The Blue Solutions of Sulphur in Oleum

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Summary The blue colour and the two-line e.s.r. absorption at 90°K of solutions of sulphur in oleum are ascribed to a planar S_4^+ ion which is in equilibrium with a yellow S_8^{2+} ion and another radical exhibiting a double-headed optical absorption band at 10,600/13,900 cm^{-1} and a three-line e.s.r. spectrum at 90°K.

RECENT investigations by P. J. Stephens[1] and R. J. Gillespie and his co-workers[2] have shown that the colourless (ν_{max} 30,400 cm^{-1}) and yellow (ν_{max} 24,400 cm^{-1}) solutions obtained by the reaction of S and Se respectively with oleum over extended periods of time at room temperature are due to S_4^{2+} and Se_4^{2+} ions. Freshly prepared solutions of sulphur in oleum are blue, and recently this colour has been ascribed to a diamagnetic S_8^{2+} ion.[3] These sulphur solutions, however, are paramagnetic[4] and exhibit strong e.s.r. signals[5] which suggest the presence of two different radicals, R^1 and R^2, in contrast to freshly prepared selenium solutions which are green and have been shown to contain the analogous Se_8^{2+} ion absorbing at 14,600 cm^{-1}, but to be diamagnetic.[2] The present work suggests that S_8^{2+} is yellow and that the blue colour of the solutions is due to a S_4^+ ion in agreement with the observed paramagnetism of the solutions.

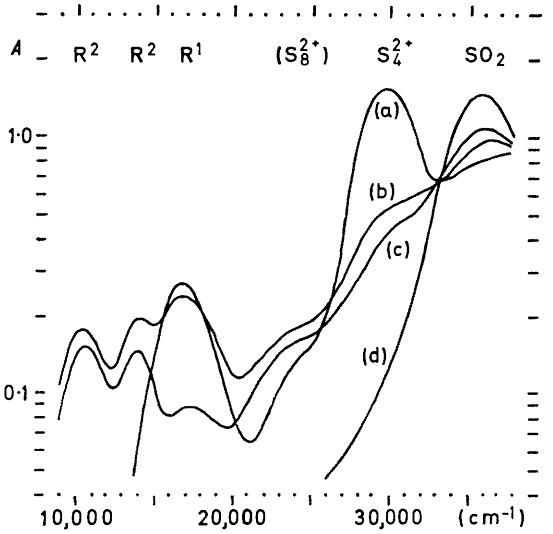

FIGURE 1. *Spectra of solutions of sulphur* (10 *mg atom/l*) *in oleum containing* (a) 40% (b) 20%, *and* (c) 10% SO_3 *measured* 1 *h after preparation. Curve* (d) *shows the spectrum of a solution containing* 10% SO_3 *after* 100 *h*. (d = 0·2 cm).

Investigations by H. Lux and E. Böhm[6] demonstrated that the blue solutions of sulphur in oleum are unstable with time whether a high or a low concentration of SO_3 is present. In the first case the absorption band at 17,000 cm^{-1} causing the blue colour decreases together with the weaker band at 24,000 cm^{-1} while the band at 30,400 cm^{-1} due to the S_4^{2+} ion increases. It has been found in this work that the decrease of the absorptions at 17,000 and 24,000 cm^{-1} is directly related to the decrease in the strength of the e.s.r. signal of R^1 which is characterized by $g_{\text{liq}} = 2{\cdot}0131$, $g_{\parallel} = 2{\cdot}0004$, and $g_{\perp} = 2{\cdot}0192$ at 90°K. Two months old solutions of sulphur in 65% oleum are colourless and do not show any e.s.r. absorption due to the sole presence of S_4^{2+} ions.

On gradual dilution to SO_3 concentrations of less than 40% a new double-headed band appears in the optical spectra with maxima at 10,600 and 13,900 cm^{-1}, and the colour of the solution changes from blue through greenish brown to brown (Figure 1). The appearance of these bands coincides with the emergence of a second e.s.r. signal with the previously reported value of $g_{\text{liq}} = 2{\cdot}0260$ at room temperature.[5] Present investigations, however, show that this signal splits into three lines with $g_1 = 2{\cdot}0024$, $g_2 = 2{\cdot}0311$, and $g_3 = 2{\cdot}0421$ at 90°K indicating lower than axial symmetry for the second radical R^2 (Figure 2). In these solutions of low SO_3 concentrations, however, all four bands at 10,600/13,900, 17,000, 24,000, and 30,400 cm^{-1} decrease with time while the absorption at 36,000 cm^{-1}

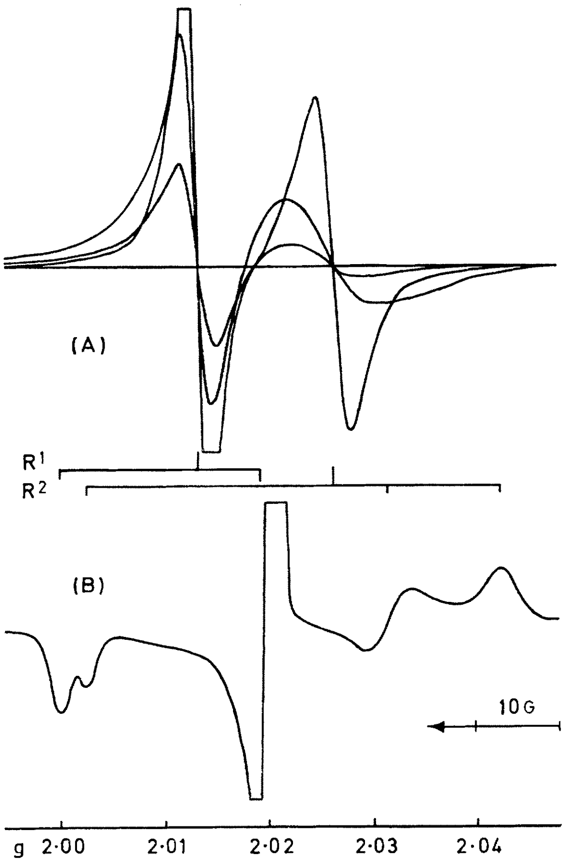

FIGURE 2. *X-Band e.s.r. spectra of a solution of sulphur* (10 *mg atom/l*) *in* 20% *oleum measured* 1 *h after preparation.*

(A) *Succession of spectra obtained during slow cooling to* 210°K.
(B) *Spectrum of the same solution after rapid cooling to* 90°K.

ascribed[4,6] to SO_2 increases. The rate of this reaction is strongly dependent on the SO_3 concentration. In solutions containing 10% SO_3 all the sulphur present is oxidized to SO_2 within 4 days (Figure 1).

The solutions of different SO_3 concentrations were prepared by mixing equal amounts of a solution of sulphur in 40% oleum with equal amounts of premixed acids of such SO_3 concentrations as to give the desired SO_3 and S concentrations in the final mixture. Thirty minutes after mixing, equilibrium between R^1 and R^2 is reached. From then on the ratio of the concentrations of R^1 and R^2 as indicated by their optical and e.s.r. absorptions remains constant as both radicals are slowly oxidized to SO_2. In these solutions large variations of the ratio $A_{17,000}/A_{24,000}$ are observed, the strength of the e.s.r. absorption of R^1 being always proportional to $A_{17,000}$.

The close relationship between R^1 and R^2 is indicated by their common behaviour towards decreasing temperatures. Whereas rapid cooling with liquid nitrogen preserves the two signals, slow cooling causes both signals to disappear (Figure 2), while at the same time the colour of the solution changes from blue to yellow. This reversible colour change, however, could only be observed in solutions containing less than 35% SO_3. The higher melting points of higher concentrated SO_3 solutions appear to prevent the association of the radicals R^1 and R^2 to form the yellow product.

The reflectance spectrum of the yellow, frozen solutions shows a band at 23,000—24,000 cm^{-1} which coincides with the position of the weak band at 24,000 cm^{-1} observed at room temperature. The separation of 7000 cm^{-1} between this band and that of the S_4^{2+} ion at 30,200 cm^{-1} is comparable to the separation of 9800 cm^{-1} for the Se_8^{2+} and Se_4^{2+} bands[2] and supports the assumption of the yellow colour being due to the S_8^{2+} ion. Its partial dissociation into radicals at higher temperatures then may tentatively be explained by assigning the two-line e.s.r. spectrum of R^1 at 90°K to a planar S_4^+ ring, and the three-line spectrum of R^2 to an open S_n^+ chain. Similar blue solutions were obtained by oxidizing a suspension of sulphur in $NaAlCl_4$–$AlCl_3$ melts with $K_2S_2O_8$, S_2Cl_2, or $KClO_3$. At room temperature the frozen melts were yellow. The blue colour of the solid $S_8(AsF_6)_2$ as prepared by R. J. Gillespie and J. Passmore[3] then may be explained by assuming the presence of small quantities of $S_4(AsF_6)$ with a molar absorptivity considerably higher than that of the dimer.

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