Spectrophotometric Study of the Electrochemical Reduction of Sulphur in Organic Media

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Summary Reduction of elemental sulphur in dimethyl sulphoxide or dimethylformamide on an inert electrode has been studied, and spectrophotometric absorption bands obtained in the visible region attributed to various polysulphide ions.

Polysulphide solutions in dimethyl formamide (DMF) or dimethyl sulphoxide (DMSO) are generally coloured. The three absorption bands (referred to as A, B and C in the Table) observed in the visible region in spectrophotometric analysis of these solutions have been interpreted as due to neutral[1,2] or ionic[3,4] species (see Table). The 618 nm absorbing species which causes the "blue coloration of sulphur" is observed in both DMF and DMSO. The ionic character of this species is proved by electrophoresis experiments,[5] Lux's interpretation[1,2] favouring neutral species is thus placed in doubt. However, Lux's results like ours show the similarity of polysulphide ion behaviour in DMSO and DMF and may be compared with the results in refs. 3 and 4. The table indicates the contradictory nature of Sawyer's[4] and Giggenbach's work: they both attribute the same A band to two different anion radicals and they both suggest the formation of a dimeric species of anion radical, but the dimer is characterised by the band C in ref. 3 and by the band B in ref. 4.

Various interpretations of the absorption bands observed in polysulphide solutions

		DMF		DMSO		DMF and DMSO
	nm	Ref. 3	Ref. 2	Ref. 1	Ref. 4	this work
A	618	$S_2{\cdot}^-$	S_4	S_4	$S_8{\cdot}^-$	$S_6{}^{2-}$
B	505	$S^{2-}_{n>4}$			S^{2-}_{16}	$S_8{}^{2-}$
C	435	$S_4{}^{2-}$	S_3	S_3		$S_4{}^{2-}$

A solution of sulphur in DMSO or DMF gives rise, on an inert electrode (platinum, gold or vitreous carbon) to two cathodic waves ($E_{1/2} = -0{\cdot}11$ *V* and $-0{\cdot}83$ *V vs* Ag/10^{-3}M $AgCl_2$ 10^{-1}M LiCl on vitreous carbon electrode in DMSO 10^{-1}M Et_4NClO_4) of nearly equal intensity. These two successive reductions are bielectronic steps and not one electron steps as previously assumed.[4] Electrolysis at controlled potential at the limiting current of the first wave, and spectrophotometric measurements in the visible region performed directly on the electrolysis cell, show that B band goes through an intensity maximum when the number z of electrons involved in the electrolysis is 2 for one molecule of S_8. (z is measured as the ratio of experimentally determined quantity of electricity and the theoretical quantity involved in a one electron process). The optical density of A band goes through a maximum when $z = 8/3$, and the coloration of the solution is at its most intense. This corresponds to a global process (1) which is

$$3\,S_8 + 8\,e \rightleftarrows 4\,S_6{}^{2-} \tag{1}$$

interpreted as a bielectronic electrochemical reduction, (2),

$$S_8 + 2\,e \rightleftarrows S_8{}^{2-} \tag{2}$$

followed, in solution, by the dismutation, (3). The band C

$$4\,S_8{}^{2-} \rightleftarrows 4\,S_6{}^{2-} + S_8 \tag{3}$$

appears (for $z > 8/3$) when the reduction potential is chosen at the limiting current of the second wave and its intensity gradually rises until $z = ca.\ 4$. These results also show that the B band intensity decreases in the interval $z = 2$—$8/3$ whereas A band increases, as z increases, producing an isosbestic point [Figure (I)]. As z values rise from 8/3 to 4, the A band decreases while the C band increases giving a second isosbestic point, Figure (II). The relation between the quantity of electricity consumed and the optical density shows that the three absorption bands cannot be attributed to species of the same reduction state, as assumed in refs. 3 and 4, and excludes any monomer–dimer equilibrium between the species which give these absorption bands.

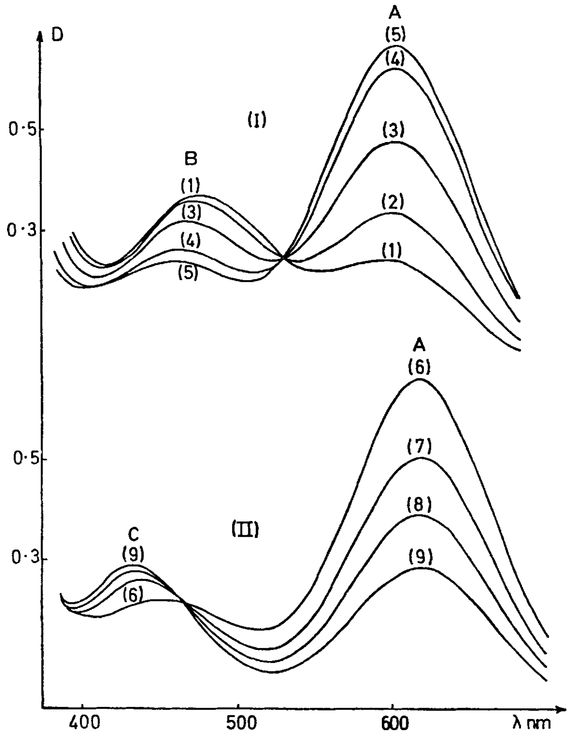

Figure. *Spectrophotometric curves recorded during the electrolysis of a solution of sulphur in* DMSO Et_4NClO_4 10^{-1}M [S_8] = 1·2 mM. *Optical pathway:* 1 mm.
(I) (1) $z = 2$; (2) $z = 2{\cdot}2$; (3) $z = 2{\cdot}4$; (4) $z = 2{\cdot}6$; (5) $z = 2{\cdot}7$. (II) (6) $z = 2{\cdot}9$; (7) $z = 3{\cdot}3$; (8) $z = 3{\cdot}5$; (9) $z = 3{\cdot}8$.

Using our results and a careful analysis of voltamperometric curves[6] we related the A, B and C bands to $S_6{}^{2-}$, $S_8{}^{2-}$ and $S_4{}^{2-}$ polysulphide ions respectively.

E.s.r. measurements of electrolysed solutions in DMF as well as DMSO indicate the existence of two paramagnetic species, (not observed by Sawyer[4] in DMSO). The e.s.r. signals are similar to those described in ref. 3. One is symmetrical and its intensity goes through a maximum at $z = 8/3$. It is caused by the $S_3\cdot^-$ anion radical which is produced by partial homolytic dissociation of S_6^{2-}. The second one which is partially superimposed on the first one, at $z = 2$, arises from a $S_3\cdot^-$–$S_4\cdot^-$ mixture, the latter radical anion being formed through S_8^{2-} partial homolytic dissociation. While our e.s.r. results agree with Giggenbach's[3] we attribute the blue coloration not to the $S_2\cdot^-$ radical anion but to the S_6^{2-} polysulphide ion (dimer of the $S_3\cdot^-$ radical anion). This conclusion is supported by the fact that both e.s.r. signal intensity and A band optical density go through a maximum value when $z = 8/3$ and also by the comparison of the relative intensities of the e.s.r. signal and of the A band on both sides of the maximum. For example, in DMF and for an initial sulphur concentration $[S_8] = 2 \times 10^{-3}$M, a 10% decrease of the e.s.r. signal is measured either for a variation from $z = 8/3$ to $z = 8/3 - 0{\cdot}22$ or from $z = 8/3$ to $z = 8/3 + 0{\cdot}22$ while the same variations of z cause a 22% decrease of the intensity of the A band. These two different figures may be interpreted as the result of an increase in homolytic dissociation of S_6^{2-} into $S_3\cdot^-$ with the decrease in dimer concentration. High water concentration and decreased temperature, which cause, in DMF,[3] the disappearance of the blue coloration, should be interpreted as a modification in the relative positions of the redox potentials of the different polysulphide ions. This modification is due either to water–ion interactions (the hydrogen bonding increasing the charge localisation) or to a change in stability of S–S bonding through temperature variations.

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