

# The Molecular Composition of Hydrophilic Sulfur Sols Prepared by Acid Decomposition of Thiosulfate [1]

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Hydrophilic sulfur sols prepared from sodium thiosulfate and concentrated sulfuric acid and purified by repeated NaCl precipitation and peptization in water have been studied by chemical analysis, vibrational spectroscopy, ion-pair chromatography and reversed-phase HPLC. The composition of the sol is  $\text{Na}_{1.64}\text{S}_{28.6}\text{O}_6 \cdot 5.9/n \text{ S}_n \cdot 1.0 \text{ NaCl}$ . The elemental sulfur  $\text{S}_n$  ( $n = 6-14$ ; mainly  $\text{S}_8$ ) accounts for 17% the total sulfur; 83% of the S are present as long-chain polythionates which form micelles in which the  $\text{S}_n$  molecules are dissolved. On aging of the sol at 20 °C the polythionate micelles decompose to give water-soluble short-chain polythionates and elemental sulfur which precipitates from the solution. The micelle structure of hydrophilic sulfur sols may serve as a model for the so-called sulfur globules ( $\text{S}^0$ ) formed intra- or extracellularly by many sulfur bacteria which oxidize reduced sulfur compounds to  $\text{S}^0$ . – Infrared and Raman spectra of  $\text{K}_2\text{S}_m\text{O}_6$  ( $m = 3-6$ ) are reported. The photodecomposition of aqueous tetrathionate yields sulfite, thiosulfate, and polythionates with up to 9 sulfur atoms.

## 1. Introduction

Sulfur sols can be classified as hydrophobic or hydrophilic. Hydrophobic sulfur sols are prepared by pouring solutions of  $\text{S}_8$  in organic solvents like ethanol or acetone into water. The finely precipitated sulfur remains in a colloidal state for some time; these milky sols are usually termed Weimarn sols. They are neither very concentrated nor of high stability. The particles of this sol are hydrophobic, soluble in  $\text{CS}_2$ , and most probably consist of  $\text{S}_8$  [2].

Hydrophilic sulfur sols can be prepared by two different routes. So-called Selmi sols are obtained by reaction of  $\text{SO}_2$  (or sulfites) with  $\text{H}_2\text{S}$  (or sulfides) in water, while the acid decomposition of sodium thiosulfate in water provides so-called Raffo sols which sometimes have also been termed as Oden or LaMer sols [2]. In this paper we are concerned with a thorough analytical characterization of Raffo sols; a corresponding investigation of Selmi sols will be published elsewhere.

The decomposition of sodium thiosulfates in aqueous acids has been studied numerous times [3] and the following reaction products have been identified, the relative importance of which depends on the reaction conditions: elemental sulfur ( $\text{S}_8$ ,  $\text{S}_7$ ,  $\text{S}_6$  [4–7]), polythionates  $\text{S}_m\text{O}_6^{2-}$  [8–11], sulfate [3],  $\text{SO}_2$  [3], and  $\text{H}_2\text{S}$  [3]. The colloidal sulfur [12] is isolated

and purified by repeated precipitation by NaCl followed by either filtration or centrifugation and re-peptization in water. In this way a clear solution of hydrophilic sulfur is obtained with a particle size of ca. 0.1–0.2  $\mu\text{m}$  [13, 14]. Freshly prepared sols are free of lower polythionates ( $m = 3-6$ ) [8] but after standing at 20 °C for some hours or days (aging) the mentioned polythionates can be detected in the aqueous phase (after precipitation of the sol by NaCl); at the same time elemental sulfur precipitates from the solution and slowly crystallizes as  $\alpha\text{-S}_8$  [2, 8, 9].

The freshly prepared sol particles are negatively charged and can be precipitated by a number of cations the efficiency of which increases with increasing ionic charge ( $\text{Na}^+ < \text{Ca}^{2+} < \text{Al}^{3+}$  etc.) [2, 8, 9]. Only with HCl, LiCl and NaCl a reversible precipitation is achieved [9]. The solubility of hydrophilic sulfur increases rapidly with temperature [15]; NaOH,  $\text{NH}_3$  and thiosulfate destroy the sol with sulfur precipitation [2, 9].

It has been suspected that the sol particles consist of elemental (polymeric) sulfur covered and peptized by lower polythionates ( $m = 3-6$ ) [8, 9], but Weitz *et al.* [16] argued that the properties of Raffo sols can be explained by the assumption that long-chain polythionates ( $m = 40-140$ ) and no elemental sulfur are present. However, no direct evidence for the presence of polythionates with  $m > 6$  in Raffo sols has so far been presented. Therefore, we have extensively analyzed these sols by reversed-phase high-pressure

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liquid chromatography (HPLC) as well as ion chromatography (IC) to search for homocyclic sulfur molecules  $S_n$  ( $n = 6, 7, 8 \dots 30$ ) and polythionates  $S_mO_6^{2-}$  ( $m = 3, 4 \dots 25$ ) which can be detected and determined by these techniques [17–20] unless the ring size  $n$  exceeds 30 atoms or the chain-length is more than 25 atoms. No direct analytical methods are available at present for these large molecules and ions, respectively.

## 2. Preparation and Properties of Raffo sols

Within 15 min an aqueous solution of sodium thiosulfate (3 mol/l; 30 ml) is added dropwise with stirring to concentrated sulfuric acid (96%; 10 ml) resulting in heat generation (70–80 °C), evolution of  $SO_2$  and some  $H_2S$ , and formation of a yellow precipitate. The mixture is cooled in an ice-bath to 0 °C for 30 min, and 50 ml of a saturated sodium chloride solution (20 °C) are added to complete the precipitation. After 15 min the yellow solid is isolated by centrifugation and careful decantation of the aqueous phase.

For purification [16] the precipitate is suspended in 200 ml  $H_2O$  and the insoluble part removed by centrifugation (10 min). To the greenish-yellow aqueous phase containing the colloidal sulfur are added 50 ml of a saturated aqueous NaCl solution whereupon the sol is precipitated. Centrifugation, peptization in 200 ml  $H_2O$  followed by precipitation by NaCl are repeated 10 times. Resuspending the precipitate thus obtained in 200 ml  $H_2O$  results in a light-yellow opalescent clear solution of  $pH \approx 6$  which after dilution shows a Tyndall effect. This purified sol which does not smell after  $SO_2$  has been used for all of the following experiments.

Investigation of the sol by ion-pair chromatography (IC) [19, 20] showed that thiosulfate and lower polythionates  $S_mO_6^{2-}$  ( $m = 4–10$ ) were absent (see Fig. 1a) in contrast to the original thiosulfate-sulfuric acid mixture which contained all of these species and which smelled strongly after  $SO_2$ .

When 20 ml of freshly prepared Raffo sol were evaporated to dryness in a vacuum at 45–50 °C bath temperature followed by drying in an evacuated de-

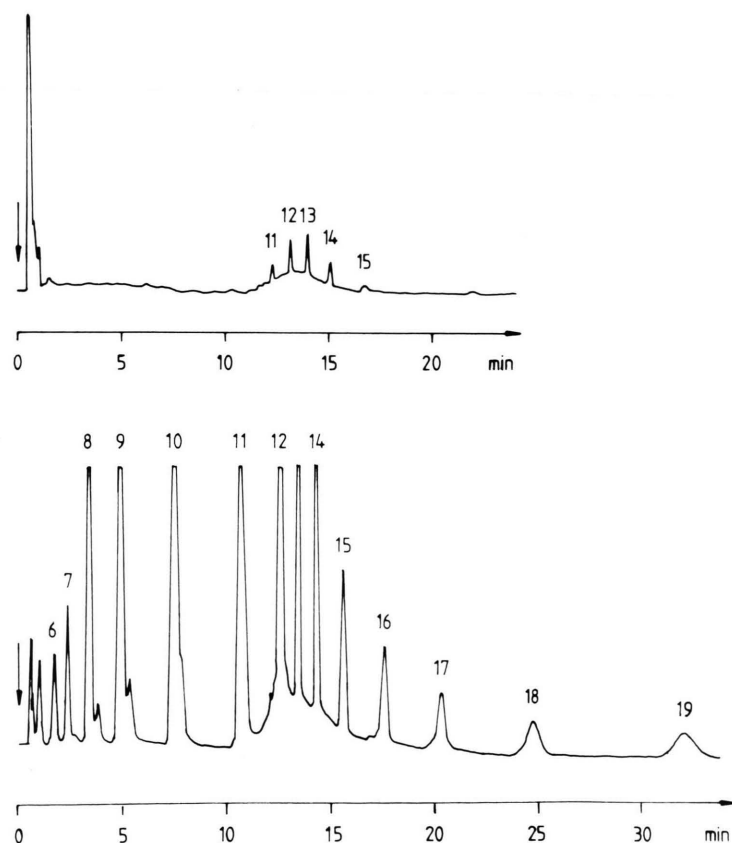


Fig. 1. Ion-pair chromatogram of a freshly prepared Raffo sol (a: above) and of the same sol after aging for 36 h at 20 °C (b: below) showing the formation of thiosulfate (first peak) and of lower polythionates  $S_mO_6^{2-}$  ( $m = 5–19$ ). The ordinate gives the UV absorbance at 240 nm. Eluent: 30%  $CH_3CN$ , 70%  $H_2O$ . The additional peaks neighboring the peaks due to  $S_8O_6^{2-}$  and  $S_9O_6^{2-}$  are caused by overloading of the column (see “Experimental”).

siccator over  $P_2O_5$  for 3–5 days, a yellow, in parts shiny and flaky residue (159.2 mg) was obtained the composition of which corresponded to the “formula”  $Na_{1.64}S_{34.5}O_6 \cdot 1.0 NaCl$  (85.3% S, 2.9% Na, 2.7% Cl, no H). Sulfur was determined after bromine oxidation as sulfate by titration; combustion and gas-chromatographic analysis did not show any C or H; heating of the flaky residue in air to 600 °C for 60–90 min resulted in a colorless mixture of  $Na_2SO_4$  and NaCl (13.4% of the original weight) the Cl con-

tent of which was determined by argentometric titration thus yielding the NaCl value (4.47%). The remaining weight (8.9%) must have been  $Na_2SO_4$  originating from the oxidation of sodium polythionate resulting in a total Na content of 2.9%. The missing 7.4% of the evaporation residue were interpreted as oxygen.

The presence of oxygen in the form of  $-SO_3^-$  groups was confirmed by the infrared spectrum of the flaky evaporation residue which showed strong

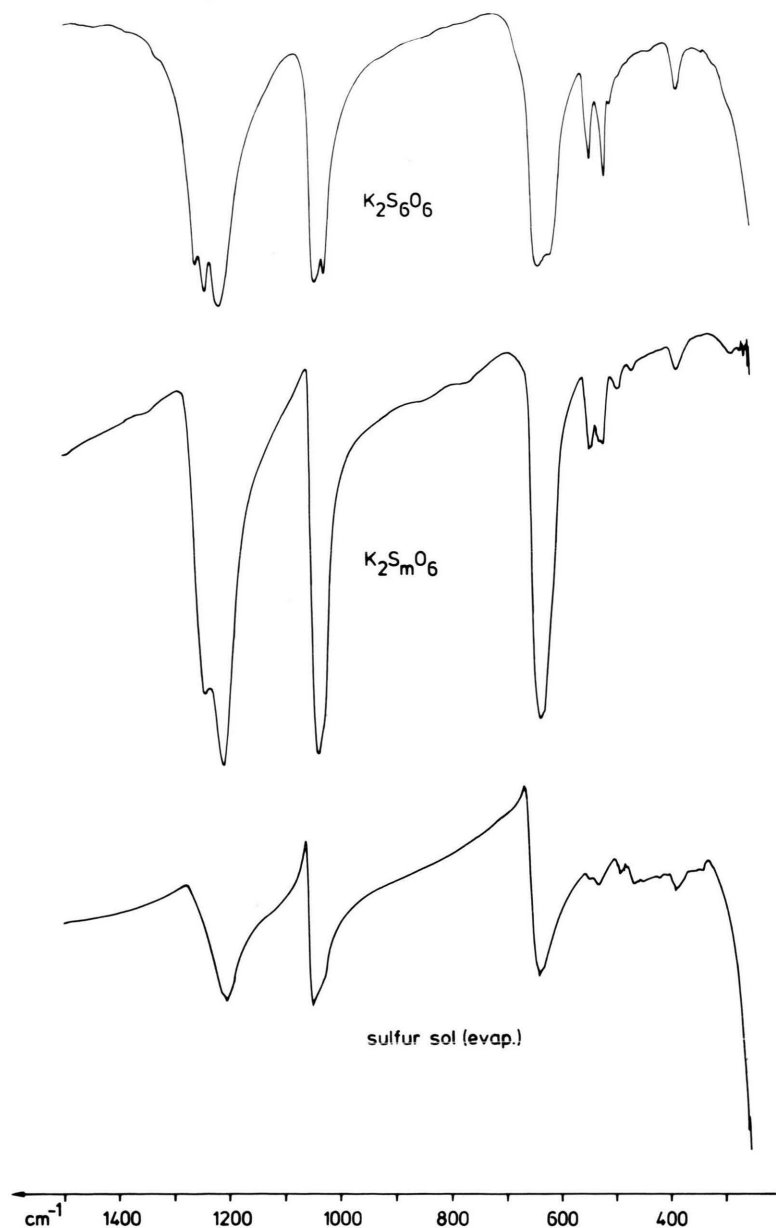


Fig. 2. Infrared spectrum of an evaporated Raffo sol (KBr disc), and of  $K_2S_6O_6$  and a polythionate mixture “ $K_2S_mO_6$  ( $15 < m < 40$ )” after Weitz *et al.* [24]. For wavenumbers see Table I.

but broad absorptions at 1205, 1050–1030 and 640  $\text{cm}^{-1}$  and weak bands at 525, 460 and 385  $\text{cm}^{-1}$  (KBr disc; see Fig. 2) which all are typical for

polythionates as a comparison with the spectra of various polythionates in Fig. 2 and 3 shows (see also ref. [21]).

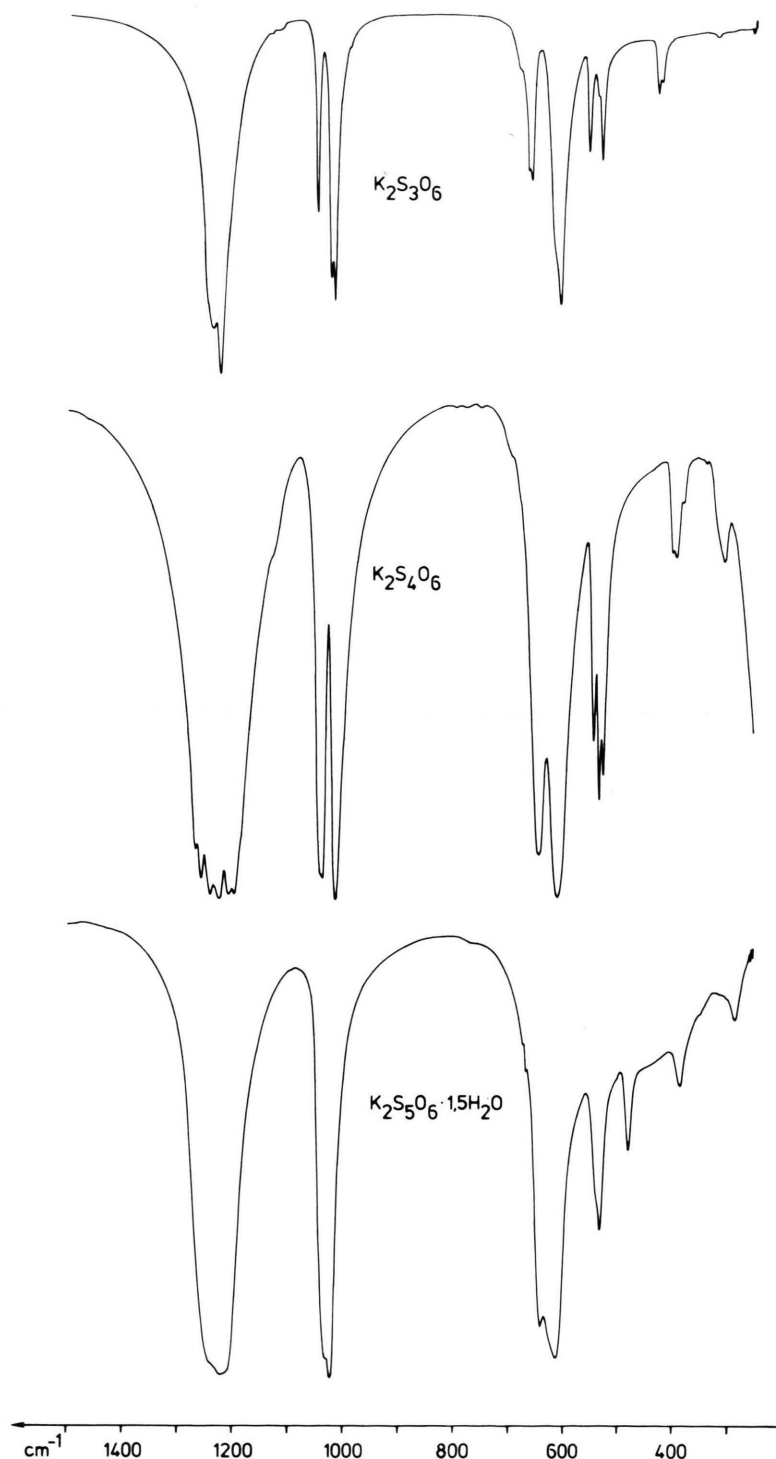


Fig. 3. Infrared spectra (KBr discs) of  $\text{K}_2\text{S}_3\text{O}_6$ ,  $\text{K}_2\text{S}_4\text{O}_6$ , and  $\text{K}_2\text{S}_5\text{O}_6 \cdot 1.5\text{H}_2\text{O}$ . For wavenumbers see Table I.



Both the aqueous Raffa sol and the evaporation residue were investigated by Raman spectroscopy. The lines observed for the solid at 471, 437, 393, 244, 217, 150, 80, 48 and 40  $\text{cm}^{-1}$  can all be assigned to  $\text{S}_8$  [22] excepting the 393  $\text{cm}^{-1}$  signal which is a typical line of polythionates and also observed in the case of  $\text{K}_2\text{S}_4\text{O}_6$  and  $\text{K}_2\text{S}_5\text{O}_6$  (see Fig. 4 and [23]). Most probably this line represents the stretching mode of a weak SS bond like the one neighboring to the  $\text{SO}_3^-$  group. The aqueous sol itself showed only lines at

471, 217 and 149  $\text{cm}^{-1}$  (Fig. 2) which are identical with the strongest Raman signals of the  $\text{S}_8$  molecule [22], although other sulfur-rich species like polythionates seem to contribute to the 471  $\text{cm}^{-1}$  line too.

X-ray powder diagrams of the evaporation residue of the Raffa sol and of the freshly precipitated sol (by NaCl) revealed only lines typical for  $\alpha\text{-S}_8$  and NaCl ( $\text{CuK}_\alpha$  radiation, 40 kV, exposure time 6 h at 20 °C).

Since the Raman spectra of the Raffa sol indicated

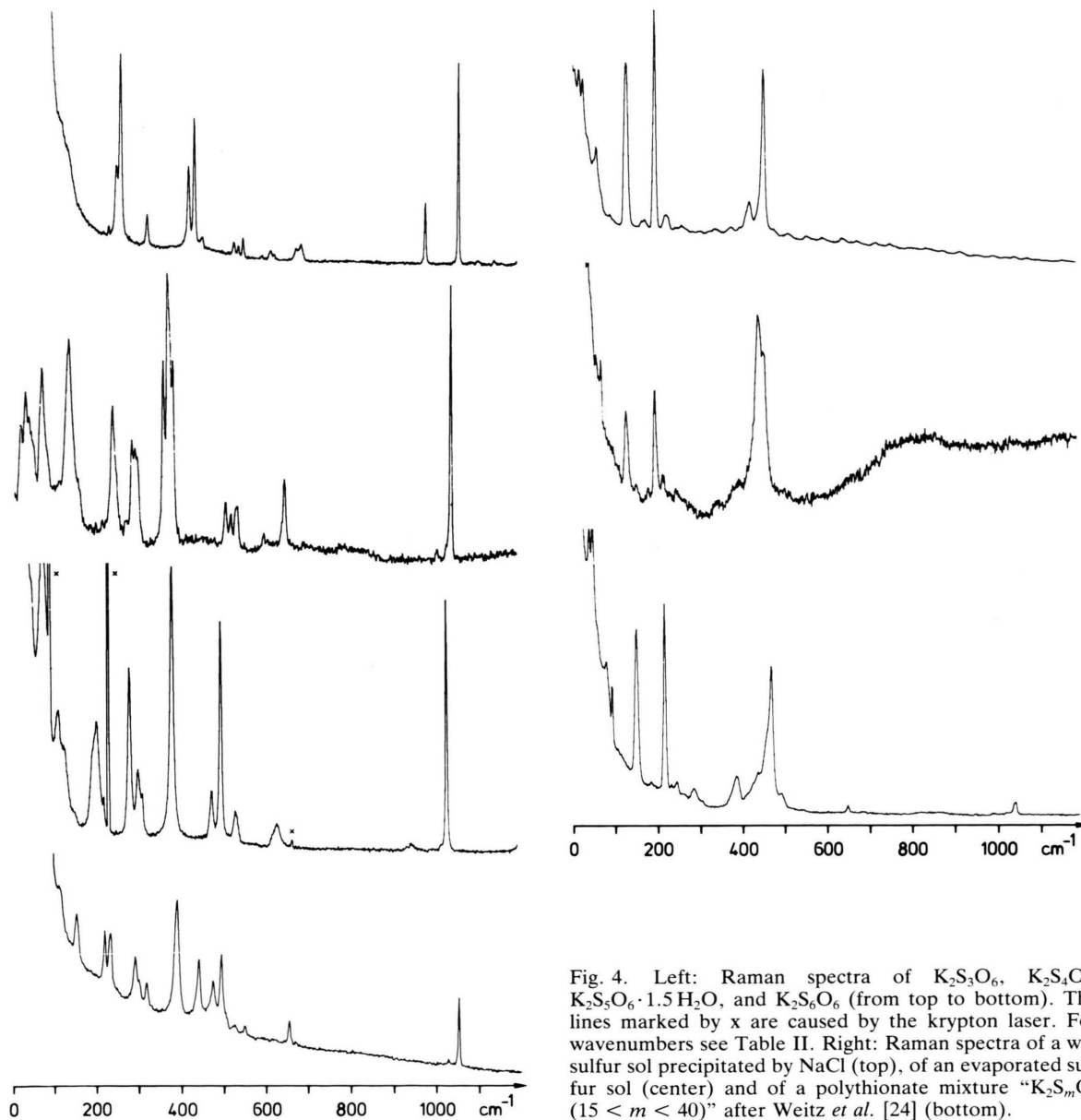


Fig. 4. Left: Raman spectra of  $\text{K}_2\text{S}_3\text{O}_6$ ,  $\text{K}_2\text{S}_4\text{O}_6$ ,  $\text{K}_2\text{S}_5\text{O}_6 \cdot 1.5\text{H}_2\text{O}$ , and  $\text{K}_2\text{S}_6\text{O}_6$  (from top to bottom). The lines marked by x are caused by the krypton laser. For wavenumbers see Table II. Right: Raman spectra of a wet sulfur sol precipitated by NaCl (top), of an evaporated sulfur sol (center) and of a polythionate mixture " $\text{K}_2\text{S}_m\text{O}_6$  ( $15 < m < 40$ )" after Weitz *et al.* [24] (bottom).

the presence of  $S_8$ , a reversed-phase HPLC analysis was carried out using octadecylsilane as a stationary phase and methanol as mobile phase [17, 18]. The freshly prepared and filtered sol was diluted (1:25) and directly introduced into the loop injector of the chromatograph.

The results presented in Fig. 5 and Table III demonstrate the presence of elemental sulfur  $S_n$  but in addition to  $S_8$  molecules other sulfur rings are present too. The order of decreasing concentrations is  $S_8 > S_7 > S_6 > S_9 > S_{12} > S_{10}, S_{11}, S_{13}, S_{14}, S_{15}$ . Using empirical calibration functions [18] the exact concentrations of four species have been determined as follows (in mg/l):  $S_6$  6.14,  $S_7$  9.92,  $S_8$  27.58,  $S_{12}$  0.22. Using these data the sum of all  $S_n$  concentrations can be estimated from Fig. 5 as 45 mg/l. Consequently, 20 ml of the undiluted Raffo sol prepared as described above contain about 22.5 mg of elemental sulfur  $S_n$  ( $n = 6-15$ ). Since the total sulfur content of the sol (85% of the dry-mass of 159.2 mg) has been found as 135.7 mg, most of the sulfur (113 mg or 83%) must be present in a form other than elemental!

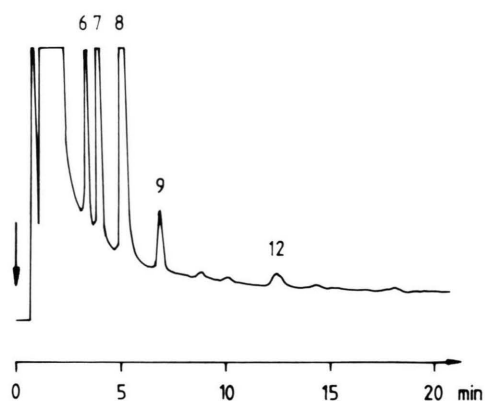


Fig. 5. HPLC analysis of a freshly prepared Raffo sol showing the presence of the sulfur homocycles  $S_n$  ( $n = 6-12$ ). The strongest peak near 1.5 min is caused by polythionates. Eluent:  $CH_3OH$ . The ordinate gives the UV absorbance at 254 nm.

The yellow flaky evaporation residue of the Raffo sol dissolved to a large extent in carbon disulfide on stirring for 4–6 h. On HPLC analysis the solution obtained showed all sulfur rings  $S_n$  with  $n = 6-17$ .

Table I. Infrared spectra of a Raffo sulfur sol and of various polythionates in the region  $250-1400\text{ cm}^{-1}$  (wavenumbers in  $\text{cm}^{-1}$ ; relative intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, b = broad, sh = shoulder). No anion absorptions were observed above  $1400\text{ cm}^{-1}$ .

Dried Raffo sol	$K_2S_3O_6$	$K_2S_4O_6$	$K_2S_5O_6 \cdot 1.5 H_2O$	$K_2S_6O_6$	$K_2S_mO_6$ [24]	Assignment
385 w		303 w 375 vw 390 w 397 vw	280 w 380 vw	385 w	388 w	$\delta(OSS)$ and $\nu(SS)$
460 vw 490 vw	420 vw 428 w		480 w		465 vw 494 vw	
525 w	530 w 548 vw 565 w 605 m 615 sh	525 w-m 532 w-m 543 w-m 610 s	530 m 610 s	505 vw 520 w 545 w 615 sh	522 w 545 w	$\delta_{as}(SO_3)$
640 vs	660 w 668 vw 1020 m 1026 m 1050 m	644 s	640 w	640 s, b	633 vs	
1030 sh, b 1050 vs, b		1015 s 1038 s 1042 sh	1020 s 1030 sh	1025 m 1045 s	1035 vs	$\nu_s(SO_3)$
1205 vs, b	1225 vs 1240 s 1250 sh	1195 1210 1225 } vs 1240 1258 1268 sh	1220 vs, b	1215 vs 1245 s 1260 m	1208 vs 1242 s	
						$\nu_{as}(SO_3)$

Raffo sol		$K_2S_3O_6$	$K_2S_4O_6$	$K_2S_5O_6 \cdot 1.5 H_2O$	$K_2S_6O_6$	$K_2S_mO_6$ [24]
wet	dry					
	41 w					39 s
	48 w	58 s			48 w	47 s
	80 w			74 m, b		80 m
				114 m, b	112 w	
149 m	150 vs		153 vs		153 m	150 vs
	194 w					183 vw
				206 s, b		
217 m	217 vs				220 m	216 vs
	244 w				233 m	243 w
		251 m	255 s			
		262 s		284 s	291 m	284 w
		325 w	300 s, b	303 m	299 sh	
			374 m		318 w	
			384 s	384 vs	389 s	384 m, b
			396 m			
	438 m	443 m			440 m	438 vw
		455 s				450 sh
471 s	472 vs			477 m	472 m	470 vs
476 sh			518 m	501 s		494 w
		530 vw		534 m	524 w	
		542 vw	546 m		550 w	
		552 vw				
		620 w		636 m, b		
			657 m		655 w	651 vw
		680 w				
		692 w				
		984 m		948 w	1040 vw	
		1062 vs	1045 s	1037 vs	1053 m	1047 w

Table II. Raman spectra of wet and dry Raffo sols and of various polythionates in the region 20–1200 cm<sup>-1</sup> (wavenumbers in cm<sup>-1</sup>; definition of intensities as in Table I).

The areas of the chromatographic peaks decreased in the order  $S_8 \gg S_7 \gg S_{12} > S_6 > S_9 > S_{15} > S_{10}, S_{14}, S_{16}, S_{17} > S_{11}, S_{13}$ . The peak areas of  $S_8$  and  $S_7$  accounted for 92% of the sum of all peak areas (Fig. 6).

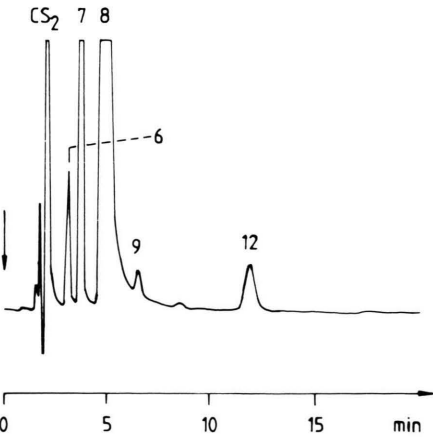


Fig. 6. HPLC analysis of an CS<sub>2</sub> extract of the evaporated Raffo sol showing the presence of  $S_6, S_7, S_8, S_9, S_{10}$ , and  $S_{12}$ . Eluent: CH<sub>3</sub>OH. The ordinate gives the UV absorbance at 254 nm.

Table III. HPLC analysis of a freshly prepared Raffo sol ( $t = 0$  h) and of the same sol after aging for 18 h and 45 h, respectively ( $t_R$  = retention time;  $c_i$  = concentration of species  $i$ ; death time 1.21 min).

	$t_R$ (min)	$S_6$	$S_7$	$S_8$	$S_{12}$
		3.24	3.82	5.04	12.38
$t = 0$	$c_i$ (mg/l)	6.14	9.92	27.58	0.22
$t = 18$ h	$c_i$ (mg/l)	2.91	7.09	25.94	0.20
$t = 45$ h	$c_i$ (mg/l)	–	3.34	16.03	0.19

3. Aging of Raffo sols

Hydrophilic sulfur sols are thermodynamically unstable both with respect to interconversion reactions resulting in stable species like  $S_8$  and with respect to hydrolytic reactions with the solvent. We have therefore studied extensively the change in molecular composition on standing at 20 °C as well as on extraction with organic solvents.

On standing of Raffo sols for several days at 20 °C pale-yellow flakes precipitated and settled on the bottom of the vessel. This sulfur-like material did not

show peptization in a large excess of water and dissolved only partly in  $\text{CS}_2$  the solution containing  $\text{S}_8$  (98%),  $\text{S}_7$  (1.9%) and traces of  $\text{S}_9$  and  $\text{S}_6$ . Basically the same result was obtained on extraction of the precipitate with methanol and subsequent HPLC analysis.

To study the time-dependend composition change two types of experiments were performed:

- the sol was stirred at 20 °C and at certain time intervals was analyzed for polythionates by IC and for elemental sulfur by HPLC,
- the sol was stirred with either cyclohexane (upper layer) or carbon disulfide (lower layer) to continuously extract elemental sulfur, and the organic layer was analyzed for  $\text{S}_n$  by HPLC and the aqueous phase for  $\text{S}_m\text{O}_6^{2-}$  by IC.

Type a) experiments showed that the concentration of polythionates  $\text{S}_m\text{O}_6^{2-}$  ( $m = 5-10$ ) increased from nothing to considerable values after 88.5 h (see Table IV and Fig. 1b). The concentration of penta-, hexa-, hepta- and octathionate increased steadily, while that of the higher polythionates ( $m = 9-14$ ) went through a maximum followed by a definite decrease after 3 days. When the stirring was continued for 8 days, the concentrations of hepta- and octathionate also started to decrease and only those of penta- and hexathionate went further up. Tetra-thionate was also formed but its concentration remained low at all times; the same holds for thiosulfate. Simultaneously the flaky sulfur-rich precipitate appeared which has already been mentioned above. The pH value of *ca.* 5.6 did not change within 5 days.

HPLC analysis of the Raffo sol after aging for 18 and 45 h, respectively, resulted in lower values for

the  $\text{S}_6$ ,  $\text{S}_7$ ,  $\text{S}_8$  and  $\text{S}_{12}$  content as compared to the freshly prepared sol (see Table III). The total  $\text{S}_n$  content ( $n = 6, 7, 8, 12$ ) of 20 ml sol decreased from 22.5 mg at  $t = 0$  via 18 mg after 18 h to 10 mg after 45 h. These results will be discussed below. The aging process could be greatly accelerated by addition of 2 or 3 drops of an aqueous iodine solution (0.05 mol( $\text{KI}_3$ )/l) to 1 ml of sol: after 1–2 h elemental sulfur had precipitated and penta-, hexa- and some heptathionate could be detected in the aqueous phase but no or only traces of higher polythionates.

Type b) experiments allowed to study the aging process under homogeneous conditions since no precipitate was observed when Raffo sols were stirred for up to 8 days with an excess of cyclohexane. These experiments had the additional advantage, that unstable sulfur rings ( $\text{S}_n$ ,  $n \neq 8$ ), which decompose to  $\text{S}_8$  or polymeric sulfur in the solid state, were preserved in the organic phase and could thus be determined quantitatively.

20 or 25 ml of Raffo sol were stirred with the ten-fold volume of cyclohexane at 20 °C for 8 days. Both phases remained clear. After certain time intervals HPLC analysis of the organic phase provided the concentrations of  $\text{S}_6$ ,  $\text{S}_7$  and  $\text{S}_8$  (see Fig. 7). The only other sulfur molecule detected was  $\text{S}_{12}$  the concentration of which was zero within the first 5 days and reached the value of  $\leq 0.4\%$  by weight of the total elemental sulfur ( $\text{S}_n$ ) after 8 days. The concentrations of  $\text{S}_6$ ,  $\text{S}_7$  and  $\text{S}_8$  increased with time and reached some kind of equilibrium value after 8 days (see

Table IV. Ion-chromatographic analysis of Raffo sols after aging at 20 °C for up to 88.5 h. Given are the chromatographic peak areas in arbitrary units.

	Aging time (h)				
	20.5	42.5	44.5	64.5	88.5
$\text{S}_5\text{O}_6^{2-}$	0.07	0.17	0.18	0.32	0.47
$\text{S}_6\text{O}_6^{2-}$	0.11	0.29	0.29	0.53	0.75
$\text{S}_7\text{O}_6^{2-}$	0.47	1.03	1.06	1.68	2.04
$\text{S}_8\text{O}_6^{2-}$	0.75	1.39	1.52	1.96	2.08
$\text{S}_9\text{O}_6^{2-}$	0.90	1.53	1.50	1.87	1.79
$\text{S}_{10}\text{O}_6^{2-}$	1.02	1.31	1.28	1.36	1.18
$\text{S}_{11}\text{O}_6^{2-}$	0.87	1.32	1.18	1.12	0.58
$\text{S}_{12}\text{O}_6^{2-}$	0.76	0.81	0.70	0.68	0.49
$\text{S}_{13}\text{O}_6^{2-}$	0.59	0.56	0.49	0.45	0.35
$\text{S}_{14}\text{O}_6^{2-}$	0.45	0.41	0.34	0.32	0.26

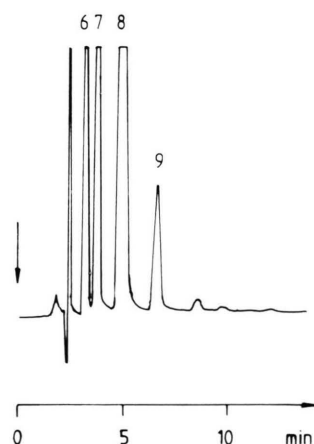


Fig. 7. HPLC analysis of the cyclohexane extract of a Raffo sol showing the presence of  $\text{S}_n$  molecules ( $n = 6-10$ ). The first large peak represents the solvent  $\text{C}_6\text{H}_{12}$ .

Table V). 20 ml of Raffo sol contained 135.7 mg total sulfur (see above). The amount of  $S_n$  extracted after 9 days amounted to 39.5 mg leaving 96.2 mg S in the aqueous phase. A sulfur determination of the aqueous phase (by bromine oxidation to sulfate and titration with barium perchlorate) resulted in 95.5 mg S. With other words, only 0.7 mg S had escaped the determination.

The composition of the aqueous phase was monitored by IC and it was observed that the concentra-

Table V. Concentration of sulfur rings  $S_n$  (mg/l) in the cyclohexane phase (200 ml) during the extraction of a Raffo sol (20 ml) at 20 °C.

Extraction time (h)	$S_6$	$S_7$	$S_8$	$S_{12}$	$\Sigma S_n$ (mg)
0.5	11.9	26.0	54.6	0	18.5
19.5	14.6	31.2	119.6	0	33.1
42.5	17.3	33.5	123.7	0	34.9
65.0	19.0	34.9	126.8	trace	36.1
89.0	20.8	36.3	130.9	trace	37.6
164.5	22.8	37.7	136.9	0.3	39.5

Table VI. Concentrations of polythionates in the aqueous phase of a Raffo sol during extraction by cyclohexane at 20 °C. Given are the chromatographic peak areas in arbitrary units.

Extraction time (d)	$S_5O_6^{2-}$	$S_6O_6^{2-}$	$S_7O_6^{2-}$	$S_8O_6^{2-}$	$S_9O_6^{2-}$
0	0	0	0	0	0
1	0.44	0.72	1.73	1.75	1.24
4	1.20	1.77	2.35	1.43	0.80
7	1.95	2.56	2.56	1.42	0.81
8	2.17	2.69	2.53	1.43	0.81

tions of the lower polythionates  $S_mO_6^{2-}$  ( $m = 5, 6$ ) steadily increased within 8 days, while those of hepta-, octa- and nonathionate went through maximum values, the maxima being reached as earlier as longer the sulfur chain (see Table VI).

The extractions with carbondisulfide yielded basically the same results. The  $S_n$  content of the  $CS_2$  phase increased first rapidly, later slowly, and after 162 h 47.7 mg  $S_n$  ( $n = 6, 7, 8, 12$ ) had been extracted from 20 ml of Raffo sol. The sulfur content of the remaining aqueous phase was determined as 88.4 mg resulting in a total sulfur value of 136.1 mg as compared to the 135.7 mg expected from the S content of the evaporation residue. The concentrations of the polythionates in the aqueous phase changed in the very same way as in the extraction experiments with cyclohexane. In contrast to the latter, however, the  $CS_2$  phase became turbid after stirring with the sulfur sol for several days. In addition to the sulfur rings mentioned, traces of  $S_9$ ,  $S_{10}$  and  $S_{11}$  could also be detected by HPLC but have not been determined.

#### 4. Properties of Long-Chain Polythionates

After it had become obvious that Raffo sols contain long-chain polythionates, we found it useful to study the properties of these compounds independently. For this purpose, a polythionate mixture supposed to consist of  $K_2S_mO_6$  with  $15 < m < 40$  was prepared from potassium thiosulfate and  $S_2Cl_2$  in concentrated hydrochloric acid following the procedure of Weitz *et al.* [24]. The IC analysis of the product obtained revealed the presence of  $S_mO_6^{2-}$  anions with  $n = 4 \cdots 18$  (see Fig. 8a), longer-chain anions

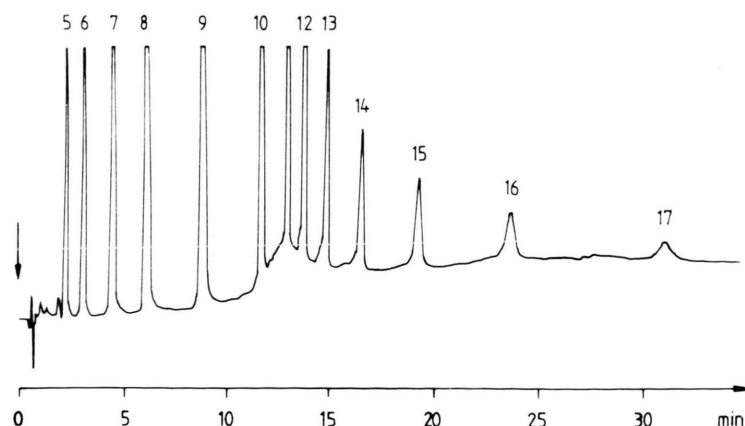


Fig. 8. Ion-chromatographic detection of the polythionates  $S_nO_6^{2-}$  ( $m = 5-17$ ) in " $K_2S_mO_6$  ( $15 < m < 40$ )" prepared after Weitz *et al.* [24]. Eluent:  $CH_3CN/H_2O$  (30/70 v/v), detector wavelength 240 nm.

Time (d)	$S_5O_6^{2-}$	$S_6O_6^{2-}$	$S_7O_6^{2-}$	$S_8O_6^{2-}$	$S_9O_6^{2-}$	$S_{10}O_6^{2-}$	$S_{11}O_6^{2-}$	$S_{12}O_6^{2-}$
0	0.56	0.49	0.82	1.17	1.14	0.68	0.83	0.71
2	0.67	0.67	1.23	1.37	1.07	0.63	0.57	0.32
7	0.93	0.99	1.47	1.04	0.58	0.25	0.39	0.07

Table VII. Chromatographic peak areas (in arbitrary units) of eight polythionates as a function of the aging time (20 °C, aqueous solution).

were probably present too but could not be detected with the present version of our IC analysis. After standing of the solution for up to 8 days at 20 °C the composition had changed similarly as observed for Raffa sols: the relative concentrations of  $S_5O_6^{2-}$  and  $S_6O_6^{2-}$  had increased while that of anions with more than seven sulfur atoms had decreased (Fig. 8b; Table VII).

The infrared spectrum of " $K_2S_mO_6$  ( $15 < m < 40$ )" shown in Fig. 3 is very similar to the one of the evaporated sol indicating that both materials mainly consist of long-chain polythionates.

Extraction of the solid salt  $K_2S_mO_6$  (205 mg) by cyclohexane (200 ml) for 2 h at 20 °C resulted in a solution of only 2.0 mg  $S_n$  ( $n = 6, 7, 8$ ) as determined by HPLC. However, when 205 mg  $K_2S_mO_6$  were dissolved in 20 ml  $H_2O$  and the milky solution extracted by 200 ml cyclohexane for up to 8 days, the sulfur content of the organic phase increased as follows:

	$S_6$ (mg)	$S_7$ (mg)	$S_8$ (mg)	total S (mg)
1 day	4	1	14	19
2 days	8	5	49	62
8 days	9	6	58	73

It is obvious that  $S_6$ ,  $S_7$  and  $S_8$  are formed from  $S_mO_6^{2-}$  as will be discussed below. Except for the first measurement, the  $S_6:S_7:S_8$  ratio remained approximately constant during the extraction.

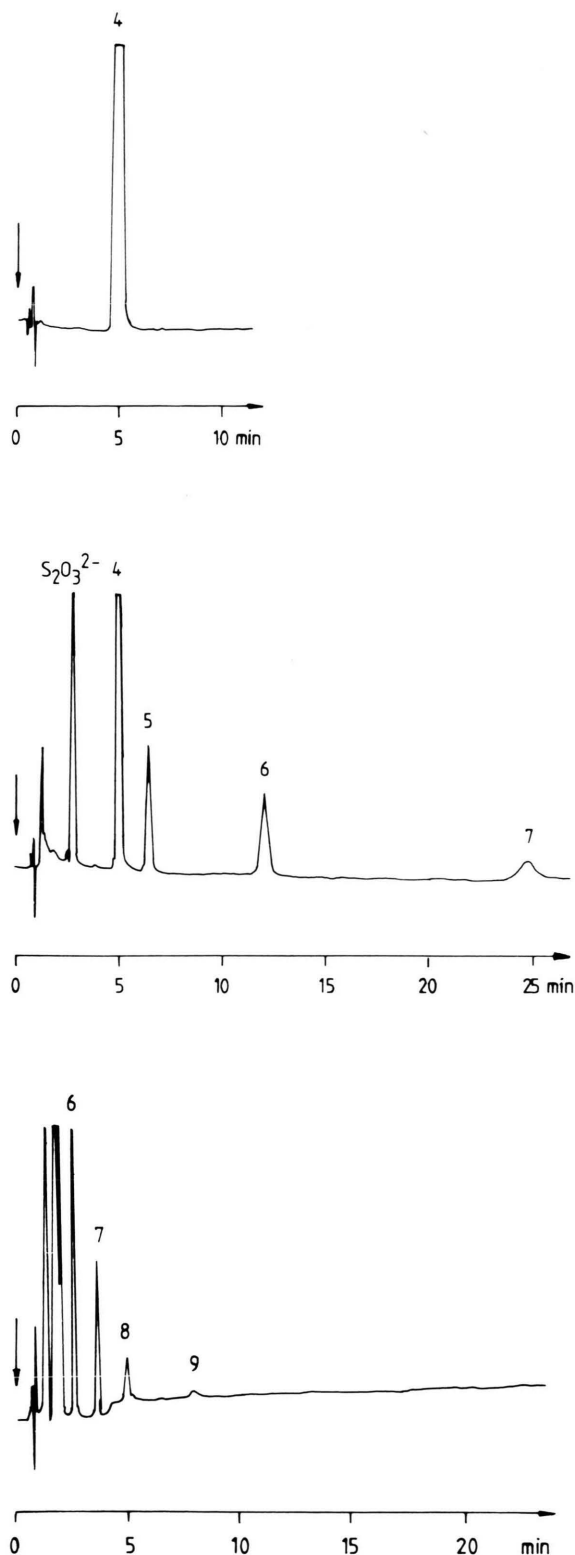
## 5. Irradiation of Aqueous Polythionates

Hydrophilic sulfur sols are light-sensitive [2] and direct illumination by sun-light accelerates the aging process which is characterized by sulfur precipitation and formation of short-chain polythionates [8]. To our knowledge, the photochemical decomposition of aqueous polythionates has never been investigated. Therefore, we have studied both the reaction products and the wavelength dependence of the photo-decomposition of tetra- and pentathionate in water

at 20 °C using a high-pressure mercury immersion lamp in combination with various optical filters [25, 26]. Two types of experiments have been carried out. In the first type the lamp and its water-cooled jacket (made from either quartz or borosilicate glass) were immersed into the tetra- or pentathionate solution. Using the quartz jacket the aqueous phase was exposed to the full power of the lamp (40 W in the range 200–600 nm) while the borosilicate glass jacket (DURAN 50) transmitted only above 290 nm. When an aqueous solution of pure  $K_2S_4O_6$  (477 mg/l) was irradiated for 10 min with 200–600 nm radiation the solution smelled strongly after  $H_2S$ , sulfur precipitated, and an IC analysis showed the presence of sulfite, thiosulfate and all polythionates  $S_mO_6^{2-}$  with  $m = 4-9$  (see Fig. 9). Thiosulfate was definitely the main product, and the concentrations of the polythionates decreased with increasing chain-length. About 75% of the initial  $S_4O_6^{2-}$  had disappeared. An HPLC analysis of the precipitated sulfur showed the presence of  $S_8 \gg S_7$ ,  $S_6 > S_9$ ,  $S_{12} > S_{10}$ , the concentrations of which decreased in that order. Application of the 290–600 nm radiation to an aqueous  $K_2S_4O_6$  solution (410 mg/l) resulted in a much slower decomposition although the same products were formed. Using empirical calibrations [19] the results in Table VIII were obtained which show that after 50 min only 40% of the initial  $S_4O_6^{2-}$  had decomposed. Thiosulfate was again the main product; the concentrations of sulfite and hepta-, octa-, and nonathionate have not been determined.

Table VIII. Photolysis of potassium tetrathionate in water at 20 °C by 290–600 nm radiation. Initial concentration: 410 mg  $S_4O_6^{2-}$ /l. Concentrations in mg/l.

t (min)	$c(S_2O_6^{2-})$	$c(S_4O_6^{2-})$	$c(S_5O_6^{2-})$	$c(S_6O_6^{2-})$
10	10	381	8	10
20	36	340	14	12
50	74	251	15	8



When the irradiation time was extended to 5 h (using the DURAN jacket) the concentrations of all higher ( $m > 4$ ) polythionates decreased to very low values and thiosulfate also started to disappear in agreement with the well known hydrolysis of tetrathionate yielding sulfite, sulfate and elemental sulfur [27]; thiosulfate is an intermediate in this reaction [27].

The photolysis of  $K_2S_5O_6$  in water (500 mg/l) applying either 200–600 or 290–600 nm radiation for 10 min resulted in the same products as in the case of tetrathionate. The main products were  $S_2O_3^{2-}$  followed by  $S_4O_6^{2-}$ ,  $S_5O_6^{2-}$ , and  $S_6O_6^{2-}$ . Sulfite was formed too, and the precipitated sulfur consisted of  $S_8$  mainly.

The second type of experiments was supposed to demonstrate which wavelengths are effective in the decomposition of tetrathionate. In this case the lamp with quartz cooler was mounted in a horizontal metal housing. The sample contained in an Erlenmeyer flask was illuminated through a window in the lamp house. This window could be covered by optical filters (SFK 18 through 22a by Schott, Mainz) which transmit at 313, 365, 436, 546, and 578 nm, respectively (halfwidths *ca.* 30 nm). The distance from the mercury lamp to the bottom of the flask amounted to *ca.* 5 cm. The duration of the photolysis was 1 h each, and IC and HPLC analyses were applied. In all experiments the tetrathionate solution (250 ml; 525 mg/l) remained clear and the temperature did not exceed 30 °C. Only with the 313 nm filter a slight decomposition (less than 1%) to pentathionate could be observed. The only other decomposition product observed were traces of  $S_8$ . Radiation of wavelength  $> 350$  nm was completely ineffective, which can be understood from the UV absorption spectrum of aqueous  $S_4O_6^{2-}$  which shows only a very weak continuous absorbance at wavelengths of  $> 300$  nm [28].

## 6. Discussion

Our results show that freshly prepared Raffa sols contain about 1125 mg/l of elemental sulfur in the form of various cyclic  $S_n$  molecules with  $n = 6–15$ ; of

Fig. 9. Formation of thiosulfate and of polythionates  $S_mO_6^{2-}$  ( $m = 5–9$ ) on irradiation of aqueous tetrathionate at 20 °C; top: prior to irradiation, center and bottom: after irradiation (chromatographic analysis with two different eluent compositions). Ordinate: UV absorbance at 240 nm.



these  $S_8$  is by far the most frequent species. The solubility of orthorhombic  $\alpha$ - $S_8$  in water at 20 °C amounts to only 5  $\mu\text{g/l}$  [29]. Since the elemental sulfur content of the sol is about 225,000 times this figure, this sulfur must be linked to some hydrophilic material which keeps it in solution.

The hydrophilic substance must also have a high sulfur content since only 17% of the total sulfur content of the sol (6790 mg/l) has been identified as elemental sulfur. The only compounds which can explain all the experimental facts are long-chain polythionates which in water will form globular micelles because of the hydrophobic interaction of the sulfur chain with the polar solvent resulting in the observed Tyndall beam. In these micelles the hydrophobic sulfur chains are stored in the core of the globule while the hydrophilic sulfonic acid groups will be concentrated on the surface where they are responsible for the overall hydrophilic character and the negative ionic charge of the whole globule. These globules will repel each other which stabilizes the sol, but addition of a high concentration of univalent cations like  $\text{Na}^+$  (or of multivalent cations in lower concentrations [2, 9]) will precipitate the particle as less soluble “salts”. Resuspension of the sodium “salt” in an excess of water results in peptization.

It seems reasonable to assume that the amorphous sulfur-rich core of the globules dissolves a certain amount of homocyclic sulfur rings ( $S_n$ ,  $n = 6, 7, 8, \dots$ ) which in this way are kept in a liquid-like state, and therefore do not interconvert to give  $S_8$  which would easily crystallize. This sulfur mixture is protected from the attack of the surrounding water.

The surface of the micelles will be covered by a layer of water containing a certain amount of  $\text{H}_3\text{O}^+$  or  $\text{Na}^+$  cations. This structural model (Fig. 10) explains all observations reported above and in the literature.

The chemical composition of  $\text{Na}_{1.64}\text{S}_{34.5}\text{O}_6 \cdot 1.0 \text{ NaCl}$  can now be rewritten as  $\text{Na}_{1.64}\text{S}_{28.6}\text{O}_6 \cdot 5.9/n S_n \cdot 1.0 \text{ NaCl}$  accounting for the 83% polythionate sulfur and 17% elemental sulfur,  $S_n$ . Since the NaCl will be dissolved in the aqueous phase, the sol particles consist of 89.2% S, 3.04% Na, and 7.74% O. The “missing” 0.36 mol cations may be either a consequence of experimental errors or may be present as  $\text{H}_3\text{O}^+$  which would result in a hydrogen content of only 0.2% which is close to the detection limit.

The average chain length of 28.6 S atoms of the polythionate constituent of Raffa sol seems to be

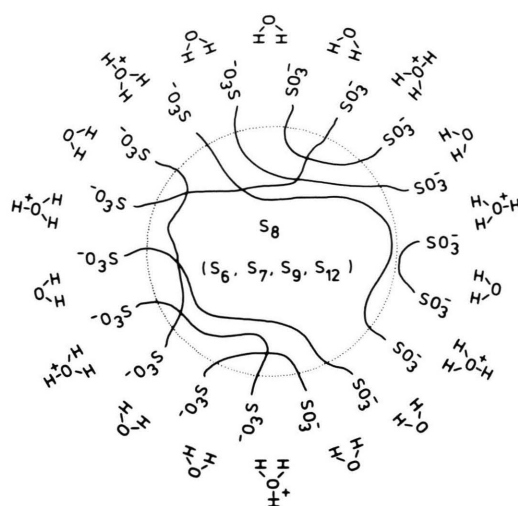
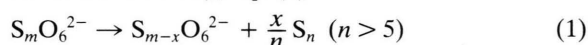


Fig. 10. Globule model of the particles in Raffa sol. The main constituents are long-chain polythionates of average chain length  $m = 29$ , which form a micelle in the core of which elemental sulfur ( $S_n$ ,  $n = 6-12$ ) can be dissolved. The hydrophilic surface of the globule is hydrated, and  $\text{H}_3\text{O}^+$  as well as  $\text{Na}^+$  cations may be present in the water layer. The  $S_n$  molecules make up for about 17% of the total sulfur content.

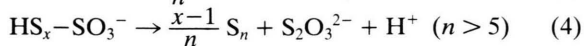
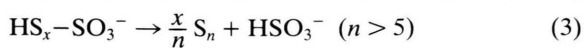
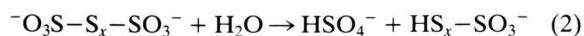
sufficient to make these compounds so sparingly soluble that micelle formation takes place. These micelles are, however, not stable but slowly decompose with formation of lower polythionates (detected by IC) and more elemental sulfur (which precipitates from the solution); eq. (1):



The short-chain polythionates are soluble in water and do not form micelles. Therefore, the elemental sulfur content of the sol drops (see Table III) and part of the sulfur precipitates both as rings  $S_n$  (soluble in  $\text{CS}_2$ ) and as insoluble polymeric sulfur. This polymeric  $S_\infty$  must be formed by decomposition of unstable  $S_n$  ( $n \neq 8$ ) molecules in a secondary reaction [30] since in the presence of cyclohexane no  $S_\infty$  is observed but all  $S_n$  species dissolve in the organic phase. It is obvious that from polythionates with 28 or more S atoms small and large rings  $S_n$  ( $n = 6 \dots 17$ ) and short-chain as well as medium-sized polythionates  $S_m O_6^{2-}$  ( $m = 5 \dots 14$ ) will be formed by reaction (1), as have in fact been detected by HPLC and IC, respectively. This decomposition (disproportionation) will be catalyzed by traces of nucleophiles like



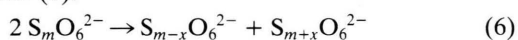
$\text{HS}^-$  or  $\text{S}_2\text{O}_3^{2-}$  which may be formed by the slow hydrolysis of the polythionates [27]:



Equations (2), (3) and (4) provide an alternative route for the disproportionation of polythionates with formation of elemental sulfur [31], but reaction (2) is known to be slow at 20 °C [27]. The mechanistic implication of reactions like (1) and (3) have been discussed elsewhere [32, 33].

It has been reported [34], that freshly prepared Raffo sols do not consume iodine, while after aging a considerable iodine consumption can be observed. Reactions (2) through (5) provide an explanation since a number of reduced sulfur compounds are formed which all are oxidized by  $\text{I}_2$  in water at 20 °C. Sulfanemonosulfonic acids  $\text{HS}_x\text{SO}_3\text{H}$  are oxidized by  $\text{I}_2$  to give polythionates  $\text{S}_{2x}(\text{SO}_3\text{H})_2$  [35]. However, iodine may also oxidize lower polythionates more rapidly to sulfate than long-chain anions.

If equation (1) is a major decomposition reaction for long-chain polythionates, then species with less than six sulfane sulfur atoms should accumulate because of the thermodynamic instability of  $\text{S}_n$  molecules with  $n < 6$ . This is exactly what has been observed: the concentration of  $\text{S}_5\text{O}_6^{2-}$  and  $\text{S}_6\text{O}_6^{2-}$  increase on aging, while long-chain species decrease. Medium-sized anions first increase, too, but later seem to be destroyed by reactions of type (6), which also favor the accumulation of short-chain species since only  $\text{S}_{m+x}\text{O}_6^{2-}$  with  $m+x > 8$  will enter reaction (1):



In the presence of water cyclooctasulfur dissolved in organic solvents is in equilibrium with about 0.8%  $\text{S}_7$  and 0.3%  $\text{S}_6$  at 20 °C [36]:



However, the  $\text{S}_6/\text{S}_8$  and  $\text{S}_7/\text{S}_8$  ratios observed in this work are much higher and show that the mentioned equilibrium (7) is established slowly. In particular the elemental sulfur dissolved in the hydrophobic core of the micelles is surprisingly rich in  $\text{S}_6$  and  $\text{S}_7$  ( $\text{S}_6:\text{S}_8 = 0.22$ ;  $\text{S}_7:\text{S}_8 = 0.36$  by weight; see Table III). The evaporation residue also contains much more  $\text{S}_n$  ( $n \neq 8$ ) molecules as what might have been expected

from the instability of these species. It is therefore not surprising that hydrophilic sulfur sols are much more reactive than pure finely divided  $\text{S}_8$  since both  $\text{S}_n$  ( $n \neq 8$ ) and  $\text{S}_m\text{O}_6^{2-}$  species are more reactive than  $\text{S}_8$ . On prolonged aging or drying or heating the unstable species decompose and finally only  $\alpha\text{-S}_8$  as well as some lower polythionates ( $m = 4, 5$ ) will be left as the dominating compounds.

## 7. Nature of the “Elemental Sulfur” ( $\text{S}^0$ ) Produced by Certain Sulfur Bacteria

It has been known for more than 100 years [37] that certain sulfur bacteria living in aquatic environments containing sulfide ( $\text{HS}^-$ ), thiosulfate, or tetrathionate under certain conditions produce sulfur-like transparent droplets (“globules”) which are stored within or outside the bacterial cell [38]. For photographs of sulfur-containing bacteria see, for instance, ref. [39–43]. These droplets reach diameters of up to 1  $\mu\text{m}$  [38, 42, 43] and seem to consist of sulfur in the zero oxidation state ( $\text{S}^0$ ), but the exact molecular nature has long been unknown. The spherical or ellipsoidal globules [38, 42–44] are at least partly soluble in acetone, chloroform, ethanol, and carbondisulfide [44–47], are of white or pale-yellow color [37], show a high index of refraction [39–43], and have been described as liquid-like [39] and amorphous (no X-ray diffraction) [39]. When allowed to stand in the wet state [39] or on drying [48] these sulfur globules eventually convert into crystalline  $\alpha\text{-S}_8$ .

Very recently we have shown by HPLC and IC analysis that the extracellular sulfur globules produced by *Thiobacillus ferrooxidans* have a micelle structure very similar to the Raffo sols; these globules contain  $\text{S}_8$ ,  $\text{S}_6$ ,  $\text{S}_7$ ,  $\text{S}_9$ , and  $\text{S}_{12}$  as well as polythionates  $\text{S}_m\text{O}_6^{2-}$  with  $m$  ranging from 4 to 17 [20]. For the following reasons we believe that a similar elemental sulfur-polythionate micelle structure can also be assumed for the globules produced by certain other bacteria living in neutral or acidic environments:

- Polythionates have been detected in the media of many *Thiobacilli* species [49, 50] as well as in media of *Chlorobium vibrioforme f. thiosulfatophilum* [51] and *Chlorobium limicola thiosulfatophilum* 6230 [52].
- The globules show a high sulfur content but do not crystallize for hours at 20 °C in the presence of water. Therefore, they cannot be liquid sulfur

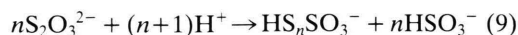
which despite its tendency to supercooling is not stable at 20 °C. Only a mixture in which S<sub>8</sub> is not dominating will remain liquid at 20 °C for longer periods of time.

- c) The globules have been described as pale-yellow or white which fits the properties of Raffa sol particles whereas supercooled liquid sulfur is of deep-yellow color.
- d) Liquid sulfur is an extremely hydrophobic material while bacterial sulfur globules are hydrophilic [40] like Raffa sol particles. Hydrophilic properties and a high sulfur content can only be realized by a long sulfur chain with polar end groups as in polythionate anions.
- e) On drying or aging sulfur globules crystallize partly as α-S<sub>8</sub> [39, 48] as do Raffa sols.
- f) The density of sulfur globules produced by two types of *Chromatium* has been determined as 1.22 g·cm<sup>-3</sup> [47] which is much lower than the density of liquid sulfur (extrapolated to 20 °C) of 1.85 g·cm<sup>-3</sup>. The micelle structure with an electrical double layer on the surface and a relatively high water content is qualitatively in agreement with the experimental density.
- g) It has been observed [53] that sulfur (S<sup>0</sup>) produced by *Thiobacillus denitrificans* does not move in electrophoresis experiments. This can be explained by the very high molecular weight of hydrophilic sol particles compared with the molecular mass of the short-chain polythionates like S<sub>4</sub>O<sub>6</sub><sup>2-</sup> which were used as reference materials [53]. The same authors found that the S<sup>0</sup> decomposed in the presence of iodine with formation of soluble polythionates which is exactly the behavior of Raffa sol particles as described above.
- h) Long-chain polythionates will react with cyanide in a similar way as elemental sulfur and will also exhibit a strong UV absorption. This can be expected from the corresponding reactions [54] and the UV spectra [28] of S<sub>4</sub>O<sub>6</sub><sup>2-</sup>, S<sub>5</sub>O<sub>6</sub><sup>2-</sup>, and S<sub>6</sub>O<sub>6</sub><sup>2-</sup>:
 
$$\begin{aligned} \text{S}_x\text{O}_6^{2-} + (x-3)\text{CN}^- + \text{H}_2\text{O} &\rightarrow \\ \text{S}_2\text{O}_3^{2-} + (x-3)\text{SCN}^- + \text{H}_2\text{SO}_4 \end{aligned} \quad (8)$$

Both types of compounds may therefore easily be mistaken for each other especially in complex mixtures.
- i) It may seem a contradiction that bacterial S<sup>0</sup> dissolves in CS<sub>2</sub> while long-chain polythionates do not. However, it has been observed by many microbiologists that the CS<sub>2</sub> extraction of S<sup>0</sup> is dif-

ficult and takes many hours which is understandable since the aging process is slow (see Table V). Only the S<sub>n</sub> molecules produced will dissolve in CS<sub>2</sub> while the lower polythionates remain in the aqueous phase.

The formation of long-chain polythionates in bacteria and in Raffa sols most probably proceeds by reactions of the following type [31, 56]:



Reaction (11) is reversible and can be used to reduce the particle size of Raffa sols by treatment with sulfite [55]; it may also serve for the re-activation of the S<sup>0</sup> sulfur in bacteria since it transforms poorly soluble higher polythionates in better soluble smaller anions.

The so far only poorly characterized sulfanemono-sulfonic acids HS<sub>n</sub>SO<sub>3</sub>H [35] obviously are key intermediates and should therefore be studied carefully in the future.

## 8. Experimental

### Materials

The reference materials K<sub>2</sub>S<sub>3</sub>O<sub>6</sub> [57], K<sub>2</sub>S<sub>4</sub>O<sub>6</sub> [57], K<sub>2</sub>S<sub>5</sub>O<sub>6</sub> [57], and K<sub>2</sub>S<sub>6</sub>O<sub>6</sub> [57] were prepared by published procedures (and their purity checked by infrared spectroscopy) using SCl<sub>2</sub> (freshly distilled with addition of PCl<sub>3</sub> [57]), K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (Fluka, purum), Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5 H<sub>2</sub>O (Merck, reinst), S<sub>2</sub>Cl<sub>2</sub> (techn.), and aqueous HCl (36%, Fluka, analytical grade). All organic solvents were distilled from drying agents: CCl<sub>4</sub>(P<sub>4</sub>O<sub>10</sub>), CH<sub>3</sub>OH(MgSO<sub>4</sub>), CS<sub>2</sub>(P<sub>4</sub>O<sub>10</sub>); C<sub>6</sub>H<sub>12</sub> was of analytical grade.

### Methods

The equipment used for IC [19, 20], HPLC [17, 18, 30] and Raman spectroscopy [58] as well as the photolysis apparatus [15, 26] have been described elsewhere. Infrared spectra were recorded by a Perkin-Elmer 580 B grating spectrometer (180–5000 cm<sup>-1</sup>) equipped with data processing terminal. The centrifuge operated at 5200 r.p.m. (9000 g).

Solutions analyzed by IC or HPLC were filtered through an Acro LC 13 filter (0.45 μm). To further protect the chromatographic column used for the IC analysis both a solvent saturation column (l = 10 cm; installed before the loop injector) and a guard-column (after the injector) were used; both columns

contained the same Spher C 18 material as the separation column. Acetonitrile concentrations of either 22 or 30% by volume were applied; the UV detector operated at a wavelength of 240 nm. When sulfur sols after aging were injected for IC analysis it was occasionally observed that the peaks due to penta- till octathionate split into two peaks (see, for instance, Fig. 1b). Sometimes the second peaks showed up as shoulders only. These additional peaks at higher retention times disappeared when the sol was diluted (1:5) prior to analysis. Obviously, overloading of the column by too high a total concentration of polythionate is responsible for the

observed peak splittings. Furthermore, the retention times of the polythionates turned out to depend on the sample concentration. Dilution by water (doubly distilled) resulted in an increase of the retention time. Reference and sample concentrations should therefore not be too different.

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