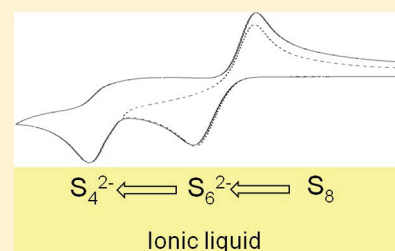


Electrochemistry of Sulfur and Polysulfides in Ionic Liquids

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ABSTRACT: The electrochemistry of elemental sulfur (S_8) and the polysulfides Na_2S_4 and Na_2S_6 has been studied for the first time in nonchloroaluminate ionic liquids. The cyclic voltammetry of S_8 in the ionic liquids is different to the behavior reported in some organic solvents, with two reductions and one oxidation peak observed. Supported by in situ UV–vis spectro-electrochemical experiments, the main reduction products of S_8 in $[C_4mim][DCA]$ ($[C_4mim]$ = 1-butyl-3-methylimidazolium; DCA = dicyanamide) have been identified as S_6^{2-} and S_4^{2-} , and plausible pathways for the formation of these species are proposed. Dissociation and/or disproportionation of the polyanions S_6^{2-} and S_4^{2-} appears to be slow in the ionic liquid, with only small amounts of the blue radical species $S_3^{\cdot-}$ formed in the solutions at r.t., in contrast with that observed in most molecular solvents.



INTRODUCTION

The occurrence of sulfur in fuels has become an important subject in petroleum refining industry, as sulfur contributes to a large extent to air pollution from exhaust gases (SO_x) released from motor vehicles and is also known to poison the catalyst converter.^{1,2} Environmental regulations on the limit of sulfur concentration in gasoline (i.e., <10 ppm)^{2,3} has prompted the development of novel processes in order to achieve such a target.^{1,4} In particular, ionic liquids (ILs) have been proposed as convenient media for the removal of sulfur compounds from liquid fuels.^{2,4–6} In these processes, the ILs can be used merely as extractant solvents or in combination with chemical oxidation processes.² Compared to organic solvents, ILs are stable at higher temperatures, are compatible with a wide range of oxidizing reagents and catalysts, and can be regenerated and recycled after the extraction of sulfur compounds.^{5,7} In addition, sulfur has been found to be a good cathode material in Li–S batteries containing ionic liquids as electrolytes,^{8,9} and it can be an efficient catalyst in ILs, for example, in carbonylation reactions.¹⁰ Despite the increasing interest in the use of ionic liquids in the sulfur-related processes described above, fundamental studies on the speciation of sulfur in ILs are still lacking, and the electrochemistry of sulfur in nonchloroaluminate ILs is yet to be explored. These studies are of interest as ILs can promote electrochemical behavior different to that observed in traditional molecular solvents, as can favor the stabilization of unusual species.¹¹

The electrochemistry of sulfur-polysulfide systems has been studied extensively in organic molecular solvents^{12–21} as well as in some molten salts,^{22–25} with only one work in a chloroaluminate ionic liquid ($AlCl_3$ – $[C_4py]Cl$; C_4py = 1-butylpyridinium)

published to date.²⁶ These studies have shown that the reduction of sulfur is very complicated, where one or more electron-transfer reactions followed by a series of chemical transformations occur at each reduction wave. These processes are dependent on the solvent, the nature of the working electrode, and/or the supporting electrolyte. The electrochemical reduction of S_8 in organic solvents such as THF, DMF, DMSO, or CH_3CN , at various working electrodes (Pt, graphite, glassy carbon, or Au), normally occurs in two 2-electron steps. An additional, smaller wave situated between the two main reduction peaks has been observed in some cases^{14,15,18,20} and has been attributed to the presence of acidic impurities by most authors.^{14,15,20}

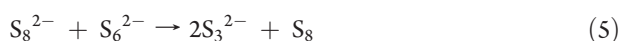
It is generally agreed that the first reduction peak for S_8 corresponds to its 2-electron reduction to S_8^{2-} (eq 1),^{13–18,20,21} often proposed to be followed by the reactions shown in eqs 2 and 3; the latter resulting in the blue radical species $S_3^{\cdot-}$.^{13–15,17} Kim and Park¹⁷ also suggest formation of S_4^{2-} and S_3^{2-} (i.e., through follow-up reactions 4 and 5) based on UV–vis spectro-electrochemical experiments.



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The second reduction wave has been attributed to different processes, including the 2-electron reduction of S_8^{2-} to S_8^{4-} , which may dissociate into S_4^{2-} (eqs 6 and 7),^{14,16,17,20,21} or the reduction of S_6^{2-} and/or S_3^{*-} to S_3^{2-} (eqs 8 and 9).^{15,17,18,20,21} In most cases, one or several reactions have been proposed to follow the reduction process, such as those shown in eq 10¹⁵ or 11.¹⁷ More complicated series of follow-up reactions involving formation of species such as S_2^{2-} , S^{2-} , S_7^{2-} , and/or S_5^{2-} have also been suggested.^{18,20,21}



Jung et al.²¹ have shown that the reversibility of the two reduction waves depends on the solvent and supporting electrolyte used. In particular, using $LiCF_3SO_3$ as electrolyte, two quasi-reversible waves are recorded in DMF, dimethylacetamide or DMSO, but the oxidation peak corresponding to the second reduction is not seen in dimethoxyethane, diglyme, or CH_3CN . In addition, the second process becomes fully reversible in DMF when $[Et_4N][BF_4]$ is used as electrolyte.

In chloroaluminate mixtures (e.g., $AlCl_3/NaCl$ ^{24,25} or $AlCl_3-[C_4py]Cl$ ($[C_4py]^+ = N$ -butylpyridinium)),²⁶ the electrochemistry of elemental sulfur is further complicated by the formation of chlorinated species such as S_2Cl_2 and SCl_3^+ , with up to four oxidation and four reduction waves observed in some systems.²⁵ However, reduction to S_8^{2-} is also proposed to occur at the first voltammetric wave in $AlCl_3/NaCl$ melts.^{24,25} It has also been shown that elemental sulfur can be easily reduced to other sulfur species (S_6^{2-} or S_3^{*-}) by dissolving it at certain temperature in some phosphonium and imidazolium ionic liquids.²⁷

In this paper, the electrochemistry of S_8 and of the polysulfide anions S_4^{2-} and S_6^{2-} is studied in a range of room temperature ionic liquids. UV-vis spectroscopy and spectro-electrochemical studies have been carried out to aid the identification of the various sulfur species formed in the IL media.

EXPERIMENTAL SECTION

The ionic liquids $[C_4mim][X]$ ($[C_4mim]^+ = 1$ -butyl-3-methylimidazolium; $[X]^- = DCA$ (dicyanamide), OTf , $[C_4mpy][NTf_2]$ ($[C_4mpy]^+ = 1$ -butyl-3-methylpyridinium; $NTf_2^- = bis$ -{(trifluoromethyl)sulfonyl}imide) and $[C_4mpyr][NTf_2]$ ($[C_4mpyr]^+ = N$ -butyl- N -methylpyrrolidinium)) were obtained from Merck KGaA, whereas $[C_4mim][X]$ ($[X]^- = NTf_2$, NO_3) were prepared following literature methods.^{28,29} All the ionic liquids were purified before use, as previously described.²⁹ Na_2S_4 and Na_2S_6 were obtained as yellow powders following literature procedures³⁰

and were characterized by X-ray powder diffraction on a X'Pert Pro PANalytical diffractometer with $Cu K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$).³¹ Sulfur (purum, >99.5%; Sigma-Aldrich) and sodium metal (stick in mineral oil, 99%; Alfa Aesar) were used as received.

The cyclic voltammograms (CVs) in ILs were obtained in a glovebox at constant temperature ($32.8 \pm 0.2^\circ \text{C}$) using a PC controlled Autolab PGSTAT12/30/302 potentiostat/galvanostat and a three-electrode cell. The working electrode was a glassy carbon (GC) disk (diameter: 3 mm), a Pt disk (diameter: 1.5 mm), or a gold disk (diameter: 1.5 mm). Platinum wire was used as the counter electrode and the reference electrode consisted of a Ag wire immersed in a 0.01 M solution of $AgNO_3$ in $[C_4mim][NO_3]$ which was separated from the bulk solution by a glass frit. The GC electrode was polished with a water based diamond slurry and rinsed with ultrapure water before use. The Pt and Au working electrodes were polished with aluminum oxide (3 μm particle size). For the CVs in anhydrous DMF and in IL/DMF mixtures, the solution (3 mM) was purged with N_2 for 2 min at r.t. before the experiment was carried out in a fume cupboard. $LiCF_3SO_3$ (1 M) was used as supporting electrolyte and the reference electrode was a Ag wire immersed in a 0.1 M solution of tetraethylammonium perchlorate (TEAP) in acetonitrile.

Saturated solutions of S_8 in ionic liquids were prepared by adding 0.002 g of S_8 to 2 cm^3 of the corresponding IL. The mixtures were stirred at r.t. in a glovebox for 24 h and in all cases some S_8 remained undissolved. Solutions (10 mM) of Na_2S_4 and Na_2S_6 were prepared by adding 0.0017 g of Na_2S_4 or 0.0024 g of Na_2S_6 to 1 cm^3 of $[C_4mim][DCA]$, and leaving the mixtures to stir for 24 h in a glovebox.

The UV-vis spectra shown in Figure 2 were obtained on a Perkin-Elmer Lambda 800 UV Vis spectrometer. In situ UV-vis electrochemical studies (Figure 4) were carried out using a Perkin-Elmer Lambda 9 UV Vis spectrometer and an Autolab PSTAT 10 potentiostat. For these, a 0.1 cm UV-vis cell was used with modification on the top for the electrodes to stand. The cell was loaded and sealed inside a glovebox, but the spectra were taken outside. The lid of the UV/vis cell had a rubber O-ring on it to make the seal as closed to the air as possible. A Pt mesh was used as working electrode, Pt wire in a separate container as counter electrode and Ag/Ag^+ was used as reference electrode. The cell and electrodes with $[C_4mim][DCA]$ was used as a blank. A saturated solution of sulfur in $[C_4mim][DCA]$ was placed into the UV-vis cell and the three electrodes were carefully immersed into the solution. The cell was then placed into the UV-vis spectrometer and the electrodes connected to the potentiostat. The first UV-vis spectrum was recorded with the electrodes setup and no potential applied. From the second spectrum onward, the selected potential (-0.85 or -1.40 V) was applied to the solution and the UV-vis absorption was monitored. Thirty spectra were recorded in total for each potential applied.

RESULTS AND DISCUSSION

Electrochemistry of Sulfur in $[C_4mim][DCA]$. The cyclic voltammetry of a saturated solution of S_8 in $[C_4mim][DCA]$ was studied over a Au, Pt, or GC electrode, at 100 mV/s (Figure 1). All of the CVs showed similar features, and contained two reduction peaks, R_1 (Pt, -0.97 V; GC, -0.84 V; Au, -0.76 V) and R_2 (Pt, -1.17 V; GC, -1.12 V; Au, -1.11 V), and one oxidation peak, O_1 (Pt, -0.35 V; GC, -0.43 V; Au, -0.56 V). The cathodic wave R_1 is associated with the oxidation peak O_1 , as indicated by the back sweeps after R_1 (Figure 1a–c). The shapes

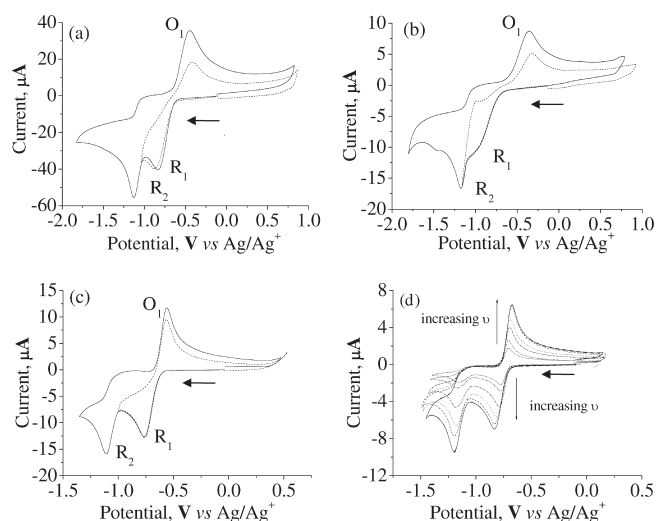


Figure 1. Cyclic voltammograms of S₈ in [C₄mim][DCA] (saturated solution) at (a) GC, (b) Pt, and (c) Au electrode; scan rate 100 mV s⁻¹. (d) Cyclic voltammograms of S₈ in [C₄mim][DCA] (saturated solution) at Au electrode at various scan rates (ν = 100, 75, 50, 25, 10, 5 mV s⁻¹). The arrows show the scan direction.

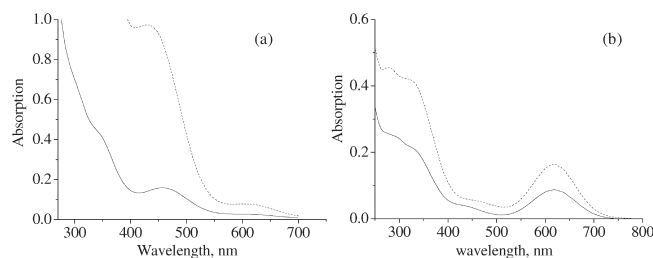


Figure 2. UV-vis spectra of solutions (ca. 3 mM) of Na₂S₆ (solid line) and Na₂S₄ (dashed line) in (a) [C₄mim][DCA] and (b) DMSO.

of the voltammograms in the IL differ from those reported in DMF or DMSO,^{14,18,21} as well as in some chloroaluminate melts,^{22,26} where two reduction and two oxidation waves are observed. However, they are similar to the CVs in organic solvents such as dimethoxyethane, diglyme or CH₃CN,²¹ where the reverse wave for the second reduction is very weak or not observed.

Both reduction peaks, R₁ and R₂, shift toward negative potential when the working electrode changes from Au to GC and to Pt. In addition, the R₁/O₁ peak separation (ΔE₁) increases in the order Au < GC < Pt [i.e., ΔE₁ = 201 (Au), 409 (GC), 628 mV (Pt)]. These observations are also in agreement with previous studies in organic media. For example, Jung et al.²¹ have shown that R₁ appeared at lower potentials at Pt than at GC and the peak separation at Pt was larger. The authors attributed this behavior to the higher affinity of sulfur for GC. Similarly, an even higher affinity would be expected for Au. Merritt and Sawyer also found sulfur to behave more reversibly at Au electrodes than at Pt or graphite.¹²

Further experiments were carried out in [C₄mim][DCA] using a Au electrode, given the well-defined voltammetry obtained at this electrode. Figure 1d includes the CVs of S₈ at various scan rates. The ratio between the peak currents of R₁ and R₂ is approximately 1:1 at 100 mV s⁻¹. However, as the scan rate decreases, R₂ becomes relatively smaller (e.g., the R₁:R₂ ratio at 5 mV s⁻¹

is ca. 1:0.5), suggesting that chemical transformation takes place after the electron transfer process at R₁. The plots of peak current versus square root of scan rate (see Supporting Information) show almost linear relationships for the three peaks, R₁, R₂ and O₁, indicating that the processes are largely diffusion controlled.

UV-vis Spectroscopy and Cyclic Voltammetry of Na₂S₄ and Na₂S₆ in [C₄mim][DCA]. In order to assign the oxidation and reduction processes of S₈ in the ILs, the UV-vis absorption spectra and the electrochemistry of Na₂S₄ and Na₂S₆ were studied in [C₄mim][DCA]. Na₂S₄ and Na₂S₆ formed light brown mixtures in [C₄mim][DCA] which turned into almost colorless solutions after stirring overnight in a glovebox. The UV-vis spectra of these solutions are shown in Figure 2a. The spectrum of Na₂S₄ shows an absorption band at ca. 440 nm whereas that of Na₂S₆ depicts a band at 460 nm with a shoulder at ca. 350 nm. These data agree well with the absorption spectra reported for the two dianions S₄²⁻ and S₆²⁻ in organic solvents (Table 1).^{14,20} The spectra for both compounds also have a small band at ca. 620 nm, characteristic of S₃⁻ (Table 1).^{13,14,17,18,20,32} This species results from the dissociation of S₆²⁻ (eq 3), and can form upon disproportionation of S₄²⁻, for example through reaction 12a²⁰ or 12b,³³ followed by eq 3. Polysulfide anions are known to form solutions containing several species in equilibrium,³³ and the presence of other polysulfide ions in the IL cannot be ruled out. However, it is interesting to note that the IL appears to prevent fast decomposition of the salts, with formation of the blue radical S₃⁻ occurring only to a small extent. This is in contrast to that observed in molecular solvents, where S_x²⁻ (x > 3) anions usually form significant amounts of S₃⁻ at room temperature.^{14,34,35} For example, complete decomposition of S₄²⁻ into S₃⁻ and other species such as S₂²⁻ has been reported in DMF or acetonitrile.³⁴ It has also been shown that the dissociation of S₆²⁻ is temperature dependent (e.g., in liquid ammonia, the 610 nm absorbance of S₃⁻ decreases with temperature and disappears completely at 200 K).³⁵



For comparison, the UV-vis spectra of Na₂S₄ and Na₂S₆ were also performed in anhydrous DMSO (Figure 2b). Both compounds immediately formed blue solutions that turned colorless after approximately 1 h when kept under N₂ or 5–10 min if left in air. The UV-vis spectra of the blue solutions performed under N₂ immediately after preparation are shown in Figure 2b. The spectra are similar for both salts and show an absorption band at 620 nm together with a small peak at 450 nm and absorptions at ca. 280 and 350 nm, in agreement with the presence of S₃⁻ (620 nm), S₆²⁻ (350 and 450 nm), and S₂²⁻ (280 nm; see eq 12a and Table 1).²⁰

Figure 3 shows the cyclic voltammetries of Na₂S₆ and Na₂S₄ in [C₄mim][DCA] over a gold electrode. The CV of S₈ is also included for comparison. In the case of Na₂S₆ (Figure 3a) one reduction peak is observed at -1.10 V when the potential was scanned from the open circuit potential (OCP) to -1.8 V, whereas one oxidation peak is found at -0.53 V when scanning back from -1.8 to 0.5 V. A new reduction peak at -0.75 V was observed when a second scan was continuously recorded after the first scan. When the potential was scanned positively from the OCP to 0.5 V, the oxidation wave O₁ was observed, followed by the two reduction peaks on the reversed sweep (not shown in the

Table 1. Absorption Maxima (λ_{max} /nm) Assigned to Sulfur Species Observed during the Electrochemical Reduction of S_8 in Molecular Solvents (DMSO and DMF; Literature Values) and λ_{max} Obtained in This Work for $[\text{C}_4\text{mim}][\text{DCA}]$

solvent	S_2^{2-}	S_2^{2-}	S_3^{2-}	S_4^{2-}	S_5^{2-}	S_6^{2-}	S_7^{2-}	S_8^{2-}	$\text{S}_3^{\bullet-}$	$\text{S}_4^{\bullet-}$	ref
DMSO				435				505	618		13
				420		475		492	618		14
			260	350, 450		340, 450		370, 490	610	770	17
DMF								498	617		18
	250	280	334	420	435	340, 450	470	490 (S_8^{2-} linear), 355 (S_8^{2-} cyclic)	600	~700	20
$[\text{C}_4\text{mim}][\text{DCA}]$				440		350sh, 460			620		this work

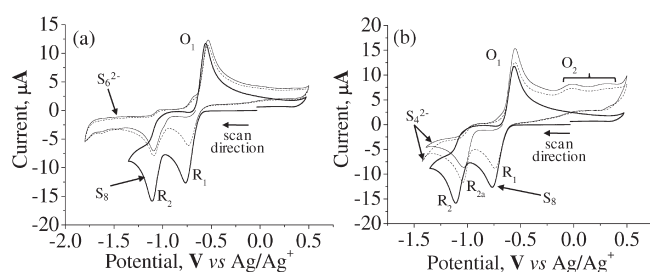
**Figure 3.** Cyclic voltammetry of (a) Na_2S_6 and (b) Na_2S_4 in $[\text{C}_4\text{mim}][\text{DCA}]$ (10 mM) over a Au electrode. The dashed lines show a second scan recorded continuously after the first scan. Overlaid is the cyclic voltammogram of S_8 (gray line) for comparison. Scan rate: 100 mV s^{-1} .

figure). Therefore, the peak at -0.75 V is coupled to the oxidation at -0.53 V . These three waves correspond well with the position of the peaks R_1 , R_2 , and O_1 observed in the voltammetry of S_8 .

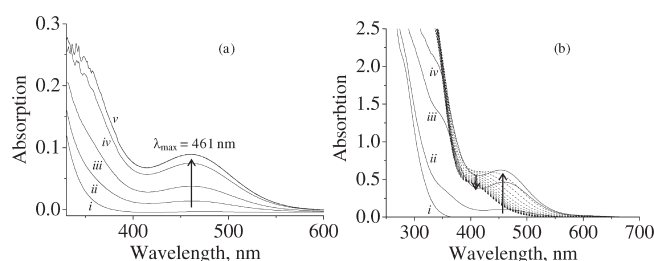
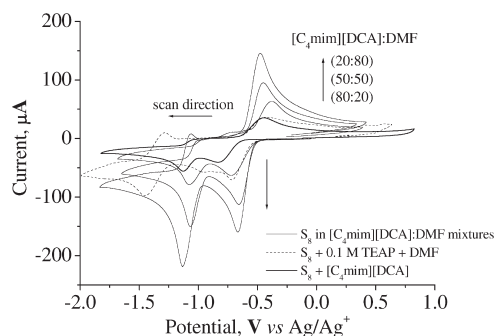
Qualitatively similar behavior was observed on the voltammograms of Na_2S_4 (Figure 3b). However, the reduction peak (R_{2a}) was observed at -1.00 V , i.e., at slightly more positive potential than R_2 . This peak was followed by O_1 (-0.55 V) on the reverse sweep and by R_1 when a second continuous scan was recorded. Two small oxidation waves (O_2) are also seen at ca. -0.02 and $+0.3 \text{ V}$ which may be related to the disproportionation of S_4^{2-} in solution.³³ The oxidation peaks O_1 and O_2 are also present in scans run from the OCP toward positive potential.

Therefore, the reduction wave R_2 appears to be related mainly to the reduction of S_6^{2-} , possibly to S_3^{2-} (eq 8). Both polysulfides are oxidized to S_8 at the same potential at O_1 (eq 13) on the reverse scan, as reported in DMSO.¹⁴ Peak R_1 on the second scan is then assigned to the 2-electron reduction of S_8 to S_8^{2-} (eq 1) followed by rapid disproportionation into S_6^{2-} and S_8 (eq 2).



Spectroelectrochemical Studies of the Reduction of S_8 in $[\text{C}_4\text{mim}][\text{DCA}]$. To further confirm the nature of the reduction products at both cathodic waves, the absorption spectra of saturated solutions of S_8 in $[\text{C}_4\text{mim}][\text{DCA}]$ were recorded in situ during bulk electrolysis carried out at both reduction features.

Figure 4(a) shows the UV-vis spectra obtained during bulk electrolysis at the first reduction peak, R_1 . The applied potential (-0.85 V) was maintained during ca. 15 min and a total of 30 spectra were recorded during this time. All the spectra show an absorption band at 461 nm which increases with time and that

**Figure 4.** UV-vis spectra obtained in situ during bulk electrolysis of a saturated solution of S_8 in $[\text{C}_4\text{mim}][\text{DCA}]$. (a) Potential (-0.85 V) applied for ca. 15 min during which a total of 30 spectra were run; shown in the figure are the 1st (i; no potential applied), 10th (ii), 20th (iii), 25th (iv), and 30th (v) spectra. (b) Solid lines: No potential applied (i) and potential (-1.40 V) applied during first 15 min (ii–iv). Dashed lines: Potential (-1.40 V) applied for further 15 min.**Figure 5.** Cyclic voltammograms over a Au electrode of saturated solutions of S_8 in mixtures of DMF and $[\text{C}_4\text{mim}][\text{DCA}]$ (gray lines) overlaid with the CVs of S_8 in pure DMF (with 1.0 M TEAP , dotted line) and in pure $[\text{C}_4\text{mim}][\text{DCA}]$ (black line). Scan rate: 100 mV s^{-1} .

corresponds well with the formation of S_6^{2-} (see Figure 2a). This agrees with the cyclic voltammetry results, where the process at R_1 results in the formation of S_6^{2-} , presumably through eqs 1 and 2 (see above). At the conditions of the experiments there was no evidence of formation of the blue radical $\text{S}_3^{\bullet-}$.

Bulk electrolysis at the second reduction peak, R_2 , was carried out by applying a potential of -1.40 V during ca. 30 min. The UV-vis spectra obtained during the experiment (Figure 4b) showed initially a peak at ca. 460 nm and a shoulder at around 360 nm , both of which grew in intensity with time. After 15 min, the peak at 460 nm started to shift and decrease in intensity, giving rise to a new absorption band at ca. 410 nm . The bands at 460 and 360 nm correspond well with those of S_6^{2-} in $[\text{C}_4\text{mim}][\text{DCA}]$

Table 2. Peak Potentials (V vs Ag/Ag⁺) from the Cyclic Voltammograms of Saturated Solutions of S₈ in Ionic Liquids at GC, Pt, or Au Working Electrode (Scan Rate: 100 mV s^{−1})

ionic liquid	peak potential (V vs Ag/Ag ⁺)								
	Pt			GC			Au		
	R ₁	R ₂	O ₁	R ₁	R ₂	O ₁	R ₁	R ₂	O ₁
[C ₄ mpyrr][NTf ₂]	−0.74	−1.14	−0.35	−0.68	−1.11	−0.46	−0.61	−1.13	−0.51
[C ₄ mpy][NTf ₂]	−0.70	−0.96	−0.38	−0.69	−0.96	−0.43	−0.57	−0.95	−0.50
[C ₄ mim][NTf ₂]	−0.69	−1.03	−0.58	−0.55	−0.93	−0.45	−0.59	−0.92	−0.47
[C ₄ mim][OTf]	−0.75	−1.02	−0.37	−0.70	−1.00	−0.42	−0.61	−0.99	−0.50
[C ₄ mim][DCA]	−0.97	−1.17	−0.35	−0.84	−1.12	−0.43	−0.76	−1.11	−0.56

while the peak at ca. 410 nm can be assigned to S₄^{2−} (see Figure 2b). The second reduction peak, R₂, can therefore be assigned to the reduction of S₆^{2−} to S₃^{2−} (eq 8) followed by reaction 10 to yield S₄^{2−}. The observation of S₆^{2−} during the initial part of the process may be due to the reaction of electrogenerated S₄^{2−} with S₈ (eq 14).



Electrochemistry of Sulfur in DMF:[C₄mim][DCA] Mixtures. In some organic solvents, such as DMF or DMSO, the CV of elemental sulfur shows two quasi-reversible processes,^{14,18,21} in contrast to that found herein in [C₄mim][DCA]. This solvent-dependent behavior has been attributed to the different ability of the media to solvate the reduction products.²¹ To investigate if the presence of small amounts of IL may be sufficient to influence the voltammetry of S₈ in organic media, the electrochemical behavior of S₈ has been studied in DMF/[C₄mim][DCA] mixtures.

Figure 5 shows the CVs of S₈ at a Au electrode in mixtures of DMF and [C₄mim][DCA] at various ratios (see the Supporting Information for CVs at other DMF:[C₄mim][DCA] ratios). For comparison, the CVs of saturated solutions of S₈ in DMF and in [C₄mim][DCA] are also included. The CVs show that [C₄mim][DCA] influences the electrochemical behavior of sulfur when only 20% w/w is used. This can be seen by the position of the second reduction peak which shifts from −1.45 V in pure DMF to −1.20 V in a 20:80 mixture of [C₄mim][DCA]:DMF. In addition, the first oxidation wave in the reverse scan starts to disappear. However, the behavior of elemental sulfur is not fully like that in [C₄mim][DCA] until the mixture is 50:50.

It is also noted that the reduction peak at higher potential is shifted to a lower potential, and the peak at lower potential is shifted to higher potential for the sample in the IL compared to that in the organic-based electrolyte (i.e., black and dotted lines, respectively, in Figure 5). Similar observations have been previously reported⁹ and may be due to the different solvation properties of the IL compared to the organic media. The second reduction peak in DMF has been attributed by some authors to the reduction of S₃^{•−} (eq 9)^{18,20,21} and/or the reduction of S₈^{2−} to S₄^{2−} (eqs 6 and 7);^{20,21} and the significant shifting of this peak between DMF and [C₄mim][DCA] may be related to the ability of the IL to stabilize the S₆^{2−} anion formed at the first reduction wave, which is then reduced at a more positive potential than S₃^{•−} or S₈^{2−}. This effect of the IL appears to be dominant in 1:1 DMF:[C₄mim][DCA] mixtures.

Electrochemistry of sulfur in other ILs. In order to analyze the effect of the IL cation/anion on the electrochemical behavior

of sulfur, the cyclic voltammetry of S₈ was studied in four additional ionic liquids ([C₄mim][X] (X = OTf, NTf₂), [C₄mpy][NTf₂], and [C₄mpyrr][NTf₂]) at 100 mV/s, over a Au, Pt, or GC electrode. In all cases, saturated solutions were used. Although the exact concentration of the solutions was not determined, the solubility of sulfur in these ILs was found to be significantly lower than in [C₄mim][DCA]. All of the CVs showed similar features to those found in [C₄mim][DCA] and contained two reduction peaks, R₁ and R₂, and one oxidation peak, O₁ (see ESI). The peak potentials are summarized in Table 2, where the data for [C₄mim][DCA] are also included for comparison.

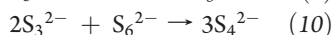
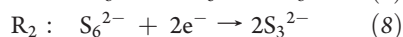
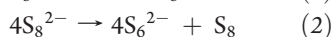
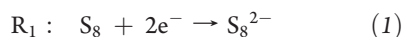
Systematic shifts in the reduction and oxidation potentials were not observed in the NTf₂-based ILs as a function of the cation. Small differences in the potentials are either within error or can be attributed to peaks becoming less reversible as the viscosity increases where, at 293 K, [C₄mim][NTf₂] (52 cP)³⁶ is less viscous than [C₄mpy][NTf₂] (80 cP)³⁷ and [C₄mpyrr][NTf₂] (89 cP).³⁶ Although it has been shown that features such as hydrogen bonding to [C_nmim]-based ILs³⁸ or π – π stacking interactions³⁹ can dramatically influence electrochemical processes, these appear to have no significant effect on the voltammetry of sulfur.

A small but more systematic shift in peak potential can be seen when varying the anion (i.e., in the series [C₄mim]X; X = DCA, NTf₂, OTf), where the reduction potentials become more negative in the order DCA > OTf > NTf₂. In this case, the viscosities of the ILs do not follow the same trend (i.e., 39 cP, 83 cP, and 52 cP, respectively).^{36,40} However, delocalization of the negative charge on the ion can be seen to decrease in the order DCA > OTf > NTf₂, potentially resulting in stronger solvation of the neutral S₈ species (in agreement with the higher solubility of S₈ in [C₄mim][DCA]) and/or decreasing ability to solvate the anionic reduction products.

CONCLUSIONS

The electrochemistry of sulfur and polysulfides has been studied in ionic liquids with special attention paid to [C₄mim][DCA]. The CVs of elemental sulfur in all the ILs investigated showed two reduction and one oxidation waves, in contrast to that found in DMF or DMSO (which shows two reduction and two oxidation waves), but similar to the CVs seen in other organic solvents (e.g., acetonitrile, dimethoxyethane, diglyme). Varying the cation or anion of the IL resulted in some shifting in peak potential which is possibly related to the viscosity of the ionic liquid or the ability of the IL to solvate the various sulfur species. With the support of in situ spectroelectrochemistry studies, the main reduction products have been identified as

S_6^{2-} (formed mainly at the first reduction wave, R_1) and S_4^{2-} (formed at the second reduction, R_2). The first reduction peak is thus assigned as the two electron reduction from S_8 to S_8^{2-} , which then disproportionate to S_6^{2-} and S_8 (eqs 1 and 2), whereas the second wave is attributed mainly to the reduction of S_6^{2-} to yield S_4^{2-} as the final product (eqs 8 and 10).



Interestingly, formation of significant amounts of the blue radical $S_3^{\cdot -}$ was not observed in $[C_4mim][DCA]$ under the conditions used. The electrochemistry of S_8 in DMF is influenced by the addition of $[C_4mim][DCA]$, with 1:1 mixtures showing the same behavior as in pure IL.

■ ASSOCIATED CONTENT

Supporting Information. Cyclic voltammograms of S_8 in $[C_4mim][X]$ ($X = OTf, NTf_2$), $[C_4mpy][NTf_2]$, and $[C_4mpyr][NTf_2]$ at GC, Pt, and Au electrodes. Plot of peak current versus the square root of the scan rate for S_8 in $[C_4mim][DCA]$. CVs of S_8 at a Au electrode in mixtures of DMF and $[C_4mim][DCA]$ at various ratios. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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