# The Molecular Nature of the Hydrophilic Sulfur Prepared from Aqueous Sulfide and Sulfite (Selmi Sulfur Sol) [1]

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Hydrophilic sulfur sols prepared by reaction of aqueous sulfide and sulfite at low pH have been studied by chemical analysis, ion-pair chromatography, and reversed-phase HPLC. The approximate composition of the sol is  $x(\text{NaHSO}_4/\text{Na}_2\text{SO}_4) \cdot y\text{S}_n \cdot z\text{Na}_2\text{S}_m\text{O}_6$  with n=6-10 and m=4-16. The elemental sulfur  $\text{S}_n$  accounts for 17% and the polythionate sulfur for 10% of the dry weight (sulfate: 18%). On aging of the sol at 20 °C the long-chain polythionates decompose to elemental sulfur and tetrathionate as well as pentathionate. The higher chemical reactivity of this sol compared to  $\text{S}_8$  is explained by the fact that 45% of the zero oxidation state sulfur (S°) are present as non-S<sub>8</sub> molecules.

#### Introduction

Elemental sulfur is often used as a substrate for certain sulfur bacteria which take advantage of the energy released on oxidation of S° to sulfate either to support their metabolism or to reduce carbon dioxide [2]. Various allotropes of elemental sulfur are of different reactivity [3]. Orthorhombic  $S_8$  ( $\alpha$ - $S_8$ ) obtained by recrystallization of commercial sulfur from carbon disulfide will be least reactive because it is the most stable allotrope. Commercial elemental sulfurs are always mixtures of  $S_8$  with traces of  $S_7$ , and sometimes  $S_6$ ,  $S_9$ ,  $S_{12}$ , as well as polymeric sulfur  $(S_{\infty})$  are present also [4]. Pure polymeric, insoluble sulfur can be obtained commercially or is prepared by repeated extraction of flowers of sulfur or of quenched liquid sulfur with CS<sub>2</sub> at 20 °C [5]. These forms of sulfur are more reactive than  $\alpha$ -S<sub>8</sub>, but they are all hydrophobic and practically insoluble in water. The solubility of  $\alpha$ -S<sub>8</sub> in water at 25 °C amounts to 5  $\mu$ g/l [6]. However, in the presence of surfactants a considerably higher solubility of  $S_8$  in  $H_2O$  is observed [7]. Truly hydrophilic sulfur can be prepared by two kinds of reactions, in which chains and rings of S atoms are built up from compounds containing only one or two S atoms:

a) Acid decompositions of aqueous thiosulfate under suitable conditions yields hydrophilic sulfur, which can be peptized in water to yield colloidal solub) The reaction of H<sub>2</sub>S with SO<sub>2</sub> in water at pH values below 7 yields a variety of polysulfur compounds [14] including elemental sulfur, polythionates [15], and polysulfuroxides [16] (later termed as polysulfane oxides [17]). Colloidal solutions of this hydrophilic sulfur are known as Selmi sols [10] and can conveniently be prepared according to Janek [18] from Na<sub>2</sub>S, Na<sub>2</sub>SO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>.

In this work we report for the first time a detailed analytical characterization of Selmi sulfur sols, prepared after Janek [18], using modern techniques.

## Results [19]

Preparation of the sulfur sol [18]: 3.6 g of dry sodium sulfite and 6.4 g of sodium sulfide ("Na<sub>2</sub>S·9H<sub>2</sub>O") are dissolved in 50 ml demineralized water each. 1.5 ml of the freshly prepared Na<sub>2</sub>SO<sub>3</sub> solution are mixed with the Na<sub>2</sub>S solution, and a mixture of 2.7 g of conc. H<sub>2</sub>SO<sub>4</sub> (1.47 ml of 95–97% H<sub>2</sub>SO<sub>4</sub>, density 1.84 g·cm<sup>-3</sup>) and 10 ml H<sub>2</sub>O is added dropwise and with stirring as long as no permanent turbidity is observed (*ca.* 8–9 ml are needed). Some H<sub>2</sub>S is evolved and the temperature of the mixture rises to a maximum of 30 °C (solution

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tions known as Raffo sols [8–10]. The particles of such solutions consist of long-chain polythionates  $(S_mO_6^{2-})$  and, to a smaller percentage, of elemental sulfur mostly in the form of  $S_8$  [8]. These particles reach diameters of up to 0.2  $\mu$ m [11, 12] and are probably composed of micelles and vesicles of polythionate anions, in which some  $S_8$  and other sulfur ring molecules are dissolved [8, 13].

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A). To the above mentioned  $Na_2SO_3$  solution are added 3 ml of conc.  $H_2SO_4$  (95–97%), and this mixture is poured rapidly and with vigorous stirring into solution A resulting in a solution temperature of *ca*. 32 °C. After standing of this mixture for 1 h at 20 °C the precipitate formed is collected on a folded paper filter, washed with 100 ml water from the outside of the filter (!), and suspended in 300 ml demineralized water. The resulting yellowish transparent suspension showed a pH of 2.5, which did not change on storage for at least 7 days.

Analytical composition: 20 ml of the freshly prepared sol were evaporated to dryness and the residue dried in a vacuum over phosphorus pentoxide. The yellow material formed (69 mg) showed the lines of  $S_8$  at 473, 439, 249, 218, 187, 153, and 84 cm<sup>-1</sup> in the Raman spectrum [20] and the absorptions of sulfate and hydrogensulfate (HSO<sub>4</sub>) in the infrared spectrum. The Raman spectrum of the liquid sol also showed the strongest lines of  $S_8$  at 485, 220, and 152 cm<sup>-1</sup> and no other compounds. On heating of the evaporation residue to 600 °C for 2 h in air a colorless salt was obtained the infrared spectrum of which was identical to that of  $Na_2SO_4$  and the mass of which (17.1 mg) corresponded to a sodium content of 18% by weight in the evaporated sol.

Titration of the aqueous sulfur sol with barium perchlorate resulted in a value of 18.1% S present as sulfate, while the total sulfur content was found by oxidation of the sol with bromine followed by Ba(ClO<sub>4</sub>)<sub>2</sub> titration as 45.1%. Consequently, 45.1 - 18.1 = 27.0% of the material must be sulfur other than sulfate (*e. g.*, elemental sulfur or polythionates).

The elemental sulfur content of the sol was determined by reversed-phase high-pressure liquid chromatography [21]. 20 ml of the freshly prepared sol were magnetically stirred with 200 ml of either cyclohexane or carbondisulfide, and after certain time intervals small samples of the organic phase were removed by a syringe and analyzed for sulfur rings  $S_n$  by HPLC. The data given in Table 1 show that after 1.5 h extraction time 12.0 mg of  $S_n$  (n = 6, 7, 8) per 20 ml of sol were determined which corresponds to an elemental sulfur content in the evaporated sol of 17% by weight. The slow increase of the S<sub>n</sub> concentrations on longer extraction times is probably caused by formation of  $S_n$  from long-chain polythionates (see below). In addition to S<sub>6</sub>, S<sub>7</sub>, and  $S_8$  small amounts of  $S_9$  and  $S_{10}$  could also be detected (see Fig. 1).

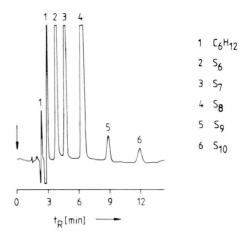
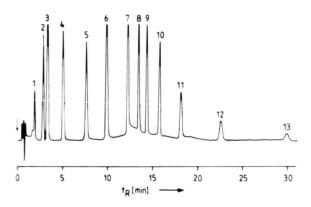


Fig. 1. Chromatogram (HPLC) of the cyclohexane extract of the sulfur sol prepared after Janek showing the presence of sulfur rings  $S_n$  (n = 6-10). Extraction time 117.5 h, flow 2.0 ml/min, ordinate: UV absorption at 254 nm.



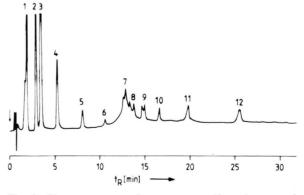


Fig. 2. Chromatograms of an aqueous sulfur sol prepared after Janek and showing the presence of thiosulfate (peak nr. 1) and polythionates (peaks 2–13; the peak number gives the number of zero oxidation state sulfur atoms in the molecule, *e. g.* peak 4 = hexathionate). Above: freshly prepared sol, below: sol after aging at 20 °C for 168 h. Ordinate: UV absorbance at 254 nm, flow 1 ml/min.

Table I. Extraction of elemental sulfur from Janek's sulfur
sol by two different solvents as a function of the extraction
time t. Values (in mg) determined by HPLC analysis.

t (h)	Cyclohexane				Carbondisulfide			
	$S_6$	$S_7$	$S_8$	$\sum S_n$	S <sub>6</sub>	$S_7$	$S_8$	$\sum S_n$
1.5 18.5 93.5 117.5	1.5 1.5	0.7 0.7	9.9 11.0 11.2 11.4	13.2 13.4	1.5 1.5	1.3 0.8	11.2	12.0 14.5 13.5 14.3

Analysis of the aqueous sulfur sol by ion-pair chromatography [8, 22, 23] using a UV absorbance detector revealed the presence of thiosulfate and polythionates  $S_m O_6^{2-}$  with up to 16 sulfur atoms per molecule. The composition very much depended on the age of the sample (see Fig. 2). The freshly prepared sol contained considerable concentrations of higher polythionates, but only traces of thiosulfate. After aging at 20 °C for 168 h, the concentrations of polythionates with more than 5 sulfur atoms had dramatically decreased, while those of thiosulfate, tetra- and pentathionate had increased. Since the concentration of elemental sulfur  $(S_n)$  as determined by HPLC (see Table I) simultaneously increased, it is assumed that a decomposition according to equations (1) and (2) takes place on aging:

$$2S_m O_6^{2-} \to S_{m-x} O_6^{2-} + S_{m+x} O_6^{2-}$$
 (1)

$$S_m O_6^{2-} \rightarrow S_{m-n} O_6^{2-} + S_n (n = 6-10)$$
 (2)

A quantitative evaluation [22] of the upper chromatogram in Fig. 2 showed that the freshly prepared sol contained 0.2 mg  $S_2O_3^{2-}$ , 1.0 mg  $S_4O_6^{2-}$ , and 0.7 mg  $S_5O_6^{2-}$  per 20 ml. After aging for 118 h the tetrathionate concentration had increased to 1.4 mg and pentathionate to 1.5 mg per 20 ml. The concentrations of the other polythionates were not determined, but from the sulfur balance it can be calculated that *ca*. 10% of the dry mass or 22% of the total sulfur must be present as sulfur in oxyanions except sulfate:

sodium: 18%, total sulfur: 45%, sulfate: 18%, elemental sulfur: 17%, sulfur in oxyanions except sulfate: 10% (all data by weight).

## Discussion

Our results indicate that the composition of the Selmi sulfur sol prepared after Janek can approximately be described by the formula  $x(NaHSO_4/$ 

 $Na_2SO_4$ ) ·  $yS_n$  ·  $zNa_2S_mO_6$  (n = 6-10, m = 4-16). Within the limits of accuracy, the sulfur balance is in accord with the ratio  $x:y:z=2:\frac{2}{n}:\frac{1}{m}$ . By dialysis the sodium hydrogensulfate and the lower polythionates as well as sulfite and thiosulfate are removed and the purified sol is composed of elemental sulfur and long-chain polythionates [24]. In Janek's sulfur sol [18] the sulfur atoms in the zero oxidation state (S°) are distributed between  $S_n$  and  $S_m O_6^{2-}$  in an approximate ratio of 2:1. Since ca. 45% of this S° is present in a form other than  $S_8$ , the sulfur sol will be more reactive than S<sub>8</sub>. It has been suspected for a long time [25] that the polythionate anions are bound to the surface of the elemental sulfur particles by hydrophobic interaction thus generating a hydrophilic particle with a hydrophobic nucleus. This nucleus may be in a liquid state since it contains  $S_6$ ,  $S_7$ ,  $S_9$ , and  $S_{10}$  besides  $S_8$  as does liquid sulfur [26]. This model resembles the micelle model proposed for the particles in Raffo sulfur sols prepared by acid decomposition of sodium thiosulfate [8]. This latter type of sol, however, prepared after Weitz et al. [9] has a much higher polythionate content than the Selmi sol prepared after Janek. This may be the reason that the Raffo sols are thermally more stable than the Selmi sol which tends to precipitate elemental sulfur more rapidly.

[16, 17]. These compounds are of deep yellow color and form S<sub>2</sub>O on pyrolysis in vacuo [17], but neither an evaporated Raffo sol nor polythionates yielded S<sub>2</sub>O on heating in vacuo. The polysulfane oxides are obviously only obtained when the reaction between H<sub>2</sub>S and SO<sub>2</sub> takes place at low temperatures and with an excess of SO<sub>2</sub> [16, 17], while the Selmi sol has been prepared at ca. 30 °C in this work. On the other hand, it is obvious now that the so-called "Wackenroder sulfur" obtained from H<sub>2</sub>S and SO<sub>2</sub> in water at 0 °C is a mixture of elemental sulfur  $(S_n)$ , polysulfane oxides and long-chain polythionates. The latter compounds are responsible for the hydrophilic nature of this material. The presence of polythionates or polythionic acids in the "sulfur" precipitated from cold reaction mixtures of H2S and SO2 in water follows not only from the analytical composition (S: ca. 88%, H: ca. 1%, oxygen being the rest) but also from infrared spectra showing absorptions at 610,

640, 1020, 1045, and 1220–1235 cm<sup>-1</sup> [27], all typical for long-chain polythionates [8]. In addition, the polysulfaneoxide absorption at 1120-1130 cm<sup>-1</sup> [27] is observed, which is to be assigned to  $\nu(SO)$  of the unit -S-S(O)-S- [28].

One common feature of the hydrophilic sulfur sols is the presence of considerable concentrations of  $S_6$ ,  $S_7$ ,  $S_9$ , and  $S_{10}$ , which are unstable in the presence of water. We believe that these species are dissolved in the probably liquid nucleus of the sol particles and are thus protected from the water by the polythionate anions which cover the particle surface. This view is supported by our observation that stirring of 10 ml of a Raffo sol [8] with 80 mg of solid  $S_7$  at either 20 °C or 50 °C resulted in a dramatic increase of the  $S_7$  concentration inside the sol particles within 20-60 min. The analysis was performed by HPLC after filtration through a  $0.45~\mu m$  filter which the sol particles can pass but not the solid  $S_7$ .

Summarizing, it can be stated that hydrophilic sulfur sols are composed of elemental sulfur  $S_n$  ( $n = 6 \cdots 10$ ) and polythionates  $S_m O_6$  ( $m = 4 \cdots 16$ ) in varying proportions depending on the preparation and the age of the sol. The thermal stability of the sol depends on the  $S_n/S_m O_6^{2-}$  ratio, since the polythionates keep the elemental sulfur in solution. Sulfur

sols are easy to prepare and provide a kind of zero oxidation state sulfur which is more reactive than  $S_8$  and, in addition, hydrophilic.

## **Experimental**

The experimental technique as well as the chromatographic equipment have been described elsewhere [8,21,22]. The chemicals used were of highest available purity. Reversed-phase HPLC analysis of sulfur rings was performed using Waters  $10\,\mathrm{C}\,18$  Radial-Pak columns contained in an MC 100 compression module and methanol as an eluent. The separation of the polythionates was achieved with a Chrompak C18 glass column (particle size  $5\,\mu\mathrm{m}$ ) and an eluent mixture of 27% acetonitrile (by volume), 73% doubly distilled water,  $2\,\mathrm{mmol/l}$  tetrabutylammoniumhydrogenphosphate, and  $1\,\mathrm{mmol/l}$  sodium carbonate applying a gradient procedure [23].

The Raman spectrometer [29] as well as the preparation of reference compounds for the peak identification and the calibration of the chromatographic systems have also been described earlier [22, 30].

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- [1] Part 126 of the Series on Sulfur Compounds; for part 125 see R. Steudel, T. Göbel, H. Schmidt, and G. Holdt, Fresenius' Z. Anal. Chem., in print.
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