

COLORED SULFUR SPECIES IN EPD-SOLVENTS

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Abstract - Alkali polysulfides dissolve in EPD-solvents (e.g. dimethylformamide, dimethylsulfoxide, and hexamethylphosphoramide) to give deep green, blue and carmine red solutions. Vis. and u.v. spectrophotometric as well as e.s.r. spectrometric investigations showed that normal polysulfides S_x^{2-} with different chain length are the carriers of the yellow and red color, whereas the radical ion S_3^- is the blue species, which gives clear blue solutions or, if it is mixed with polysulfide anions with $x < 6$ or $x > 6$, green or carmine red. U.v. and e.s.r. spectra point to the existence of two further radical ions S_2^- (yellow) and S_4^- (red) in EPD-solvents. The behaviour of polysulfides in these solvents can be understood by assuming that anions are only poorly solvated due to dipole shielding of the solvent molecules.

INTRODUCTION

It has been known for a long time that the yellow polysulfides are soluble with a deep blue color in solvents, such as dimethylsulfoxide (DMSO), and dimethylformamide (DMF) which are termed EPD or electron pair donor solvents because of their nucleophilicity. Solutions of polysulfides in EPD-solvents which are saturated or nearly saturated with sulfur exhibit a deep red color. Many chemists have been interested in these blue and red solutions of polysulfides in polar solvents. The observation of a blue solution of sulfur in water was reported first by Geitner(1). When sulfur is heated to 1800 together with water and traces of a base in a sealed tube, a deep blue color develops which disappears again at lower temperature. Gil(2) recommended a blue coloration which develops in boiling ethanol for the qualitative determination of alkali polysulfides. Lux(3,4) tried for many years to elucidate the nature of the colored sulfur particles in dimethylformamide and oleum. He was always convinced that he was dealing with neutral particles, because the blue as well as the red color could be observed in both acidic and alkaline solvents. His former coworker Giggenbach(5-7) defended until recently his opinion that the blue particle is represented by the radical ion S_2^- .

Whereas earlier investigations of Benninger(8) did not reveal an e.s.r. absorption for the solutions of polysulfides in aprotic organic solvents, Giggenbach(5) was able to confirm the presence of two different radicals in rather low concentration. He reports in his first paper on the nature of the blue solutions of sulfur in DMF that it can be demonstrated by cooling the solutions that the blue color decreases to the same extent as the symmetrical e.s.r. signal with $g = 2.027$.

The electrochemical reduction of elemental sulfur in DMSO on an inert electrode was studied first in 1969 by Merrit and Sawyer(9). They concluded that the blue anion S_8^- is formed by a one electron process and undergoes dimerization with the formation of red S_{16}^{2-} . Two years later Bonnaterre and Cauquis(10) reported that the first step of the reduction of the S_8 -molecule is really a two electron process. From spectrometric studies they concluded that S_8^{2-} exhibits a red color in DMSO as a solvent, S_6^{2-} a blue, and S_4^{2-} a yellow. E.s.r. measurements of electrolysed solutions in DMF as well as DMSO confirmed the existence of the two paramagnetic species, observed by Giggenbach(5). The two e.s.r. signals were believed to originate from S_3^- and S_4^- . It is very astonishing that the blue color was attributed to S_6^{2-} and not to S_3^- , though it was recognized by Bonnaterre and Cauquis that the blue color is

deepest and the symmetrical e.s.r. signal most intensive, if three S_8 molecules are reduced by eight electrons. Evidently the paper of the French, and a second paper of Chivers and Drummond which appeared in 1972(Ref. 11) induced Sawyer to reinvestigate the electrochemical reduction of elemental sulfur in DMSO. Two papers of our group were left unnoticed(Ref. 12,13). Subsequent experiments of Sawyer with a group of three coworkers now established that the first study was in error. The data given in a revised paper, which appeared in August 1973(Ref. 14) are consistent with the results of our own experiments.

Chivers and Drummond(15) reported at the end of 1971 that elemental sulfur is sparingly soluble in hexamethylphosphoramide [tris(dimethylamino)phosphine oxide, HMPA], which is the most efficient EPD-solvent, to give blue solutions. The color was attributed to the formation of a negatively charged species, probably S_3^- . Further arguments for this idea were given in a subsequent, more comprehensive paper which appeared one year later(Ref. 11). Direct observations, e.g., resonance Raman, infrared, and e.s.r. spectra, and indirect measurements, e.g., visible u.v. spectra, conductivity and magnetic susceptibility suggested that the blue species formed by alkali polysulfides or elemental sulfur in HMPA can be attributed to the S_3^- radical anion. The nature of the cation derived from the solvent remained unknown. In 1974 Chivers and Drummond(16) tried to elucidate the mechanism of the reduction of sulfur in pure HMPA. It now turned out that the reducing agent was a solvent impurity, probably dimethylamine. To support this idea finally the reaction between sulfur and piperidyllithium was examined. In the last paper of Chivers and Drummond many arguments against Giggensbachs hypothesis are cited. The aim of this paper is to report on experiments which have been done independently of the research work of Giggensbach, Bonnaterre and Cauquis, Sawyer et al., and Chivers and Drummond. The results may clear up the contradicting conclusions of these authors. Finally some ideas concerning the theoretical aspects of the phenomena to be observed are given.

THE NATURE OF THE BLUE AND RED SULFUR SPECIES IN EPD-SOLVENTS

According to literature data it was supposed until recently that the blue color of a polysulfide solution in EPD-solvents is deepest if disodium tetrasulfide is dissolved. However, we found that this is not the case under anaerobic conditions. Solutions of Na_2S_4 in DMF are yellow-green. They turn blue only on the addition of sulfur or by oxidation and finally they become red by adding sulfur in great excess. We consequently decided to elucidate the exact connection between the light absorption and the amount of sulfur of a polysulfide solution in DMF by titration of Na_2S_4 with sulfur using a photometric method. Because of the extremely high oxygen sensitivity of very dilute sulfide solutions we used a totally closed glass equipment, as shown in Fig. 1. It contained two small bulbs for easy mixing of the solutions, a horizontal glass tube with small glass beakers, which could be thrown one after the other into the solution by lifting the magnetic closure. Finally the solution could be filled into the cuvette.

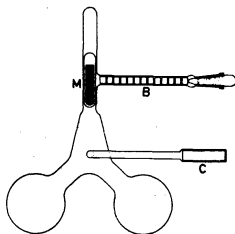


Fig. 1. Apparatus for anaerobic spectrophotometric titration of solutions with solid substances. B small beakers, M magnetic closure, C cuvette

Figure 2, a shows the absorbance curves during the first step of the titration. The green color of the starting solution originates from a blue and yellow color carrier. By further addition of sulfur the absorption of the orange light which leads to the blue color becomes stronger. It is remarkable that the blue band at 16200 cm^{-1} is totally isolated and that charge transfer transitions are not observable. This is the reason for the extreme brilliancy of the blue color. Further an isosbestic point is seen indicating that the

sum of the concentrations of the yellow and the blue colored species remains constant for a long time. Figure 2,b shows the step of the titration where the blue color is most clear and intensive. By further addition of sulfur a new band in the green region of the spectrum arises, the blue band decreases and again an isosbestic point is visible. If the absorbance curves of Fig. 2,c are shown the solution exhibits a carmine red color.

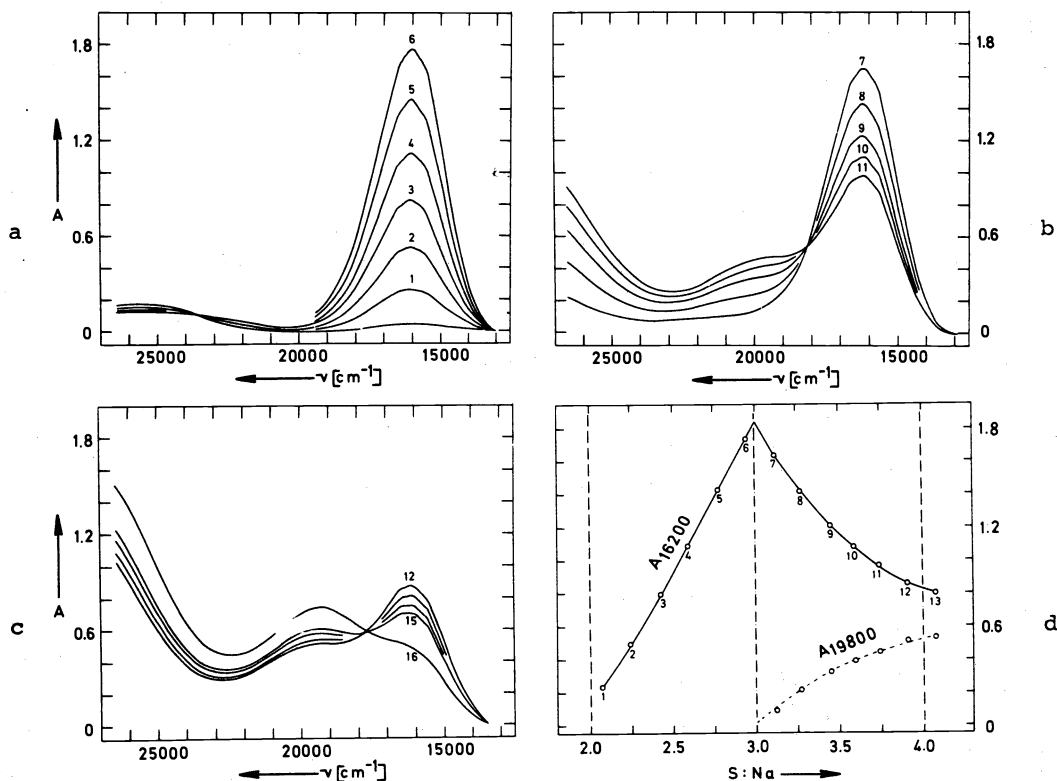


Fig. 2,a-c. Change in absorbance during the titration of a 0,00203 M solution of disodium tetrasulfide in dimethylformamide at 25°C. d. Change in the maximal absorbance at 16200 cm^{-1} . Layer thickness 1 mm.

Curve	1	2	3	4	5	6	7	8
S:Na	2.07	2.25	2.42	2.59	2.78	2.95	3.12	3.27
Curve	9	10	11	12	13	14	15	16
S:Na	3.45	3.59	3.74	3.91	4.07	4.25	4.43	8.02

The results of the photometric measurements can be presented as a titration curve (Fig. 2,d). This shows that the blue color carrier has the highest concentration if the relation between sulfur and sodium atoms is 3 to 1. It is also obvious that sulfur reacts quantitatively with sodium tetrasulfide. The further reaction is delayed. It is possible, however, to estimate from the application of tangents at the beginning of the curves in the right part of the diagram, that the second color carrier contains sulfur and sodium in the ratio 4 to 1. The photometric titration of sodium tetrasulfide also in HMPA proved convincingly that the blue color carrier shows its highest concentration if the ratio of sulfur to sodium atoms is 3 : 1. The blue band has exactly the same position as in DMF (Fig. 3,a). However, the red band seems to be shifted to lower wave numbers (Fig. 3,b). Furthermore, an isosbestic point is not so well observed. This indicates that the red color originates from more than one other carrier, which is in equilibrium with the blue. It is remarkable that a band analysis proves that the maximum of the red band, which is superimposed on the blue, is not as much displaced from its position in a DMF solution as would be expected (Fig. 3,c). Finally we observe that the red color carrier has a second band in the u.v. region, typical for normal polysulfides. We can again present the results of our photometric measure-

ments as a titration curve (Fig. 3,d). The right part of the curve reveals that the blue particle is more stable toward an excess of sulfur than in a DMF solution.

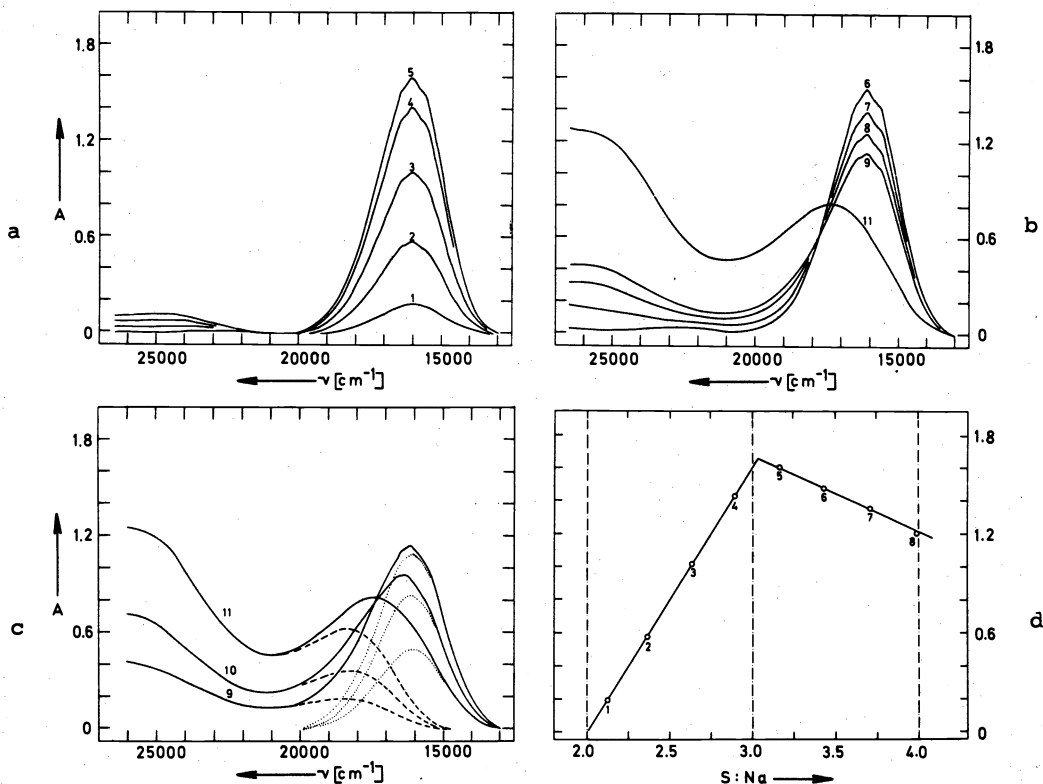


Fig. 3, a-b. Change in absorbance during the titration of a 0,00155 M solution of disodium tetrasulfide in hexamethylphosphortriamide at 25°C. c. Band analysis of curves 9-11. d. Change in the maximal absorbance at 16200 cm^{-1} . Layer thickness 1 mm.

Curve	1	2	3	4	5	6	7	8	9	10	11
S:Na	2.14	2.39	2.67	2.93	3.21	3.49	3.77	4.06	4.32	15	40

What particles are we dealing with in the case of the yellow, blue and red color carriers? Stoichiometrically we could have tetra-, hexa- and octa-sulfides. Normal polysulfides, however, are yellow! It would be also reasonable to think of small sulfur particles which are separated from polysulfide ions under the influence of the EPD-solvents. Small sulfur molecules are well known from the work of Meyer(17). Among those there is no blue particle! S_2 , S_3 , S_4 are colorless, yellow and red, respectively. The isosbestic points are a further argument against neutral sulfur molecules: During our titration we were adding sulfur continuously.

Giggenbach(5) found that the blue band reveals a weak but well defined fine structure, consisting of six to eight detectable subpeaks with an average spacing of 430 cm^{-1} . From this he concluded, that the absorbing particle has to be a small molecular ion, the S_2^- ion, or "supersulfide ion". In fact the band structure is a strong hint that we are dealing with a small molecule. But from stoichiometry we have to conclude that the S_3^- ion is the color carrier. Meyer did prove that the absorption of the neutral S_3 -molecule around 400 nm exhibits a vibration structure, too. In this case the subpeaks fit into two progressions with spacings of 420 cm^{-1} and 590 cm^{-1} .

At first we thought that the color carriers of the polysulfide solutions in EPD-solvents are consistent with the sequence S_2^- , S_3^- , S_4^- . The isosbestic points, however, can be explained by an arbitrary mixture of this sequence with the sequence of the normal polysulfides with doubly charged anions, S_2^{2-} ,

S_6^{2-} , S_8^{2-} . It is clear that we observe an isosbestic point if the molar absorptivities ϵ of the two particles S_3^- and S_4^- are equal at a certain wavelength and the sum of the concentrations of the two absorbing species remains constant. In the case of an equilibrium between S_3^- , sulfur, and S_8^{2-} the absorbance A remains constant if the molar absorptivity of S_3^- is twice that of S_8^{2-} .

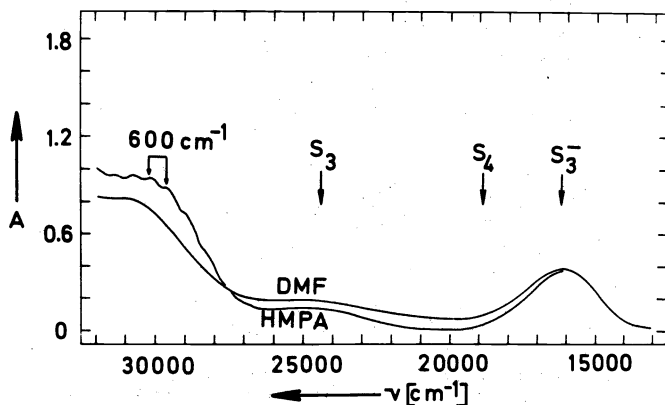


Fig. 4. Absorbance of 0,00550 M solutions of disodium tetrasulfide in DMF and HMPA at 25°C. Layer thickness 0.4 mm.

Only recently have careful experiments shown that the absorption of the singly charged S_2^- -ion can be found in HMPA-solutions around 30 000 cm^{-1} . We are able to identify this ion too by its characteristic vibration structure, as shown in Fig. 4. The spacing between the subpeaks is 600 cm^{-1} . It corresponds exactly to the position of the Raman-band of S_2^- , when the radical is trapped in alkali halides (Ref. 18). It is notable that the position of the band of S_2^- in the u.v. in HMPA-solutions lies far from literature data, which give for its position values around 25 000 cm^{-1} (Ref. 18,19).

Convincing proof that solutions of polysulfides in EPD-solvents contain radicals is given by e.s.r. spectroscopy. All blue polysulfide solutions in EPD-solvents show an e.s.r. signal with $g = 2,029$. Integration leads to a curve which lies between a Gauss- and a Lorentz-curve. The signal has an abnormal half-width value of 145 Gauss which points to a rapid exchange of electrons. The titration of a solution of disodium tetrasulfide in DMF could be also performed using e.s.r. spectrometric indication. In the first stage of the titration the result was the same as in the photometric titration. The concentration of the radicals increases until the ratio sulfur to sodium atoms becomes 3 : 1. This indicates clearly that the blue species is a radical. Moreover we could estimate that the spin concentration of a solution of Na_2S_6 in HMPA agrees with the assumption that the radical contains three sulfur atoms (Ref. 20).

Radicals exhibit two characteristic properties: They associate on lowering the temperature and they can be trapped at low temperatures in a solid matrix. We therefore reinvestigated the temperature dependence of the light absorption of the blue solutions of the S_3^- ion. On cooling, the solution at first becomes green-blue, then green and finally yellow. Benninger first reported this fact in his thesis (Ref. 8). An isosbestic point at 19 100 cm^{-1} agrees with the assumption that the S_3^- ion dimerizes to yield hexasulfide S_6^{2-} (Fig. 5). The height of the blue band and the intensity of the e.s.r. signal of the S_3^- ion decrease simultaneously. From the temperature dependence of the equilibrium we obtained for the dissociation of S_6^{2-} an enthalpy value of 47.4 $kJ \cdot mol^{-1}$, an entropy value of 138 $J \cdot K^{-1} \cdot mol^{-1}$, and the dissociation constant at normal temperature $K_{298} = 0.079$ mol. The molar absorptivity of S_3^- at 16200 cm^{-1} is 4850 $l \cdot mol^{-1} \cdot cm^{-1}$.

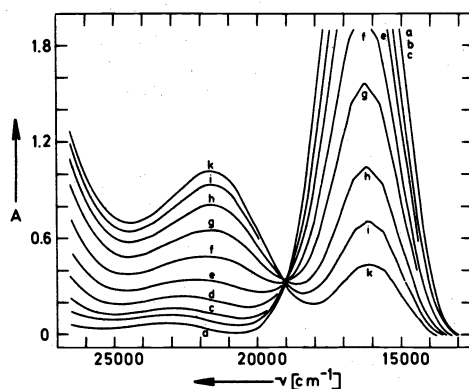


Fig. 5. Temperature dependence of the absorbance of a 0,00165 M solution of NaS_3 in DMF. Layer thickness 5 mm.

Curve	a	b	c	d	e	f	g	h	i	k
Temp. [K]	293	283	274	266	257	249	240	231	223	216

If the blue solution in HMPA is frozen, the S_3^- radicals are evidently partially conserved, because the solvent solidifies before the radical dimerization is complete. The ESR-signal now exhibits a more complicated structure (Fig. 6). It agrees with the assumption that the S_3^- ion is a bent molecule. Values of the g -tensor are given in Table 1.

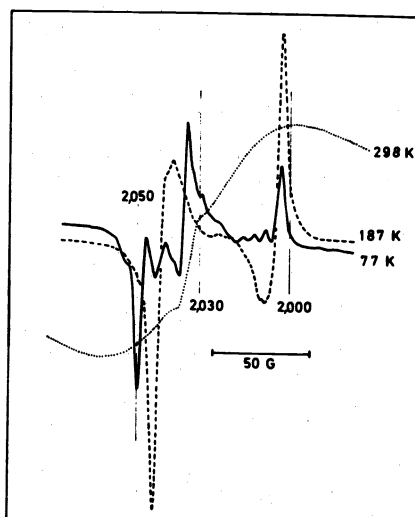


Fig. 6. E.s.r. spectrum of NaS_3 in HMPA at various temperatures.

TABLE 1. Values of the g -factors of S_3^- found in this work compared with literature data

Matrix	g_1	g_2	g_3
HMPA	2.0027	2.035	2.053
HMPA (11)	2.003	2.033	2.047
KCl (21)	2.0026	2.0319	2.0499

Our e.s.r. titration diagram informs clearly that the concentration of the radicals does not remain constant after reaching its maximum when the ratio of sulfur to sodium atoms is three. Obviously the red color carrier is not a radical or we are dealing with a radical which cannot be detected by e.s.r.

spectrometry. In contrast to Giggenbach we could not find the second e.s.r. signal of solutions of polysulfides in DMF with $g = 2.023$. We found a second radical with $g = 2.033$ only in HMPA solutions, mainly if they were frozen. It is noticeable that the second radical can be observed even in solutions of Na_2S_6 . Its concentration is higher in solutions of Na_2S_8 , but even in this case lower than the concentration of S_3^- . The band analysis shows that the maximum of the red band gradually shifts to longer waves during the titration of NaS_3 with sulfur in both solvents (cf. Fig. 3,c). This could be explained satisfactorily by the assumption that on further addition of sulfur the hepta-sulfide is formed at first.

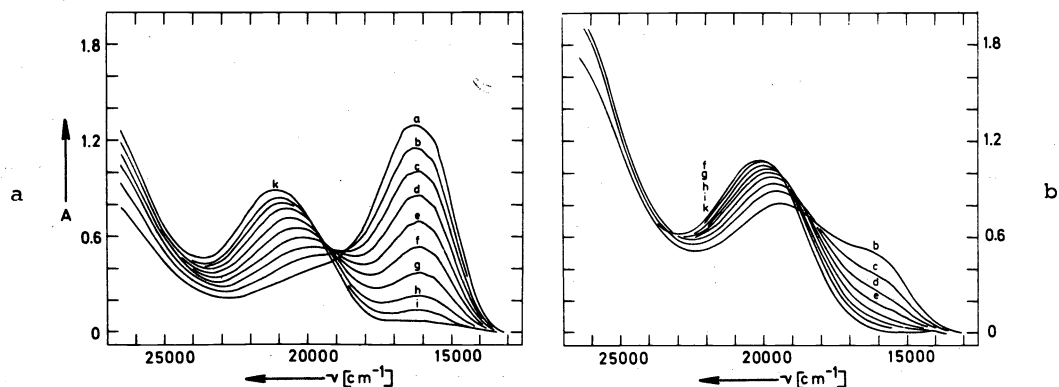


Fig. 7 Temperature dependence of the absorbance of 0.00042 M solutions of sodium polysulfides. a Na_2S_8 . b. Polysulfide solution saturated with sulfur (S:Na 55). Layer thickness 5 mm

Curve	a	b	c	d	e	f	g	h	i	k
Temp. [K]	293	283	274	266	257	249	240	231	223	216

We were now interested in the temperature dependence of the light absorption of the red solutions. If a DMF solution is cooled, the red color changes to orange. More information than from a subjective impression is given by objective measurements. Figure 7, a shows the absorbance curves of a solution of Na_2S_8 . The curves of a polysulfide solution which is saturated with sulfur give the impression that the S_3^- ion, always present in red solutions too, associates to yield S_6^{2-} , while the red color carrier remains unchanged (cf. Fig. 7, b). If a red HMPA solution is quickly frozen to liquid nitrogen temperature the deep red color remains, whereas blue solutions become yellow if they are frozen. One has the impression that a second red color carrier exists. Perhaps we are dealing with the radical S_4^- .

If we compare the bright yellow frozen solutions of Na_2S_6 or NaS_3 in DMF or HMPA, respectively, with the deep red frozen sulfide solutions containing an excess of sulfur, we no longer believe that the red color originates from a normal polysulfide only. Evidently the carmine red color derives from a mixture of colored species, normal polysulfides, the S_3^- radical and a second radical, probably S_4^- . Through personal communication with Professor Schneider at the University of Freiburg we got the information that S_4^- can be trapped in alkali metal halides, which then exhibit a red color.

Martin, Dobb, Roberts and Sawyer found by cyclic voltametry and controlled potential electrolysis that S_8 -sulfur undergoes two-electron reduction at a gold cathode in DMSO to produce S_8^{2-} and perhaps other polysulfides in equilibrium with the octasulfide ion. We found that during the reduction process the maximum of the red band does not alter its position from the beginning and that the whole band is not unusually broad. This shows that we are dealing mainly with S_8^{2-} . Supporting this fact is that the red color is very sensitive toward temperature and dilution. In an equilibrium between S_4^- and $\text{S}_3^- + \text{S}_8$ the number of particles would remain almost unaltered.

We made many efforts to find evidence of the existence of small neutral sulfur molecules in EPD-solvents. S_2 , S_3 and S_4 are electron deficient molecules which could be stabilized by electron donors. The fact that solutions of sulfur in all EPD-solvents are colorless indicates that the dissociation of sulfur to yield colored S_3 or S_4 molecules is not favoured by the solvent to an observable degree. One could suppose that the dissociation of S_8 is hindered

kinetically and only possible if catalysts, such as sulfide ions, are present. Of course one can not exclude that small sulfur molecules are always present in very low concentration. First of all we searched for the S_3 molecule, which shows a characteristic vibration spectrum in the visible region. But we got no definite hint.

Lux and Giggenbach(22) had already shown in 1966 that the blue and red color carriers migrate in DMF solutions from cathode to anode at different rates. By paper electrophoresis we discovered that the migrating spot of red particles leaves no red spot if the solution is saturated with sulfur. This experiment indicates clearly that sulfide ions do not catalyse the fission of S_8 to yield S_4 to a visible extent.

Chivers and Drummond reported that HMPA is a catalyst for reactions involving elemental sulfur (Ref. 15). We observed that ammonia, mono- and dimethylamine, but not trimethylamine and pyridine, readily react with solutions of sulfur in DMF, DMSO and HMPA even at very low pressures. Depending on the concentration of sulfur we observed the blue and red color typical of solutions of polysulfides in these solvents. Chivers and Drummond discovered the blue color of sulfur in HMPA containing traces of dimethylamine. By prolonged evacuation, amine and hydrogen sulfide can be separated from those solutions and a yellow solution remains. Evidently we are dealing with reactions which are summarized in the following equation for dimethylamine.



(The reaction under consideration was studied by Jenne and Becke-Goehring(23) in benzene and in the presence of PbO and H_2O .)

The reaction with dimethylamine explained a fascinating observation we made fortuitously. If one adds potassium fluoride to a solution of sulfur in HMPA, not dried very carefully, one can observe almost instantly a deep red color. The interface between a layer of sulfur and a layer of KF in a test tube becomes almost immediately deep red if both samples come into contact with HMPA. The effect is very astonishing in view of the low solubility of KF in HMPA. We could easily prove that KF reacts with moist HMPA with the separation of dimethylamine. If one adds HMPA to layers of sulfur and ammonium hydrogen fluoride, the sulfur becomes deep red, the layer of fluoride remains white and the supernatant solvent becomes deep blue. This experiment demonstrates that polysulfides are not stable in an acid medium. All experiments of this kind give the impression that the sulfur molecule is activated in EPD solvents. Therefore it was very unexpected to us that sulfur reacts in benzene with dimethylamine just as fast as in EPD-solvents to yield a yellow solution of polysulfuramides and yellow solid dimethylammonium polysulfides. Evidently the EPD-solvents have no special influence on the chemical behaviour of sulfur. Their influence is restricted to a change in color and the radical dissociation of hexasulfide.

How can we explain the phenomena observed, when polysulfides are dissolved in EPD-solvents? Evidently the S_3^- -radical displays an extraordinary stability. What is the difference between this and other singly-charged polysulfide ions? It is known from the structure of solid polysulfides that the trisulfide ion is bent and, of course, it is plane. The four sulfur atoms of the tetrasulfide ion, however, do not lie in a common plane. We can be sure that the same holds for the singly charged radical anions, which are formed as primary products by the fission of the chainlike polysulfide anions. The planarity of S_3^- makes electron delocalisation possible. The spectrum of S_3^- is compatible with the assumption that the ground state of the molecule is described by a delocalized orbital; we are dealing with a so-called $\pi \rightarrow \pi^*$ transition. The structure of the S_3^- band shows that there is no noticeable interaction between the ions and the solvent molecules. This means that the radical dissociation of S_6^{2-} is not enhanced by an interaction with the solvent in the case of the EPD solvents under consideration. The radical fission is evidently hindered in water.

According to the Helmholtz-Gibbs-equation two effects must be considered: Energy and entropy. Giggenbach had already pointed to the fact that the amount of "supersulfide" to be observed depends largely on temperature, leading to an order of solvents according to the temperature required to convert half of the initial polysulfide into the blue species. These temperature values are -20° for DMF, 0° for DMSO and acetonitrile, $+60^\circ$ for formamide, ethanol, ethylenediamine, $+200^\circ$ for glycerine and water, $+300^\circ$ for potassium thio-cyanate melts. Our feeling is that entropy effects play a predominant role in

the dissociation of the polysulfide ions. The fission of a doubly charged ion into a singly charged ion means that the entire charge becomes more distributed in the solvent. This causes the solvent, if it consists of dipole molecules, to lose entropy due to the orientation of dipoles in the neighborhood of charges. From this idea we can readily understand that the dissociation of S_6^{2-} in water and particularly in melts of borates, phosphates and silicates is hindered.

In view of the well known bright yellow color of solutions of polysulfide in water the carmine red color of solutions in EPD-solvents saturated with sulfur is striking. Aqueous solutions of alkali polysulfides have been studied extensively and it has been found that only the tetra- and pentasulfides form stable solutions. Therefore we can observe the color of only these polysulfides. In equilibrium with undissolved elementary sulfur a polysulfide solution cannot contain more than 4,5 excess sulfur atoms per sulfide ion. By using ethanol as solvent the sulfur excess range can be extended to six. It is remarkable that S_3^- can be found spectroscopically in these solutions even at normal temperature. In EPD-solvents the solubility of sulfur is much higher and therefore the higher polysulfides are more stable.

In his first paper on the nature of the blue solutions of sulfur in DMF, Giggenbach pointed out that on addition of DMF to aqueous solutions of disodium tetrasulfide a gradual shift of the entire spectrum to lower wavenumbers is observed without any significant change in either the shape or the molar absorptivity of the absorption maxima. This indicates a strong interaction between one of the solvents and the tetrasulfide ion. A red shift with decreasing polarity of the solvent is typical of spectra due to the transition of an electron from a non-bonding orbital to a π -orbital, it is assumed that the ground state is lowered by a strong interaction between the localized non-bonding electron and a solvent molecule. This means that we observe in the less polar EPD-solvents the color of the free or undisturbed polysulfide anions as is actually demonstrated by the structure of the band of the S_3^- -ion. Moreover we observe the red shift of the light absorption by the lengthening of the chain of sulfur atoms. According to Fehér(24) the prolongation of a polysulfane chain of six atoms by two sulfur atoms causes a red shift of 150 cm^{-1} . Finally a red shift of the polysulfide band in the visible region is caused by the superimposition with the band of S_3^- and possibly S_4^- -ions.

We now understand the role of the EPD-solvents in the case under consideration. In fact they do not act as electron donors to sulfur or sulfur anions. The clue for the understanding of the behaviour of polysulfide anions is that in EPD-solvents anions are naked. The fluorine anion exhibits therefore an unusually strong basicity, liberating amine from DMF and HMPA, and all existing polysulfide anions make their debut and reveal their true color. In an excellent paper on DMSO as a solvent for inorganic compounds which appeared in 1960 in "Angewandte Chemie" Schläfer(25) gives strong support for the fact that cations are strongly solvated, anions poorly. For instance the potassium cation is as large as the tetrabutylammonium-ion. The chloride ion proves to be smaller than the potassium cation. Evidently we are dealing with dipole shielding which prevents the interaction between anions and solvent molecules.

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REFERENCES

1. C.F. Geitner, Pharm. Annls **129**, 350 (1864).
2. J.C. Gil, Z. analyt. Chem. **33**, 54-55 (1894).
3. H. Lux and H. Anslinger, Chem. Ber. **94**, 1161-1172 (1961).
4. H. Lux, S. Benninger, and E. Böhm, Chem. Ber. **101**, 2485-2493 (1968).
5. W. Giggenbach, J. Inorg. Nucl. Chem. **30**, 3189-3201 (1968).
6. W. Giggenbach, Inorg. Chem. **10**, 1306-1308 (1971).
7. W. Giggenbach, J. Chem. Soc. (D) **1973**, 729-731.
8. S. Benninger, Dissertation, Technische Hochschule München (1967).
9. M.V. Merrit and D.T. Sawyer, Inorg. Chem. **9**, 211-215 (1970)
10. R. Bonnaterre and G. Cauquis, Chem. Comm. **1972**, 293-294.
11. T. Chivers and I. Drummond, Inorg. Chem. **11**, 2525-2527 (1972).
12. F. Seel and G. Simon, Z. Naturforsch. **27b**, 1110-1112 (1972).
13. F. Seel and H.-J. Güttler, Angew. Chem. **85**, 416-417 (1973).

14. R.P. Martin, W.H. Doub, Jr., J.L. Roberts, Jr., and D.T. Sawyer, Inorg. Chem. 12, 1921-1924 (1972).
15. T. Chivers and I. Drummond, Chem. Comm. 1972, 293-294.
16. T. Chivers and I. Drummond, J. Chem. Soc. (D) 1974, 631-633.
17. B.Meyer, T.V. Oommen, and D. Jensen, J. Phys. Chem. 75, 912-917. (1971).
B.Meyer, T. Stroyer-Hansen, and T.V. Oommen, J. Mol. Spectrosc. 42, 335-343 (1972).
18. W. Holzer, W.F. Murphy, and H.J. Bernstein, J. Mol. Spectrosc. 32, 13-23 (1969).
19. D.M. Gruen, R.L. McBeth, and A.J. Zielen, J. Amer. Chem. Soc. 93, 6691-6693 (1971).
20. F. Seel and H.J. Güttler, Z. Naturforsch. 30 b, 88-90 (1975).
21. J. Schneider, B. Dischler, and A. Räuber, Phys. stat. sol. 13, 141-157 (1966).
22. W. Giggenbach, Dissertation, Techn. Hochschule München (1966).
23. H. Jenne and M. Becke-Goehring, Chem. Ber. 91, 1950-1955 (1958).
24. F. Feher and H. Münzner, Chem. Ber. 96, 1131-1149 (1963).
25. H.L. Schläfer, Angew. Chem. 72, 618-626 (1960).