The Blue Supersulphide Ion, S_2^-

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Spectroscopic investigations into solutions of alkali polysulphides in dimethylformamide showed that the formal oxidation state of the species giving rise to the intense blue colour of these solutions is $-\frac{1}{2}$. With the actual charge found to be one half of that of a polysulphide ion, the species is identified as the supersulphide ion, S_2^-.

EARLIER work had indicated that the species giving rise to the 'blue solutions of sulphur' only contains sulphur,[1,2] assumed to be present as uncharged molecules[3,4] such as S_2 or S_4. Later work[5] on solutions of polysulphides in aprotic, polar, organic solvents led to

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[1] H. Lux and H. Anslinger, *Chem. Ber.*, 1961, **94**, 1161.

[2] H. Lux, S. Benninger, and E. Böhm, *Chem. Ber.*, 1968, **101**, 2485.

[3] J. Greenberg, B. R. Sundheim, and D. M. Gruen, *J. Chem. Phys.*, 1958, **29**, 461.

[4] J. Greenberg, *J. Chem. Phys.*, 1963, **39**, 3158.

[5] W. Giggenbach, *J. Inorg. Nuclear Chem.*, 1968, **30**, 3189.

the conclusion that the supersulphide ion, S_2^-, was responsible for the colouration and the corresponding structured absorption band at 16·2 kK observed in these solutions. An additional absorption band at *ca.* 24 kK was ascribed to polysulphide.[6] Recently, however, the blue colour of ultramarine [7,8] and of systems containing sulphur under slightly alkaline, reducing conditions [9-11] was attributed to an S_3^- ion, with the S_2^- ion assumed to absorb at *ca.* 24 kK and the implication that S_2^- is yellow. Similar blue solutions obtained by electrochemical reduction of sulphur in dimethyl sulphoxide were thought to be due to the formation of a S_8^- species [12] or hexasulphide [13] ions, S_6^{2-}.

Because of their experimental suitability, the solutions of alkali polysulphides in dimethylformamide (DMF) were reinvestigated in order to establish unambiguously the nature of the blue species for at least this one system.

EXPERIMENTAL

The identification of the blue species requires the determination of n and m of the ion or molecule S_m^{n-}. The formal oxidation state of sulphur, $-n/m$, is presumed to lie between 0 and -2. Solutions containing sulphur in these two limiting oxidation states were prepared by dissolving weighed amounts of purified, elemental sulphur directly in vacuum-distilled, deoxygenated DMF, and recrystallized, freshly analysed $Na_2S,9H_2O$ in small, known amounts of water, followed by dilution with DMF to the desired concentration. The solutions, with water contents ranging from 4 to 30 mol %, were investigated at 22 °C; all starting solutions were colourless.

All mixing operations were carried out under purified nitrogen in a reaction flask directly connected to the spectrophotometric cell. By use of a silica insert the optical path-length could be varied from 0·5 mm over 2·2 mm to 10 mm, thus allowing a wide range of concentrations to be covered. The spectrophotometer used was the Zeiss PM QII, with the monochromator M4 QIII.

RESULTS

On addition of sulphur solution to the sulphide solution the blue colouration appears instantly and the spectra of the reaction product with the strong band at 16·2 kK initially closely approximate Beer's law with respect to the amount of zerovalent sulphur, S^0, added. On further addition of sulphur solution the molar absorptivity ε_{S^0}, based on S^0, starts to drop due to the formation of a new species absorbing at *ca.* 19 kK and causing the colour of the solution finally to turn red. The Boguer–Beer law behaviour at low ratios of S^0/S^{2-} and the sharp breaks in the plots (Figure 1) of ε_{S^0} and $\varepsilon_{S^{2-}}$, the molar absorptivity of the blue species based on the total sulphide concentration, indicate that the second species is only formed after virtually all the sulphide present had been consumed by S_m^{n-}. From the value close to three (Figure 1) for the ratio S^0/S^{2-} at which these breaks occur, a formal oxidation state for S_m^{n-} of $-\frac{1}{2}$ is obtained, thus reducing the general formula of the unknown species to S_{2n}^{n-}.

The formal oxidation state thus determined corresponds to that for the well known tetrasulphide ion, S_4^{2-}, whose solutions in water [14] exhibit an absorption band at 27·2 kK.

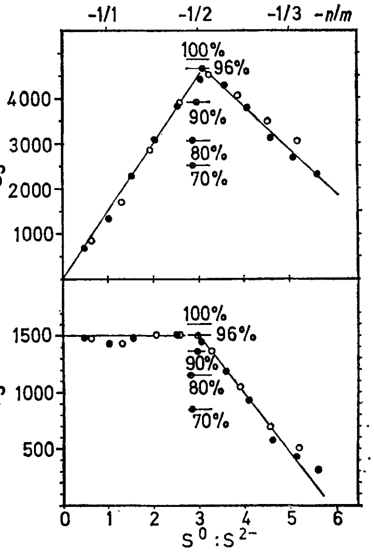

FIGURE 1 Molar absorptivities ε_{S^0} and $\varepsilon_{S^{2-}}$ at 16·2 kK based on the amounts of zerovalent sulphur S^0 added to DMF–water mixtures containing 2·8 mmol (filled circles) and 1·9 mmol (open circles) sulphide, as a function of the ratio $S^0:S^{2-}$. For DMF contents other than 96 mol % only the intersections are shown; the values for 100% DMF are extrapolated

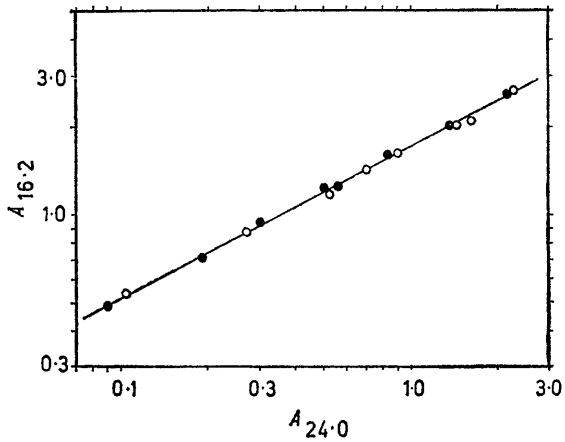

FIGURE 2 Plot of log $A_{16·2}$ *versus* log A_{24} for a series of solutions containing Na_2S_4 (filled circles) or S^0 and S^{2-} in the ratio 3 : 1 (open circles) in 70 mol % DMF (d = 0·22 cm)

On addition of DMF to these aqueous solutions the tetrasulphide absorption band gradually shifts towards lower wave numbers [5] without any significant change in either the shape or the molar absorptivity until at a DMF concentration of about 30 mol % a new band appears at 16·2 kK, that of the unknown species S_{2n}^{n-}. In solutions

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[6] W. Giggenbach, *Inorg. Chem.*, 1971, **10**, 1306.

[7] K. H. Schwarz and U. Hofmann, *Z. anorg. Chem.*, 1970, **378**, 152.

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[9] W. Holzer, W. F. Murphy, and H. J. Bernstein, *J. Mol. Spectroscopy*, 1969, **32**, 13.

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[12] M. V. Merritt and D. T. Sawyer, *Inorg. Chem.*, 1970, **9**, 211.

[13] R. Bonnaterre and G. Cauquis, *J.C.S. Chem. Comm.*, 1972, 293.

[14] W. Giggenbach, *Inorg. Chem.*, 1972, **11**, 1201.

containing 70 mol % DMF, both species were estimated to be present in approximately equal amounts. With S_4^{2-} and S_{2n}^{n-} assumed to be connected by an equilibrium $S_4^{2-} \rightleftharpoons (2/n)S_{2n}^{n-}$, the value of n can be derived from the slope σ of a plot of log $A_{16\cdot 2}$ *vs.* log A_{24}, the logarithms of the absorbances of S_{2n}^{n-} and S_4^{2-} respectively, for a series of solutions with varying total sulphur concentrations, but constant ratio S^0/S^{2-} and DMF content. From the least squares slope of 0·508 obtained from Figure 2 the value $n = 2\sigma$ is found to be close to unity, identifying the blue species as S_2^-.

From the molar absorptivities, extrapolated to 100 mol % DMF, for ε_{S^0} of 1600 ± 50 and $\varepsilon_{S^{2-}}$ of 4750 ± 100 as shown in Figure 1 a molar absorptivity for the supersulphide ion $\varepsilon_{S_3^-} = \frac{1}{2}\,\varepsilon_{S^{2-}} = \frac{3}{2}\varepsilon_{S^0}$ of 2400 ± 60 is obtained. The value of 4750 for $\varepsilon_{S^{2-}}$ is very close to that of 4600 determined for blue solutions of sulphur in sulphide-containing chloride melts [15] and suggests a close relationship between the two systems. Due to the small amounts of the thiozonide ion, S_3^-, present in DMF solutions,[5] its optical characteristics could not be determined.

DISCUSSION

The number of species proposed to explain the 'blue solutions of sulphur' is likely to be due, at least in part, to interferences from a variety of sulphur species associated with the blue species over its wide range of stability. The preparation of a solution containing only the blue species, therefore, was considered an important objective of any investigation into this problem. Of the many systems considered, dilute solutions ($<10^{-3}$M) of alkali tetrasulphides in DMF at room temperature emerged as the ones coming very close to this ideal. The main criteria used were the strict observance of the Boguer–Beer law with respect to the amount of sulphur added in various forms and the insensitivity of measured spectroscopic values (optical and e.s.r.) to variations in temperature. Whereas decreasing temperature causes a rapid drop in the absorbance of the blue species in solutions of Na_2S_4 in DMF, increasing the temperature from 25° to above 100° has only very little effect on both optical and e.s.r. spectra, suggesting virtually complete conversion of the tetrasulphide ion into the blue species at room temperature, or, as shown in this work, its complete homolytic dissociation into supersulphide ions.

During the investigations into the solvent and temperature dependence of this dissociation equilibrium it was found that the blue colour could be produced in any system as long as tetrasulphide could be expected to be stable, that is, under near neutral, to slightly alkaline, reducing conditions. The amount of supersulphide present then depends largely on temperature, leading to an order of solvents according to the temperature required to convert approximately half of the initial tetrasulphide into supersulphide: DMF (−20 °C); liq. ammonia (0°); DMSO, acetone, methyl cyanide (+20°); formamide, ethanol, ethylenediamine (60°); glycerine, water (200°); potassium thiocyanate (300°); LiCl–KCl eutectic (450°); borate, phosphate melts (600°); silicate melts (800°).

From this series it can be seen that many systems previously investigated contain polysulphide under conditions only allowing partial conversion into supersulphide, leading to serious interferences from a large number of other possible polysulphide species, especially in electrochemical work.[11-13]

With the blue species shown to be derived from polysulphide according to an equilibrium of the general form $A \rightleftharpoons 2B$, the possibilities of the blue colour being due to uncharged [2,3] or doubly charged [13,15] particles can be excluded. On the other hand, the nonexistence of polysulphide ions S_nS^{2-} with $n > 5$ in aqueous solution [14] requires that the number of sulphur atoms m of the dissociation product S_m^- does not exceed three,[12] reducing the number of possible species to S_2^- and S_3^-. The very small amounts of S_3^- radicals observed [5,13] in DMF and DMSO solution, suggest that S_2^- by far predominates in these systems. E.s.r. investigations on sulphur-doped borate glasses [16,17] and on ultramarine,[7] however, revealed the existence of considerable amounts of S_3^- ions. No additional absorption bands attributable to this ion, however, could be detected in these systems suggesting that the absorption spectrum of S_3^- is similar to that of S_2^-, and implying that S_3^- is also blue.

In low-temperature systems (DMF, DMSO) the formation of S_3^- is largely prevented by its tendency to dimerize to higher polysulphide ions.[5] At elevated temperature, however, these long chain molecules can be expected to become thermodynamically less stable, thus favouring the formation of the shorter S_3^- ions in equilibrium with monosulphide S^{2-}, disulphide S_2^{2-}, supersulphide S_2^-, and sulphur vapour according to:

$$S^{2-} \xrightleftharpoons{+S_2} S_2^{2-} \xrightleftharpoons{+S_2} 2S_2^- \xrightleftharpoons{+S_2} 2S_3^-$$

Accepting the possibility of S_3^- and S_2^- having similar absorption bands, previous findings by Gruen *et al.*[10] leading to the assignment of the 25 kK band to S_2^-, may be reinterpreted by assuming an equilibrium between disulphide ions, absorbing at *ca.* 25 kK, and S_2^- and S_3^- absorbing at 17 kK, in the ratio 2 : 1 in solutions of sulphur in sulphide containing salt melts at 600°.

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