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On the dissolution of non-metallic solid elements (sulfur, selenium, tellurium and phosphorus) in ionic liquids

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Ionic liquids are shown to be good solvents for elemental sulfur, selenium, phosphorus and tellurium, and can be designed to maximise the solubility of these elements. The presence of the $[S_3]^{•-}$ radical anion in diluted solutions of sulfur in some ionic liquids has been confirmed, and is the origin of their intense blue colour (cf. lapis lazuli).

A number of solvents (such as carbon disulfide,¹ tetrachloromethane,² pyridine² and toluene²) are known to dissolve sulfur. Of these, carbon disulfide (CS_2) is by far the most efficient solvent, exhibiting a sulfur solubility of 35.5 g per 100 g at 25 °C.³ However, carbon disulfide is a dangerous solvent due to its neurotoxicity, with a very high flammability and a low flash point.³ Also, CS_2 is fairly reactive, which limits the range of chemical reactions that can be performed in it. Selenium is slightly soluble in CS_2 , and its solubility depends on the allotrope in question.² Solvents such as 1,2-diaminoethane can be used to dissolve selenium and tellurium at low concentrations, enabling the formation of nanotubes of these elements.⁴ Tellurium is also slightly soluble in ethanolic KOH solutions, and gives rise to purple colourations.⁵ White phosphorus (P_4) is also known to dissolve in CS_2 to the extent of 89 g per 100 g of CS_2 at 10 °C.⁶ The red allotrope of phosphorus is virtually insoluble in nearly all molecular solvents due to its polymeric nature.³

Examples of sulfur being used as a catalyst,⁷ as a reagent in the Gerwald reaction in the presence of tetraethylammonium hexafluorophosphate,⁸ and as a component of an electrode⁹ in ionic liquids are known, but no details of solubility are presented. The formation of elemental selenium of different morphologies was carried out in 1,2,3-trimethylimidazolium tetrafluoroborate, but no details of its solubility are noted.¹⁰ In this work, ionic liquids are shown to be safe alternatives to conventional solvents for sulfur, and they can be designed to give the greatest known solubility for sulfur in any solvent (at atmospheric pressure).¹¹ A number of readily available ionic liquids were tested for sulfur solubility at elevated temperatures. This was achieved by portion-wise addition of sulfur to the ionic liquid and measuring the temperature at

Table 1 The solubility of sulfur (wt%) in $[C_8mim][NTf_2]$,¹² $[P(tBu)_3CH_3][OTs]$,¹³ and $[C_6mim][OTs]$ ¹⁴ at varying temperatures

Temp/°C	$[C_8mim][NTf_2]$	$[P(tBu)_3CH_3][OTs]$	$[C_6mim][OTs]$
110	<1	1	2
125	<1	1	2
140	2	3	4
155	3	5	6

which the mixture became homogeneous. The solubilities are shown in Table 1.

Generally, when sulfur is dissolved in Lewis basic solvents, the solutions display strong colours due to the formation and occurrence of polysulfides and polysulfide radicals, first observed in 1864.¹⁵ Hydroxide ions can also evoke such coloured solutions, highlighting that the Lewis basicity of the solution is important.¹⁶ Indeed, it was found in our studies that the influence of the ionic liquid anions is stronger than that of the ionic liquid cations, and that the nucleophilicity of the anion is an important factor in determining the solubility and colour. Tributylethylphosphonium diethylphosphate, for example, dissolves small amounts of sulfur (~2 wt%), adopting a bright blue colour when very dilute (<1 wt%) and becoming carmine red at higher concentrations. The blue colour is due to a broad absorption band at 616 nm in the electronic absorption spectrum (Fig. 1), typical for the $[S_3]^{•-}$ radical anion (absorbing at 600–620 nm).^{17,18} The presence of the $[S_3]^{•-}$ radical is also confirmed by EPR spectroscopy, where a broad signal is observed, and adjusted to a Lorentzian line shape centred at $g = 2.029$. The signal is about 48.7 G wide at 298 K. This is in accordance with literature reports.¹⁹ At lower temperature, the $[S_3]^{•-}$ anions dimerise to give $[S_6]^{2-}$ anions, which are carmine red. In the spectrum (Fig. 1), the

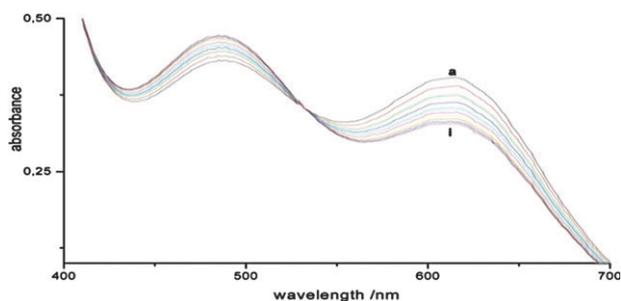


Fig. 1 Electronic absorption spectrum of a solution of sulfur in tributylethylphosphonium diethylphosphate (~1 wt%) with decreasing temperature (a: 60 °C to i: 25 °C).

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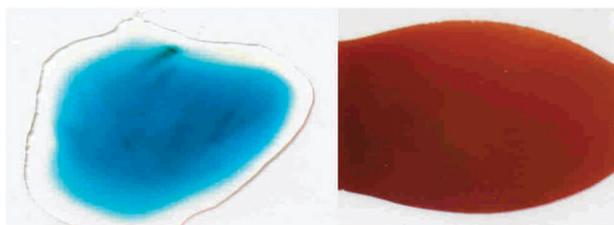


Fig. 2 The colour of the sulfur solution when dilute (blue) and concentrated (carmine red) in the ionic liquid $[P_{6,6,6,14}][\text{decanoate}]$.

presence of the $[S_6]^{2-}$ anions is confirmed by an absorption band at 485 nm (475 nm in dimethylsulfoxide).²⁰ The presence of an isosbestic point (533 nm in Fig. 1) agrees with the dissociation of the hexapolysulfide anion according to $[S_6]^{2-} \rightleftharpoons 2[S_3]^{1-}$. The dissociative equilibrium of $[S_6]^{2-}$ has been intensively studied in other solvents, such as *N,N*-dimethylmethanamide²¹ and NH_3 .²² At higher sulfur concentrations, polysulfide anions $[S_n]^{2-}$, with $n > 6$, are likely to be formed, which subsequently undergo dissociation or disproportionation.¹⁸ The concentration dependent colouration change is shown in Fig. 2. Remarkably, in contrast to reactions performed in molecular solvents, no particular precautions for the exclusion of dioxygen were required during these studies.

The solutions of sulfur, selenium and tellurium behave in a similar manner in trihexyltetradecylphosphonium decanoate, $[P_{6,6,6,14}][\text{decanoate}]$ (which contains a basic carboxylate anion), in that they can display a wide range of colours, and these colours are very concentration dependent. Examples of the dilute solutions of these elements are shown in Fig. 3, where sulfur, selenium and tellurium gave blue, orange and purple colourations, respectively. The orange colour of selenium could be due to the $[Se_3]^{1-}$ radical anion, since mass spectra of selenium solutions show a peak of $m/z = 239.79$.

These results demonstrated that ionic liquids can dissolve sulfur, and led to the design of ionic liquids with greater sulfur solubility than shown in Table 1. By choosing ions with higher polarisability, a series of new ionic liquids were synthesised. Factors that affect solubility can be due to the anion's or cation's contribution to the overall solubility. From Table 1, it can be seen that replacing a phosphonium tosylate with an imidazolium tosylate only made a modest improvement to the solubility, suggesting that 1,3-dialkylimidazolium cations (which have polarisable π -electrons) are slightly preferable to tetraalkylphosphonium cations. Changing the anions resulted in greater improvements in sulfur solubility (see Table 2), particularly those shown in Fig. 4.



Fig. 3 Dilute solutions (< 1 wt%) of sulfur (blue), selenium (orange) and tellurium (purple) in the ionic liquid $[P_{6,6,6,14}][\text{decanoate}]$ at 50 °C (S, Se) and 170 °C (Te).

Table 2 The solubility of S_8 in $[C_4\text{mim}]^+[\text{Y}]^-$ or $[C_4\text{mim}]_2^+[\text{Y}]^{2-}$ ionic liquids

Ionic liquid [Y] ⁻ or [Y] ²⁻	Solubility of S_8 /wt%		
	110 °C	125 °C	135 °C
(1a) $[S_2CN(C_2H_5)_2]^-$	25	—	33
(1b) $[S_2CN(CHMe_2)_2]^-$	19	23	31
(1c) $[S_2CSN(CH_2)_4O]^-$	18	23	31
(1d) $[S_2CSN(CH_2)_4]^-$	24	38	43
(2a) $[S_2CSC_4H_9]^-$	20	—	30
(2b) $[(S_2CSC_2H_5)_2S]^{2-}$	9	—	22
(2c) $[(S_2CS)_2CH_2]^{2-}$	5	—	13
(3a) $[S_2COCH_3]^-$	27	37	41
(3b) $[S_2COC_2H_5]^-$	18	37	37
(3c) $[S_2COCH(CH_3)_2]^-$	29	42	49
(3d) $[S_2COC_4H_9]^-$	37	47	52
(3e) $[S_2COC_5H_{11}]^-$	72	> 100	> 100

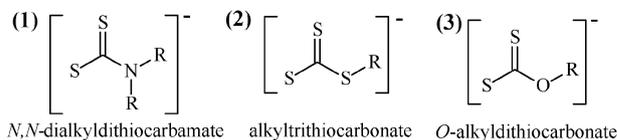


Fig. 4 Examples of ionic liquid anions which enhance sulfur solubility.

The ionic liquids (Table 2) were made by the metathesis of the sodium or ammonium salt of the desired anion with $[C_4\text{mim}]\text{Cl}$ in propanone or propan-2-ol.⁸ The sodium or ammonium salts of the anions (1), (2) or (3) were either purchased from Aldrich Chemical Company, or made by the reaction of carbon disulfide with amines, thiols or alcohols, respectively, in the presence of aqueous sodium hydroxide or ammonia.⁸ The cation (Table 2) was kept constant as $[C_4\text{mim}]^+$ in order to isolate the effect of the anion. The main point to note is that the solubilities of sulfur are all reasonable above 110 °C. The dithiocarbamates displayed solubilities of 31–43 wt% at 135 °C, with the pyrrolidine dithiocarbamate (1d) giving the best results. The trithiocarbonates (2a–c) showed moderate sulfur solubility, with the $[C_4\text{mim}][S_2CSC_4H_9]$ (2a) showing better solubility than the dianionic salts (2b and 2c). The dithiocarbonates gave the highest solubilities (3a–e). As the alkyl chain length of the dithiocarbonates increases, the solubility of sulfur increased considerably, with (3e) giving > 1 : 1 miscibility with sulfur at 125 °C. This solubility is the highest known at atmospheric pressure, although carbon disulfide may give this solubility if compressed to prevent it from boiling. There also exists the possibility that, with further optimisation, higher solubilities at lower temperatures can be achieved with ionic liquids.

In order to test if dissolved sulfur, selenium and tellurium could be used in chemical reactions, a model reaction with triphenylphosphine was investigated. It was found that sulfur, selenium and tellurium all reacted with triphenylphosphine. It was found that the reactions proceeded smoothly to give the corresponding triphenylphosphine sulfide, triphenylphosphine selenide and triphenylphosphine telluride in good yields (Fig. 5). The reactivity of the three elements was in the order $S > Se > Te$. The choice of ionic liquids avoided sulfur in the anion (to avoid chalcogen exchange), but the solubility of these elements was known to be fairly low (< 5 wt%). However, it was sufficient for the reaction to proceed.

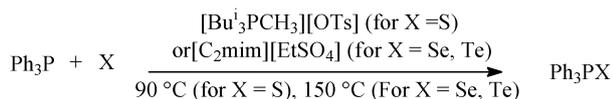


Fig. 5 The reaction of triphenylphosphine with sulfur, selenium or tellurium in ionic liquids, X = S (98% yield), Se (96% yield), and Te (40% yield).

Table 3 The solubility of white P₄ in ionic liquids at 100 °C

Ionic liquid	Weight%
[C ₁₀ mim][CyOCS ₂]	8
[C ₄ mim][CyOCS ₂]	5
[C ₄ mim][C ₆ H ₁₃ OCS ₂]	4
[C ₄ mim][C ₄ H ₉ OCS ₂]	3
[C ₄ mim][C ₂ H ₅ OCS ₂]	2
[P ₆₆₆₁₄][C ₉ H ₁₉ CO ₂]	2
[P ₆₆₆₁₄][N(CN) ₂]	1
[P ₆₆₆₁₄][NTf ₂]	Trace

The dissolution of white phosphorus was attempted in a number of ionic liquids at 100 °C. Three readily available ionic liquids from Cytec (containing [P₆₆₆₁₄]⁺ as the cation and bis((trifluoromethyl)sulfonyl)amide [NTf₂]⁻, dicyanamide [N(CN)₂]⁻ and decanoate [C₉H₁₉CO₂]⁻ as the anions) were found to exhibit low solubility for liquid P₄. With the ionic liquids (**3b**) and (**3d**), the solubility rose to 2–3 wt%. By changing from the [C₄mim]⁺ to the [C₁₀mim]⁺ cation and by combining with the *O*-cyclohexyldithiocarbonate anion ([CyOCS₂]⁻), the solubility was increased to 8 wt% at 100 °C (see Table 3). Red phosphorus was found to be sparingly soluble in these ionic liquids although, in the case of [P₆₆₆₁₄][C₉H₁₉CO₂], the colourless solution of P₄ turned red/brown in colour. This change was mapped in the ³¹P NMR spectra of phosphorus in [P₆₆₆₁₄][NTf₂], where the P₄ molecule is stable and gives a sharp peak at -520.6 ppm (Fig. 6). In [P₆₆₆₁₄][C₉H₁₉CO₂], the ³¹P signal shifted upfield to give a broader peak at -454.3 ppm, thought

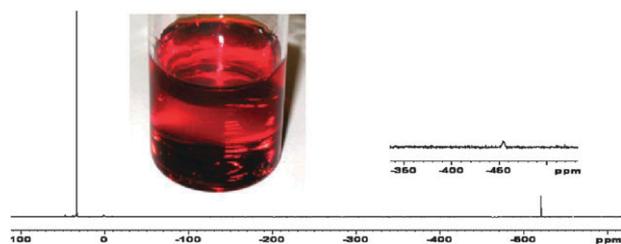


Fig. 6 The ³¹P NMR spectrum of white phosphorus in [P₆₆₆₁₄][NTf₂] with the ionic liquid phosphonium signal at 33.8 ppm and the P₄ signal at -520.6 ppm. The insets show a photograph and ³¹P NMR spectrum of red phosphorus (-454.3 ppm) in [P₆₆₆₁₄][C₉H₁₉CO₂].

to be due to the formation of a polymeric phosphorus solution, similar in nature to that of red phosphorus.

The availability of safer solvents for the dissolution of sulfur, selenium, tellurium, and phosphorus offers up a new area of reactive and synthetic chemistry, one previously hindered by the lack of suitable solvents. This has significant implications for pharmaceutical synthesis, radioisotopes, extraction of sulfur from petroleum, and the production of novel inorganic materials.

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