water, under either an argon or helium atmosphere. Prior to the formation of $O_2^{\bullet-}$, a background voltammogram was obtained after removal of O_2, using a scan rate of 100 mV/s. O_2 removal was achieved by purging the IL with dry N_2. This particular method was quite simple and effective. Purging a solution with an inert gas can reduce the partial pressure of O_2 above the solution, and consequently, the solubility of O_2 in the solution is decreased. Then, O_2 was bubbled into the IL for at least 30 min to ensure that equilibrium was achieved. Between consecutive CV runs, O_2 was bubbled into the solution briefly to refresh the system and to remove any concentration gradients. N_2 or O_2 sparging was discontinued during the CV runs.

Long-Term Stability of $O_2^{\bullet-}$

Spectroscopic grade DMSO was dried overnight in a vacuum oven at 50 °C and vacuum pressure. KO_2 was stored in a sealed vial filled with molecular sieves. The chemical generation of $O_2^{\bullet-}$ was performed by dissolving about 0.001 to 0.003 g of KO_2 in 20 to 30 ml of DMSO while stirring with a magnetic stirrer. Subsequently, 0.05 g of IL was added to 5 ml of the DMSO in which $O_2^{\bullet-}$ had been produced 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 2 s for up to 24 h. Quartz cuvettes were used (Perkin Elmer, 10-mm path length). The reference solution for the spectral measurements was DMSO or DMSO solution that contained an appropriate amount of IL. It is known from previous studies that the absorbance band of $O_2^{\bullet-}$ is in the range of 250-270 nm (Hayyan *et al.*, 2015a). The UV-vis experiments were conducted in a dry area. The cuvettes were sealed, and the necessary precautions were considered to prevent any external effects. This was verified by simultaneously measuring the $O_2^{\bullet-}$ absorbance in a cuvette containing IL and in a cuvette containing a blank solution without IL.

Destruction of Thiophene Using Potassium Superoxide

About 0.01 g of the thiophene was added to a labeled vial, after which 5 g of dried IL were added. The mixture was stirred for 30 min. After reaching equilibrium, a sample was withdrawn and diluted in AcN and then analyzed using HPLC. The HPLC specifications and analysis conditions are shown in Table 2. Then, during vigorous stirring, KO_2 was added gradually to the vial that contained the IL mixture. Samples were taken before and after the addition of KO_2 by dissolving 0.1 g of the IL-sulfur mixture in 1 g of AcN. This procedure was repeated, and more KO_2 was added until the thiophene peak was no longer detected or did not change.

Table 2: HPLC specifications and analysis conditions.

Analytical Instruments	
Shimadzu HPLC System	Liquid chromatograph LC-10AD VP
	System controller SCL-10A VP
	UV/Vis Detector SPD-10A VP
	Auto injector SIL-10AD VP
	Column oven CTO-10AS VP
	Degasser DGU-14A
	Shimadzu LC solution software
Column	Size: 4.6 x 150 mm, 5 µm
	Description: Eclipse Plus C18 Agilent
Guard column	Agilent Zorbax reliance cartridge
Analytical Conditions	
Mobile phase	AcN:Deionized Water (75:25%), HPLC grade
Flow rate	1 ml/min, low pressure gradient
Wavelength	254 nm
Column Temperature	30 °C
Injection Volume	5 µl

RESULTS AND DISCUSSION

Electrochemical Generation of $O_2^{\bullet-}$

Figure 1 shows the CVs for the reduction of O_2 to $O_2^{\bullet-}$ at sweep rates of 9 and 100 mV/s in [MOEMPip][TPTP], [MOPMPip][TFSI], [N112,1O2][TFSI], and [EDMPAmm][TFSI]. The background voltammograms after N_2 sparging indicated that all ILs were electrochemically stable in the range of potential for $O_2^{\bullet-}$ generation (i.e., ± –1 V). The reduction peak indicated the formation of $O_2^{\bullet-}$. The presence of the oxidation peak in the backward scan indicated that the $O_2^{\bullet-}$ formed was stable in these ILs within the time limits of the experiment. In the CV shown in Figure 1(c) for [N112,1O2][TFSI], the slight hump seen at – 0.7 V indicates the presence of impurities in the IL that could react with $O_2^{\bullet-}$. These impurities were not electrochemically active after nitrogen sparging, but they were activated after O_2 reduction to produce electrochemically-active compounds. Another possible reason was the adsorption of cations on the surface of the GC working electrode

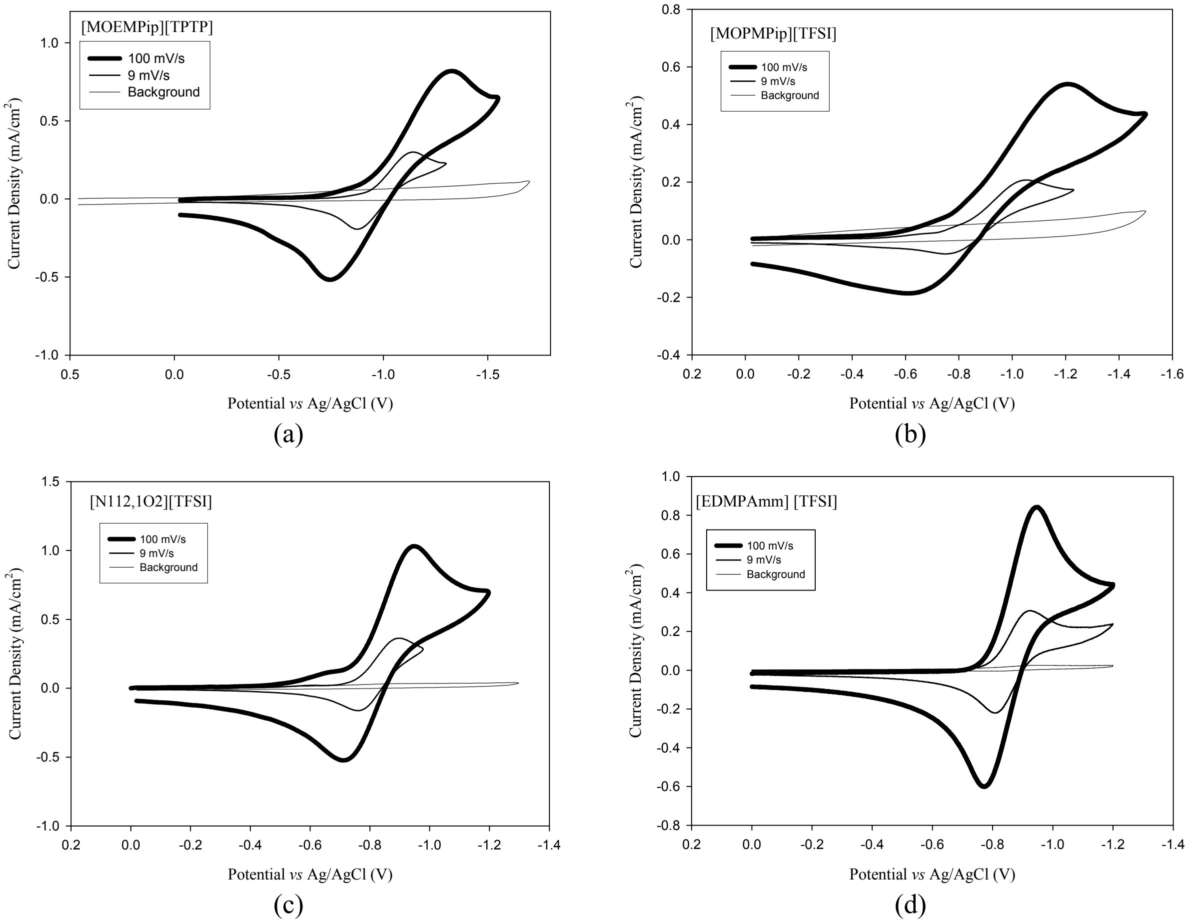


Figure 1: CVs in (a) [MOEMPip][TPTP] (b) [MOPMPip][TFSI] c) [N112,1O2][TFSI] and d) [EDMPAmm][TFSI] after sparging with oxygen and nitrogen (background) at the GC macro-electrode for different sweep rates at 25 °C.

(Hayyan *et al.*, 2012b). Previous studies have suggested that the potential shifts to more positive values as the solvating properties of the solvent increase. The asymmetry of the forward and reverse peaks reflected the difference in the diffusion of O_2 vs. $O_2^{\bullet -}$ (Buzzeo *et al.*, 2003). The main impurities in ILs are water and halide ions. Electrochemically speaking, water impurities have been shown to decrease the viscosity (Widegren *et al.*, 2005; Zhang *et al.*, 2006), increase the conductivity (Fitchett *et al.*, 2005) and shrink the electrochemical window significantly (Schröder *et al.*, 2000; Fitchett *et al.*, 2005). Although water is by far the major impurity affecting the ILs, O_2 from air is also easily dissolved in the ILs and often accompanies water; since this molecule is electroactive, its removal is required before any electrochemical measurement (Ohno, 2005). Mostly, water is present in every IL as an adventitious impurity. The presence of a trace amount of water can significantly change the physicochemical properties of ILs (and their analogous deep eutectic solvents), such as conductivity, viscosity, diffusivity and consequently mass transport properties of electrochemical processes (Schröder *et al.*, 2000; Zhao *et al.*, 2010). It has been recognized that water has a very different structure when dissolved in ILs relative to that in pure water since the water molecules in ILs are structurally associated with the ions of the ILs (Cammarata *et al.*, 2001; Köddermann *et al.*, 2006), and therefore are difficult to be eliminated. Nevertheless, it was found that O_2 removal by placing 1-*n*-butyl-3-methylimidazolium tetrafluoroborate in a nitrogen-filled glove box or in a vacuum cell also simultaneously leads to water removal and alteration of voltammetric data (Zhao *et al.*, 2010). Halide impurities are also of main concern when interpreting voltammetric responses. These impurities are generally introduced during the preparation of the

ILs, which commonly involves a halide precursor (Seddon *et al.*, 2000). Earle *et al.* (2006) stated that the color of ILs is due to chromophoric impurities in ILs during the synthesis process, and they have suggested a methodology to decolorize the ILs. However, this method can be applied only for small volumes of ILs required for fundamental spectroscopic studies but not in industrial processes.

Figure 1 shows that the ILs produce stable $O_2^{\bullet-}$ for the analysis time. However, the short timespan of the voltammetry (less than 5 min) is insufficient to confirm the long-term stability of $O_2^{\bullet-}$ in these ILs. For instance, AlNashef *et al.* (2002) reported a stable generation of $O_2^{\bullet-}$ in 1-butyl-3-methylimidazolium hexafluorophosphate [BMIm][HFP]. Conversely, it has been shown in diverse studies that $O_2^{\bullet-}$ was unstable in imidazolium-based ILs (Katayama *et al.*, 2004; Islam *et al.*, 2005; Barnes *et al.*, 2008; Islam *et al.*, 2009; Rogers *et al.*, 2009). AlNashef *et al.* (2010) reported that imidazolium cations reacted with $O_2^{\bullet-}$ to produce the corresponding 2-imidazolones. Therefore, the long-term stability of the $O_2^{\bullet-}$ with these ILs was monitored using a UV-vis spectrophotometer.

Chemical Generation and Long-Term Stability of $O_2^{\bullet-}$

Any consumption of the $O_2^{\bullet-}$ that is generated can be ascribed to the reaction of $O_2^{\bullet-}$ with the IL or with impurities that could not be removed by vacuum drying. Figure 2 shows the time course of the chemically-generated $O_2^{\bullet-}$ in DMSO that contained the corresponding IL for up to 24 h at 2-s intervals. The reaction time was divided into zones, as shown in Table 3 and Figure 2. The reaction kinetics for the zones and the overall reaction time were analyzed.

Assuming that the IL that was added to the DMSO was in large excess in comparison to $O_2^{\bullet-}$, the IL concentration was negligible, and the reaction might follow the pseudo first-order kinetics, i.e., Eqs. (1) and (2):

$$r = k\,[O_2^{\bullet-}]^1 \tag{1}$$

$$[O_2^{\bullet-}] + [A] \longrightarrow Z \tag{2}$$

where k is the rate constant, [A] is the concentration of the cation, and Z is either the new product or the ion paring of the $O_2^{\bullet-\cdots}$cation.

The calculated rate constant was also based on the assumption of a second-order kinetic mechanism, assuming that either the involvement of the cations or the order of $O_2^{\bullet-}$ is two, Eqs. (3) and 4.

$$r = k\,[O_2^{\bullet-}]^2 \tag{3}$$

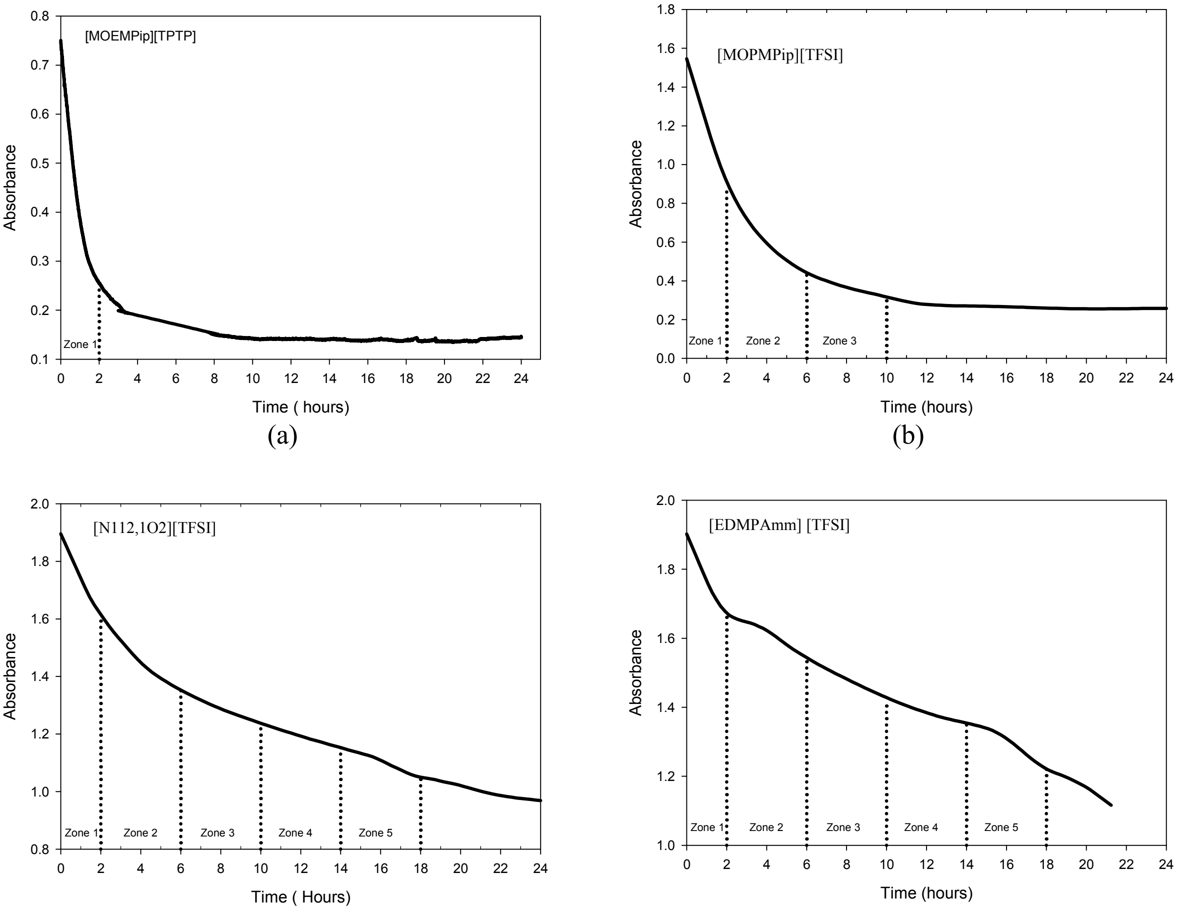
$$r = k\,[A]^1[O_2^{\bullet-}]^1 \tag{4}$$

The total consumption of $O_2^{\bullet-}$ in the ILs was calculated by comparing the initial $O_2^{\bullet-}$ concentration with the concentration after 2 h, and the consumption rate of $O_2^{\bullet-}$ was determined by dividing the concentration of $O_2^{\bullet-}$ consumed by the time period of the measurement, Eqs. (5) and (6).

$$\text{Average Rate} = -\frac{\Delta[O_2^{\bullet-}]}{\Delta t} \tag{5}$$

$$\text{Average Rate} = -\frac{[O_2^{\bullet-}]_{final} - [O_2^{\bullet-}]_{initial}}{\Delta t} \tag{6}$$

Table 3 lists the first- and second-order rate constants (k_1 and k_2) calculated for the respective ILs. As can be observed from the more gradual slope of these graphs and from the smaller values of k_1 and k_2 that were calculated, the $O_2^{\bullet-}$ was found to be more stable with the ammonium-based ILs than with the piperidinium-based ILs. This was in good agreement with the results of previous studies (Hayyan *et al.*, 2012d; Hayyan *et al.*, 2015a). This high stability of $O_2^{\bullet-}$ in the ILs consisting of ammonium cations was anticipated because $O_2^{\bullet-}$ is known to form the stable ionic salt of tetramethylammonium superoxide (Sawyer and Valentine, 1981). Furthermore, Laoire *et al.* (2010) attributed the stabilization of $O_2^{\bullet-}$ in tetrabutylammonium hexafluorophosphate [TBAmm][HFP] solutions in different solvents to Pearson's hard-soft acid-base (HSAB) theory through the formation of the TBA^+---O^{2-} complex. For the piperidinium-based ILs, the $[TFSI]^-$ showed greater stability than the $[TPTP]^-$. This was expected since ILs that contain $[TFSI]^-$ are hydrophobic (Kato *et al.*, 2008; O'Mahony *et al.*, 2008; Hayyan *et al.*, 2011; Hayyan *et al.*, 2013b). The hydrophobicity of the IL increases as the length of the alkyl chain on the cation increases (Freire *et al.*, 2007; Erdmenger *et al.*, 2008; O'Mahony *et al.*, 2008). This also could explain why $O_2^{\bullet-}$ in [MOPMPip][TFSI] is more stable than in [MOEMPip][TPTP]. The rate constants determined were highest during the first 2 h. This may have been due to the consumption of impurities, which react with $O_2^{\bullet-}$ faster than the IL. Figure 2 shows that, in general, the rate constants of $O_2^{\bullet -}$ reactions with [MOEMPip][TPTP], [MOPMPip][TFSI], [N112,1O2][TFSI], and [EDMPAmm][TFSI] follow those of second-order reactions rather than first-order reactions. This was in accordance with previous studies conducted by Chin *et al.* (1982) and Hayyan *et al.* (2015a). Figure 2 shows that different zones provide different kinetics. This clearly shows that the $O_2^{\bullet -}$ reaction mechanism varied depending on the medium, substrate, and reaction time.



(a) (b)

(c) (d)

Figure 2: Absorbance of superoxide ion in DMSO with (a) [MOEMPip][TPTP] (b) [MOPMPip][TFSI] (c) [N112,1O2][TFSI] and (d) [EDMPAmm][TFSI] monitored every 2 s for up to 24 h.

Table 3: Kinetic rate constants for $O_2^{\bullet -}$ reaction with IL (k_1= first order rate constant, k_2= second order rate constant).

	[MOEMPip][TPTP]						
	Zone 1	**Steady State**	**Steady State**	**Steady State**	**Steady State**	**Steady State**	
	0-2 h	**2-6 h**	**6-10 h**	**10-14 h**	**14-18 h**	**18-24 h**	**Overall**
k_1 (s^{-1})	5×10^{-5} $R^2 = 0.958$	-	-	-	-		5×10^{-5} $R^2 = 0.958$ (0-2 h)
k_2 ($M^{-1}s^{-1}$)	0.0365 R^2=0.971	-	-	-	-	-	0.0365 R^2=0.971 (0-2 h)

Continuation Table 3

Continuation Table 3

	[MOPMPip][TFSI]						
	Zone 1	**Zone 2**	**Zone 3**	**Steady State**	**Steady State**	**Steady State**	
	0-2 h	**2-6 h**	**6-10 h**	**10-14 h**	**14-18 h**	**18-24 h**	**Overall**
k_1 (s^{-1})	5×10^{-5} R^2= 0.997	2×10^{-5} R^2= 0.979	6×10^{-6} R^2= 0.978	-	-	-	2×10^{-5} R^2= 0.876 (0-10 h)
k_2 ($M^{-1}s^{-1}$)	0.0228 R^2= 0.999	0.0126 R^2= 0.988	0.0047 R^2= 0.979	-	-	-	0.0109 R^2= 0.922 (1-10 h)
	[N112,1O2][TFSI]						
	Zone 1	**Zone 2**	**Zone 3**	**Zone 4**	**Zone 5**	**Steady State**	
	0-2 h	**2-6 h**	**6-10 h**	**10-14 h**	**14-18 h**	**18-24 h**	**Overall**
k_1 (s^{-1})	2×10^{-5} R^2= 0.925	8×10^{-6} R^2= 0.965	3×10^{-6} R^2= 0.981	3×10^{-6} R^2= 0.978	4×10^{-6} R^2= 0.917	-	4×10^{-6} R^2=0.912 (0-18 h)
k_2 ($M^{-1}s^{-1}$)	0.0069 R^2= 0.933	0.0034 R^2= 0.969	0.0017 R^2= 0.981	0.0013 R^2= 0.978	0.002 R^2= 0.914		0.002 R^2=0.936 (0-18 h)
	[EDMPAmm][TFSI]						
	Zone 1	**Zone 2**	**Zone 3**	**Zone 4**	**Zone 5**		
	0-2 h	**2-6 h**	**6-10 h**	**10-14 h**	**14-18 h**	**18-24 h**	**Overall**
k_1 (s^{-1})	1×10^{-5} R^2= 0.941	3×10^{-6} R^2= 0.835	3×10^{-6} R^2= 0.955	2×10^{-6} R^2= 0.884	4×10^{-6} R^2= 0.930		3×10^{-6} R^2=0.959 (0-18 h)
k_2 ($M^{-1}s^{-1}$)	0.0055 R^2= 0.943	0.0014 R^2= 0.836	0.0014 R^2= 0.955	0.001 R^2= 0.884	0.0022 R^2= 0.928		0.0014 R^2=0.968 (0-18 h)

The IL was added in excess, so steady state was attributed to the complete $O_2^{\bullet -}$ consumption. $O_2^{\bullet -}$ lasted for 2 h in [MOEMPip][TPTP], 10 h in [MOPMPip][TFSI], 18 h in [N112,1O2][TFSI], and more than 21 h in [EDMPAmm][TFSI]. These findings were in accordance with our recently reported work in which we investigated the long-term stability of $O_2^{\bullet -}$ for only 2 h with 10-min time intervals of measurements (Hayyan *et al.*, 2015a). In general, in both time intervals, the rate constants were the same order of magnitude. However, the 2-s intervals provided more useful results than the 10-min intervals. Table 4 illustrates the consumption percentage and consumption rate of $O_2^{\bullet -}$ in DMSO that contained ILs. The total percentage of $O_2^{\bullet -}$ that was consumed followed the order of [EDMPAmm][TFSI] < [N112,1O2][TFSI] < [MOPMPip][TFSI] < [MOEMPip][TPTP]. This was in agreement with the order of the rate constants that were determined. This clearly showed that $O_2^{\bullet -}$ was more stable in ammonium-based ILs than in piperidinium-based ILs. However, the slight differences in the percentage of consumption can likely be attributed to the inability to remove all water or other impurities via the pre-preparation procedures.

Table 4: Total consumption percentage and consumption rate of $O_2^{\bullet -}$ in DMSO containing ILs.

IL	**Total consumption% of $O_2^{\bullet -}$ after 120 min**	**Consumption rate of $O_2^{\bullet -} \times 10^3$ (mM/min)**
[MOEMPip][TPTP]	28.3	3.71
[MOPMPip][TFSI]	26.0	5.12
[N112,1O2][TFSI]	10.0	2.30
[EDMPAmm][TFSI]	9.0	2.09

Destruction of Thiophene

The superoxide ion in [EDMPAmm][TFSI] was found to be most stable based on our kinetics studies; therefore, this IL was used as a medium to generate $O_2^{\bullet -}$ from the dissolution of KO_2 for possible reaction with thiophene. Figure 3 shows the HPLC chromotogram of thiophene in the IL before and after the addition of KO_2. Remarkably, it was found that $O_2^{\bullet -}$ destroyed close to 90% of the thiophene in [EDMPAmm][TFSI] at ambient conditions. This result was in good agreement with the findings of recent studies (Chan *et al.*, 2008; Hayyan *et al.*, 2015b; Hayyan *et al.*, 2016b). Chan *et al.* (2008) used KO_2 as an alternative oxidant for the oxidative-desulfurization process. It was shown that KO_2 was comparable to or better than H_2O_2 for the ultrasound-assisted oxidative desulfurization or for the oxidative-desulfurization process. However, they used [BMIm][HFP] as the medium, which was reported later to be an inappropriate medium for producing $O_2^{\bullet-}$ in terms of the cation or the anion. This conclusion was based on the fact that the imidazolium cation reacts with $O_2^{\bullet-}$ to produce the corresponding 2-imidazolone (Al-Nashef *et al.*, 2010), and [HFP] anion is undesired for such reactions because it produces HF when it is in contact with water.

Nevertheless, it is important to conduct studies on the extraction of sulfur compounds from diesel fuel feed using the ILs in this work, since most published studies have used pyrrolidinium-based ILs (Zhao *et al.*, 2007; Holbrey *et al.*, 2008), imidazolium-based ILs (Bosmann *et al.*, 2001; Zhang and Zhang, 2002; Lo *et al.*, 2003; Huang *et al.*, 2004; Wasserscheid and Jess, 2004; Planeta *et al.*, 2006; Cassol *et al.*, 2007; Li *et al.*, 2009b), pyridinium-based ILs (Jianlong *et al.*, 2007; Chu *et al.*, 2008; Gao *et al.*, 2008; Holbrey *et al.*, 2008; Francisco *et al.*, 2010), and quinolium-based ILs (Kumar and Banerjee, 2009).

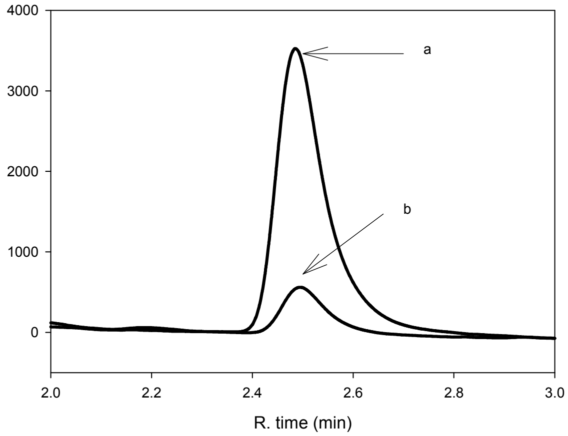


Figure 3: HPLC chromatograms of TH in [EDMPAmm] [TFSI] (a) before KO_2 addition (b) after KO_2 addition.

Cheng and Yen (2008) stated that ILs can be used as phase-transfer catalysts for deep oxygenative desulfurization. Lu *et al.* (2006) found that the sulfur removal from dibenzothiophene-containing model oil can be in the range of 60-93%, depending on the reaction temperature, and this was superior to simple extraction with ILs, but they used H_2O_2 as the oxidant. Zhao *et al.* (2007) suggested that a coordination compound was generated between H_2O_2 and the cation of the IL and that it decomposed to produce hydroxyl radicals. The sulfur-containing compounds in the model oil or diesel fuel were extracted into the IL phase and oxidized to their corresponding sulfones by the hydroxyl radicals.

Thus, a combination of catalytic oxidation and extraction in the IL can remove sulfur compounds from the model oil effectively. This clearly shows the remarkable advantage of this process over desulfurization by mere solvent extraction with IL or catalytic oxidation without IL (Zhu *et al.*, 2007; Li *et al.*, 2009a).

CONCLUSIONS

The long-term stability of $O_2^{\bullet-}$ that was produced was investigated in piperidinium-based and ammonium-based ILs by the chemical generation of $O_2^{\bullet-}$ in DMSO in the presence of the corresponding IL. A UV-vis spectrophotometer was used in the absorbance range of 190–400 nm to determine the stability of $O_2^{\bullet-}$ with [MOEMPip][TPTP], [MOPMPip][TFSI], [N112,1O2][TFSI], and [EDMPAmm][TFSI]. The rate constants were calculated based on first- and second-order reactions. It was found that the values of k followed the order of [EDMPAmm][TFSI] < [N112,1O2][TFSI] < [MOPMPip][TFSI] < [MOEMPip][TPTP]. [EDMPAmm][TFSI] was found the best IL for $O_2^{\bullet-}$ stability. These ILs potentially can be used as media to investigate the possible applications of $O_2^{\bullet-}$, such as the destruction of hazardous chemicals and the oxidative desulfurization of sulfur compounds. The $O_2^{\bullet-}$ kinetics varied depending on the medium, substrate, and reaction time. The reactions of $O_2^{\bullet-}$ and ILs require further study to isolate and analyze possible products.

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