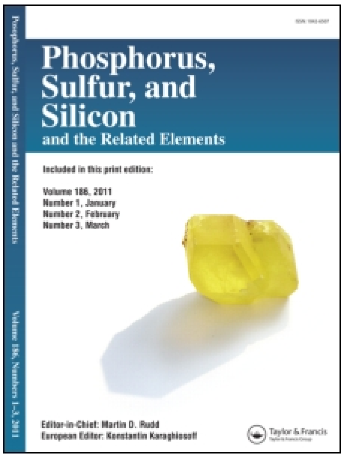

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SOLUBILIZATION OF SULFUR IN AMMONIA AND EQUILIBRIUM COMPOSITION OF SULFUR AMMONIA SOLUTIONS

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To cite this Article Seelert, S. and Schindewolf, U.(1991) 'SOLUBILIZATION OF SULFUR IN AMMONIA AND EQUILIBRIUM COMPOSITION OF SULFUR AMMONIA SOLUTIONS', Phosphorus, Sulfur, and Silicon and the Related Elements, 55: 1, 239 — 247

To link to this Article: DOI: 10.1080/10426509108045946

URL: http://dx.doi.org/10.1080/10426509108045946

Phosphorus, Sulfur, and Silicon, 1991, Vol. 55, pp. 239–247
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SOLUBILIZATION OF SULFUR IN AMMONIA AND EQUILIBRIUM COMPOSITION OF SULFUR AMMONIA SOLUTIONS

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(Received April 2, 1990)

Sulfur ammonia solutions (SAS) were separated by anion exchange HPLC into the anions S_4N^- and S_3N^-, S_3^- (and its dimer S_6^{2-}), and $S_xNH_2^-$ (sulfur in oxidized, in reduced and in neutral form resp.). The analysis of the absorption spectra of SAS yields the concentrations of the individual components and leads to the assignement $x = 4$ in $S_xNH_2^-$. The time dependence of the HPLC chromatograms and of the optical spectra of freshly prepared SAS reveals that $S_4NH_2^-$ is the primary species in the dissolution process which partly disproportionates to S_4N^- and S_3^- and to S_3N^- as another intermediate.

Key words: Anion exchange, HPLC, liquid ammonia, sulfur, sulfur ammonia solutions, UV/VIS spectroscopy.

INTRODUCTION

Recent spectroscopic investigations by Chivers *et al.*,[1] Lelieur *et al.*,[2–5] and ourselves[6–7] led to the conclusions, that on solubilization of sulfur in ammonia by disproportionation a series of anionic components are formed which contain sulfur in oxidized and in reduced states. The main components are S_4N^- and S_3N^- (formal oxidation state of sulfur $\frac{1}{2}$ and $\frac{2}{3}$ resp.) as well as S_3^- (in equilibrium with its dimer S_6^{2-}; formal oxidation state of both $-\frac{1}{3}$). In addition evidence was given for a compound of zero sulfur oxidation state,[4,5] assigned as $S_{2,am}$, which is present in relatively high concentration.

We succeeded recently to separate the components of sulfur ammonia solutions (SAS) by anion exchange HPLC.[8,9] By comparison of the UV/VIS-absorption spectra of the individual chromatographic peaks with those of known pure compounds we could confirm the presence of the anionic species with sulfur in oxidized and in reduced form given above. An additional chromatographic peak is due to an anion with absorption maxima at 300 and 420 nm. This anion in the separated form is unstable (see below) for its spectrum changes with time to that of a normal SAS; therefore it contains sulfur in zero oxidation state; we assigned it as $S_xNH_2^-$, formed by attack of ammonia on neutral sulfur. We could not detect by HPLC as prominent components in SAS uncharged (described[4,5] as $S_{2,am}$) or cationic species which all would pass the anion exchange column as a sharp peak without delay. Under some experimental conditions we observe a weak tail preceding the sharp anionic peaks (we think this tail to be due to uncharged decay or reaction products of the separated species). Neither could we detect (in agreement with Lelieur[4]) the anion S_7N^- described before by us[7] and others.[1]

In the following we will try to estimate the relative concentrations of the main species identified in SAS, to estimate the number x in $S_xNH_2^-$, its maximum extinction coefficients (ε_{420} and ε_{300}), and to give information on the process of solubilization of sulfur in ammonia and on the establishment of the final equilibrium. The preparation of the solutions, the high performance anion exchange chromatography, and UV/VIS-spectroscopy were done with the techniques described before.[8,9]

For the evaluation of the spectra of SAS we make use of the normalized spectra of S_3^-, S_4N^-, and S_3N^- as obtained from the separated chromatographic peaks or from pure synthesized compounds[8] and of the maximum extinction coefficients of their main absorption bands determined by us or others[9] (S_3^-: $\varepsilon_{610} = 5100$, $\varepsilon_{330} = 1600$ (shoulder), $\varepsilon_{270} = 6200$ (shoulder); S_4N^-: $\varepsilon_{578} = 16000$; S_3N^-: $\varepsilon_{462} = 6500$, $\varepsilon_{290} = 3700$ (all in $M^{-1}\ cm^{-1}$)).

The given extinction coefficients indicate that the three absorption bands of SAS around 300 (at low concentrations only a shoulder), between 420 and 460 and around 590 nm (Figure 1) are due to an overlap of the absorptions of S_3^-, S_3N^- and $S_xNH_2^-$, of S_3N^- and $S_xNH_2^-$, and of S_4N^- and S_3^- resp. Of course S_6^{2-} which is in equilibrium with S_3^- and which has absorption maxima around 460 and 317 nm might contribute to the bands around 300 and 450 nm. A change of intensity or a left or blue shift of a band with time, with concentration (Figure 1) or with temperature or on chemical action indicate changes of the concentrations or of the relative concentrations resp. of the species causing the band.

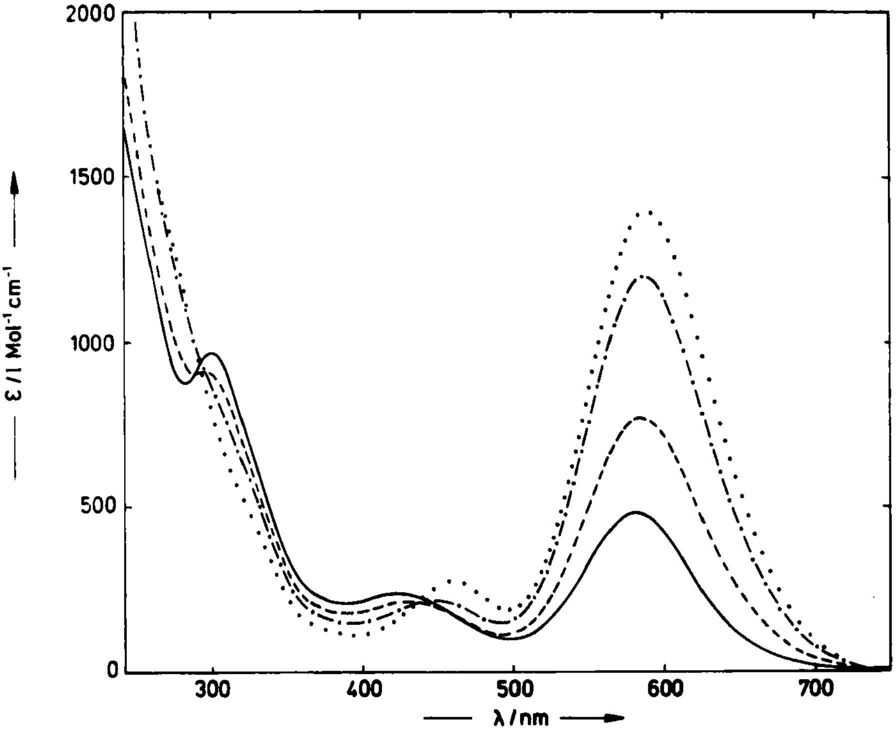

FIGURE 1 Absorption spectra of equilibrium SAS at 25°C: 1.9×10^{-2} M(S) (—), 2.8×10^{-3} M(S) (- - -), 7.5×10^{-4} M(S) (· - ·), 1.9×10^{-4} M(S) (· · · ·); mole of sulfur per litre ammonia.

EXPERIMENTAL

Decay of $S_xNH_2^-$. Anion exchange HPLC is a very powerful tool for the separation of anionic species in SAS; however quantitative data of the spectra or the concentration of the separated species cannot be obtained, because at least parts of these are unstable in the separated form and undergo further disproportionation reactions. This is shown by the changes of anion exchange chromatograms of SAS obtained at various flow rates and by the time dependence of the spectrum of separated $S_xNH_2^-$.

In Figure 2 the chromatograms of a slightly oxidized equilibrium SAS are displayed which were taken with eluation rates 10 and 0.2 ml/min resp. At high flow rate the two pronounced peaks due to S_4N^- and $S_xNH_2^-$ and a short tail due to S_3^- clearly are distinguished (for the assignments see References 8 and 9). At low flow rate the S_4N^- peak and the S_3^- tail are enhanced on the expenses of the $S_xNH_2^-$ peak and an additional weak peak inbetween is developed due to S_3N^- (the enhanced leading tail probably is caused by uncharged decay products which we could not identify yet).

Thus we can conclude that only at high eluation rate the chromatograms will reflect the equilibrium composition of the solutions; however on high eluation rates the resolution of the separation is diminished. At low rates on the other hand where high resolution would be achieved, those species which are instable when by separation taken out of the equilibrium have ample time for further disproportionation reactions.

The decay of $S_xNH_2^-$ also is demonstrated in Figure 3 by the spectral changes of its chromatographic peak after stopping the HPLC pump. The absorption bands of $S_xNH_2^-$ at 300 and 420 nm (upper part, see next paragraph) decrease in favour of the band around 600 nm due to S_4N^- and S_3^- (the band around 580 nm directly after stop of the HPLC pump is caused by S_4N^- not completely separated form $S_xNH_2^-$ or by S_4N^- and S_3^- already formed by decay of $S_xNH_2^-$).

The two figures clearly show that separated $S_xNH_2^-$ is instable and decays after separation to the normal products of an SAS, i.e. to S_4N^-, S_3N^- and S_3^- (or S_6^{2-}). Therefore we cannot obtain with

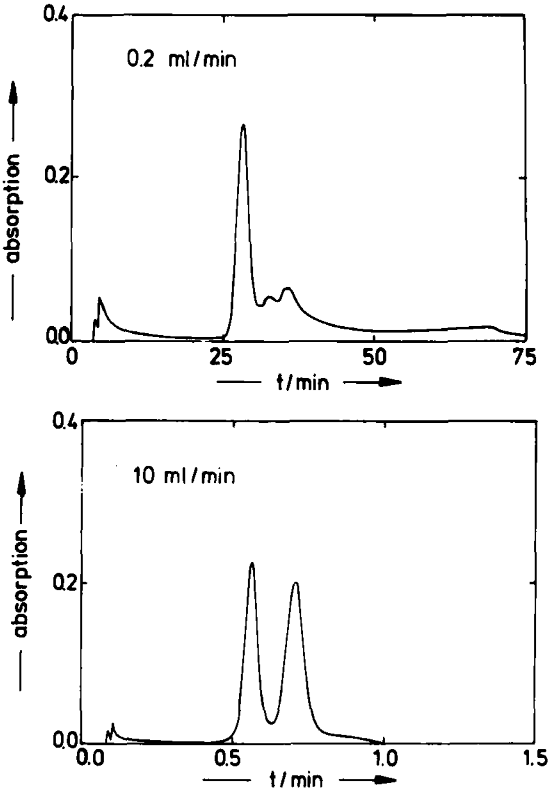

FIGURE 2 Anion exchange chromatogram of a slightly oxidized SAS at eluation rates of 0.2 and 10 ml/min (2.1×10^{-2} M(S), 25°C, 20 μl, optical path 0.8 cm, detection light 260 nm).

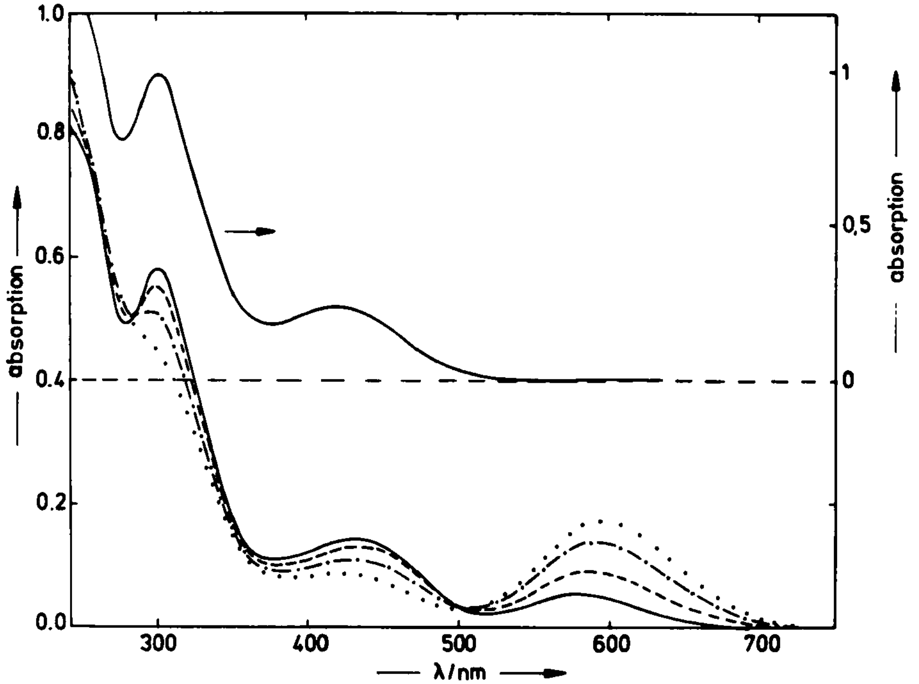

FIGURE 3 Lower part: absorption spectra of the $S_xNH_2^-$ peak of the anion exchange chromatogram immediately after stop (—), 6 min (- - -), 15 min (- · - ·) and 30 min (· · · ·) after stop of the HPLC pump (1.8 × 10^{-3} M(S), 25°C, 20 μl, optical path 0.8 cm). Upper part: spectrum of $S_4NH_2^-$ (arbitrary absorption units).

the desired accuracy the spectrum and concentration of $S_xNH_2^-$ from its chromatographic peak but have to analyse the spectrum of an unseparated SAS with all its components in equilibrium.

Spectrum of $S_xNH_2^-$ analysed from the spectra of a SAS. Assuming that the main species of SAS are those given in the last paragraph we should be able to get the spectrum of $S_xNH_2^-$ from the spectrum of a SAS by peeling off those of the other components. We start with the absorption band of SAS (Figure 1) at the longest wave length around 600 nm which is due only to S_3^- and S_4N^-, subtracting the normalized spectra[8] of these two ions both multiplied with varying weight factors. A weight factor chosen too high (or too low) will yield a difference spectrum with negative (or remaining positive) absorption above 550 nm. By trial and error finally a difference spectrum with no absorption above 550 nm is obtained. With the same procedure we subtract from the difference spectrum the normalized spectrum[8] of S_3N^- multiplied by a suitable weight factor obtaining the spectrum of $S_xNH_2^-$—unless we neglected other species with prominent absorption.

We have applied this method to the spectra of SAS in the concentration range from 1.9 × 10^{-4} to 1.9 × 10^{-2} M(S) in Figure 1 and obtained in every case a residual spectrum[8] (Figure 3, upper part) with absorption maxima at 300 and 420 nm approximately matching that of the chromatographic peak immediately after stopping the HPLC pump which we have assigned to the anion $S_xNH_2^-$ (Figure 3 full line). This corroborates that indeed the absorption spectrum of SAS is caused mainly by the four species considered so far.

Equilibrium concentration of the main species in SAS. From the weight factors obtained by peeling off the spectra and the known extinction coefficients of S_3^-, S_4N^- and S_3N^- we finally get the concentrations of these species, listed in Table I as relative concentrations. They increase with decreasing sulfur concentration.

Since sulfur (oxidation state zero) is dissolved by a redox reaction (disproportionation) the sum of the concentrations of sulfur atoms in the oxidized state multiplied by their oxidation number must equal that of sulfur atoms in the reduced state. Considering only S_4N^- and S_3N^- on the one hand and S_3^- on the other we see from the data in Table I that we have an excess of sulfur in the oxidized state

TABLE I

Relative sulfur concentrations (in %) of the individual components of an equilibrium SAS at 25°C (M/M(S) × 100 × *i* with *i* number of sulfur atoms in the compounds).

M(S)	S_6^{2-}	S_3^-	$S_xNH_2^-$	S_4N^-	S_3N^-
$1.9\ 10^{-2}$	9	6	75	10	—
$2.8\ 10^{-3}$	5	16	65	14	—
$7.5\ 10^{-4}$	4	29	46	19	2
$1.9\ 10^{-4}$	3.5	42	26.5	21	7

(e.g., in the solution with 1.9×10^{-2} M(S) we have the relative concentration of oxidized sulfur $x_{ox} = 0.1$ in S_4N^- with the oxidation number $z_{ox} = \frac{1}{2}$ or $z_{ox} \times x_{ox} = 0.05$; the relative concentration of reduced sulfur is $x_{re} = 0.06$ in S_3^- with the oxidation number $z_{re} = -\frac{1}{3}$ or $z_{re} \times x_{re} = -0.02$. Therefore there must be another species with reduced sulfur with $z_{re} \times x_{re} = -0.03$).

In analysing the absorption spectra by peeling off we have neglected the S_6^{2-} ions which are known to be in equilibrium with S_3^- ions[1,5,10,11]; however their absorbance in dilute SAS is not prominent. Assuming that the excess of sulfur in the oxidized state is compensated by S_6^{2-} we get its relative concentrations also given in Table I (in the example with $x_{re} \times z_{re} = -0.03$ and $z_{re} = -\frac{1}{3}$ for S_6^{2-} we obtain its relative concentration $x_{re} = 0.09$). This treatment is reasonable, for the equilibrium constant $K = (1.2 \pm 0.4) \times 10^{-3}$ M of the $S_6^{2-} \rightleftharpoons 2\,S_3^-$ equilibrium calculated from the corresponding data is within the limit of error of our treatment (see below) in good agreement with the literature value[11] $K = 1.4 \times 10^{-3}$ M for ammonium hexasulfide solutions of the same temperature.

Assuming that all major components with oxidized and reduced sulfur have been taken into account we can calculate from their relative concentrations that of the postulated compound $S_xNH_2^-$ listed in Table I: with increasing sulfur concentration the relative concentration of $S_xNH_2^-$ increases. (Weighing errors of sulfur and ammonia and the uncertainty of the spectra and extinction coefficients of the compounds which we used to analyse the spectra of SAS lead to uncertainties of about ± 10% for their relative concentrations).

Evaluation of the equilibrium in SAS. Since we are dealing with equilibrium concentrations we finally can determine the number x of sulfur atoms in $S_xNH_2^-$. The general equation for the equilibrium between S_4N^- and S_3^- on the one side of $S_xNH_2^-$ on the other is

$$10/x\ S_xNH_2^- + (10/x - 3)NH_4^+ \rightleftharpoons S_4N^- + 2\,S_3^- + (20/x - 4)NH_3 \qquad (1)$$

(S_6^{2-} and S_3N^- must not be taken into consideration, because their formation can be described by further independent equations, see below). The equilibrium constant is evaluated taking the concentration of ammonia equal to unity, that of NH_4^+ ions to balance the charge of the anions, making use of the activity coefficients calculated according to the Debye-Hückel theory. Thus we find in the covered concentration range for $x = 2$ a variation of the equilibrium constant from about 10^5 to 10^{16}, or for $x = 8$ from about 10^{-12} to 10^{-16} (in proper units of M), i.e., in a range of many powers of ten up or down. Only for $x = 4$ or $x = 5$ the equilibrium constant decreases or increases by approximately a factor of ten only (4×10^{-6} to 6×10^{-5} M or 2×10^{-8} to 3×10^{-9} M^2 resp.). Therefore x in $S_xNH_2^-$ should be 4 or 5 (it might average around 4 to 5 if several species $S_xNH_2^-$ were present, what we do not believe). We also obtain $x = 4$ or 5 evaluating the data of the literature[5] which lead to the assignment $S_{2,am}$.

With $x = 4$ we finally formulate the equilibrium (1):

$$5\,S_4NH_2^- \rightleftharpoons 2\,S_4N^- + 4\,S_3^- + 2\,NH_3 + NH_4^+ \qquad (2)$$

It reflects the experimental results that on oxidation, reduction, neutralization or dilution of SAS (decreasing the concentration of S_3^- or S_4N^- or NH_4^+ or all) the relative concentration of $S_4NH_2^-$ decreases (with $x \leq 3$ neutralization or dilution would lead to an increase of $S_xNH_2^-$).

Extinction coefficient of $S_4NH_2^-$. From the concentration of $S_4NH_2^-$ and its spectrum both obtained by the peeling-off-method we calculate the maximum extinction coefficients of $S_4NH_2^-$ in ammonia: $\varepsilon_{300} = 4440$ and $\varepsilon_{420} = 1080\ M^{-1}\ cm^{-1}$ (both with an error of about 10%).

Establishment of the dissolution equilibrium in SAS. The absorption spectra of freshly prepared SAS vary with time and the time dependence varies with concentration and temperature[5,9] of the solution. A dilute solution ($\leq 10^{-3}$ M(S)) prepared and kept at −35°C has a spectrum with three bands around

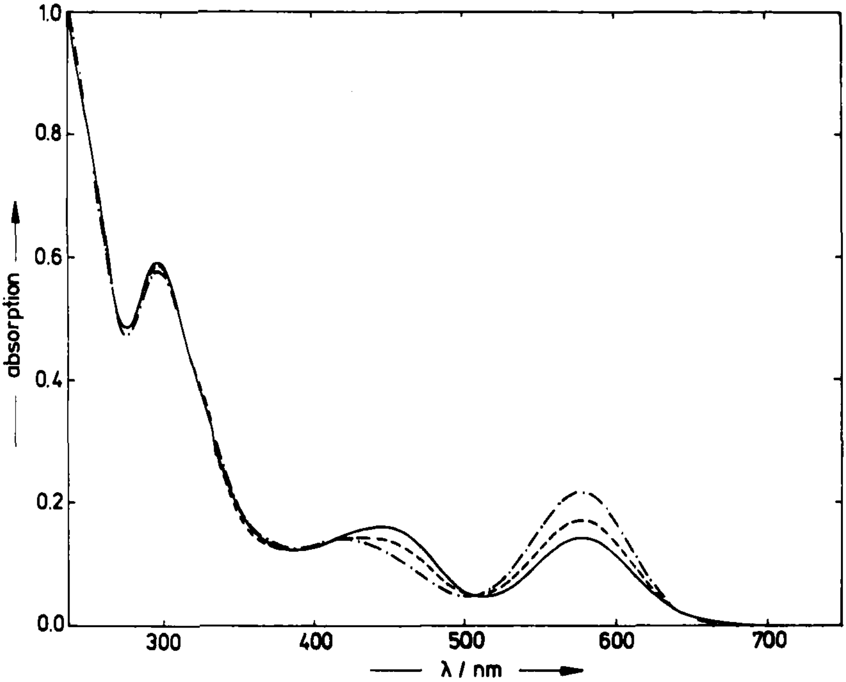

FIGURE 4 Absorption spectrum of an 1.2 × 10^{-2} M(S) SAS 4 days (—), 6 days (- - -) and 12 days (- · -) after preparation (−35°C, optical path 0.05 cm).

300 (S_3N^-, $S_4NH_2^-$, S_3^-), 450 (S_3N^-, $S_4NH_2^-$), and 600 nm (S_4N^-, S_3^-) the maxima of which decrease in the same order. No change with time could be observed after dissolution. However, after heating to 25°C (where the high temperature spectrum is developed rather fast, see below) and recooling again to −35°C the spectrum changes to a final one with again three maxima. The one at 300 nm is very little affected. The second one decreases with blue shift to 440 nm. The third one has a three to fourfold increase (reversal of the intensity ratio of the last two bands) with a blue shift to 580 nm. This confirms[5,8] that all experiments at low temperature with low concentrated SAS prepared at low temperature were carried out under non-equilibrium conditions.

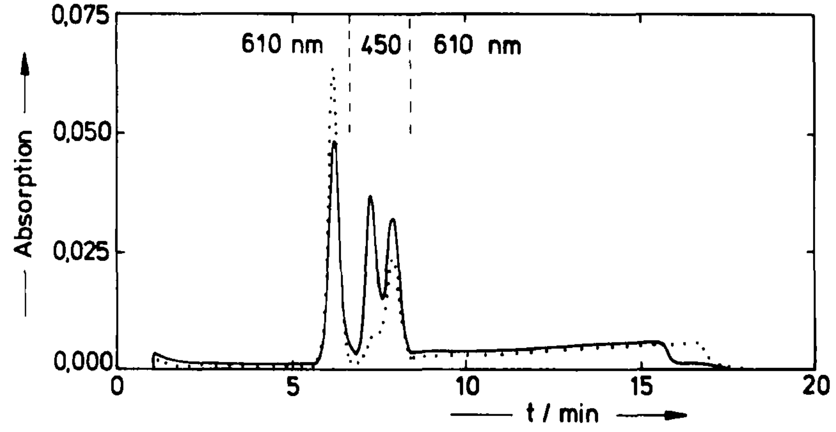

FIGURE 5 Anion exchange chromatogram of a 8.2 × 10^{-3} M(S) SAS prepared and kept at −35°C (—) and after heating to 25°C (· · · ·) (20 µl, optical path 0.8 cm; detection light in the middle part 450 nm, in the outer part 610 nm).

In a more concentrated solution ($\geq 10^{-3}$ M(S), Figure 4) prepared and kept at −35°C the spectrum with again three maxima changes with time; about 12 days after dissolution the equilibrium state is reached: heating and recooling then has no effect on the spectrum any more. During equilibration the absorption maximum at 580 nm increases in intensity, that at 450 nm (becoming less pronounced than that at 580 nm) decreases with blueshift to 420 nm; the one at 300 nm stays constant.

The interpretation of these spectra and their changes with time and concentration or after heating is facilitated by the anion exchange chromatograms of a solution of intermediate concentration taken at low temperature and after heating up (Figure 5). We clearly can identify by the retention time and the absorption spectra of the peaks[8] the four species we dealt with so far. The three peaks and the long tail (increasing retention time) are due to S_4N^- (absorption maximum 578 nm) increasing with temperature, S_3N^- (462 nm) sharply decreasing, $S_4NH_2^-$ (420 nm) slightly decreasing, and S_3^- (610 nm) increasing with temperature.

These experiments show that on dissolution of sulfur in ammonia at −35°C S_3N^- and $S_4NH_2^-$ are formed as intermediates in higher concentrations. After equilibration S_3N^- is not detectable any more in high concentrated solutions (the second absorption maximum of the concentrated SAS around 420 nm in Figure 1 is due to $S_4NH_2^-$ only), whereas some of it persists in low concentrated solutions (the absorption maximum of the dilute SAS around 450 nm in Figure 1 is due to a mixture of $S_4NH_2^-$ and S_3N^-).

The relative rate with which the equilibrium is established at −35°C is slow and in accordance with the kinetics of reactions of higher orders it goes down with decreasing concentration; actually in dilute solutions it is so slow that we never could observe any spectral changes within 10 or 20 days.

Of course at higher temperature equilibration rates are increased. Thus in high concentrated solutions at 25°C a few minutes after adding sulfur to ammonia the typical spectrum with the three maxima around 300, 420 and 580 nm has developed (the middle one with lowest intensity). During dissolution (less than 2–3 hours) it increases without change of the relative intensities of the bands. This proves that equilibration of the species in the solution is rather fast, even faster than the dissolution process, and that S_3N^- is not formed as a detectable intermediate (the middle peak is caused by $S_4NH_2^-$ only).

In lower concentrated solutions on the other hand equilibration at 25°C is slow but complete after 8 days (Figure 6). The band around 600 nm due to S_4N^- and S_3^- steadily increases; that around 450 nm passes through a maximum indicating that $S_4NH_2^-$ *and* S_3N^- are formed as intermediates which

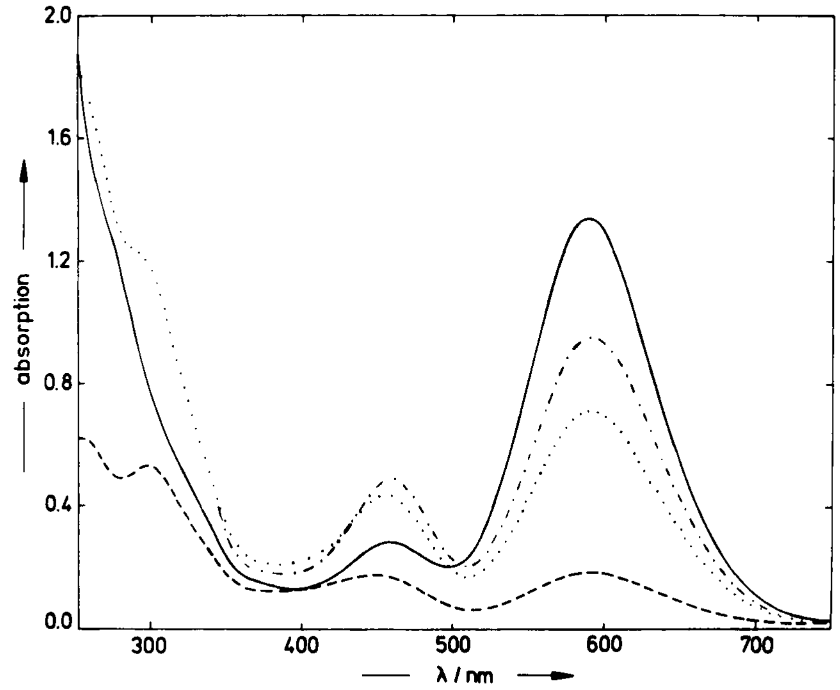

FIGURE 6 Absorption spectrum of a 2 × 10^{-4} M(S) SAS 30 min (– – –), 300 min (· · ·), 1 day (· – ·) and 8 days (—) after preparation (25°C, optical path 5 cm).

in equilibrium persist in smaller concentrations; the observed slight red shift of the band proves that during equilibration the concentration ratio of S_3N^- and $S_4NH_2^-$ slightly increases. Also the absorption around 300 nm (in the beginning a maximum, inbetween as a shoulder, at the end no structure) passes through a maximum value – again due to the intermediate formation of $S_4NH_2^-$ in higher concentration.

CONCLUSIONS

Information on the process of dissolution of sulfur in ammonia is obtained only under those experimental conditions under which we can follow formation and further reactions of intermediates, i.e., in low concentrated solutions at high temperature or high concentrated solutions at low temperature. Under these conditions we observe $S_4NH_2^-$ and S_3N^- as species which are formed in excess of their equilibrium concentrations, i.e., they are primary products. Similar conclusions were given by Lelieur[5] who however described the species with zero sulfur oxidation state as $S_{2,am}$.

Not knowing any other intermediates we do not want to speculate about mechanistic details, we only can try to describe the reaction sequences by balanced equations leading to the products we observe. Thus we formulate as the first step of solubilization the formation of $S_4NH_2^-$ by attack of ammonia on sulfur

$$S_8 + 4\,NH_3 \rightleftharpoons 2\,S_4NH_2^- + 2\,NH_4^+ \qquad \text{(a)}$$

We do not think that solubilization is initiated by the attack of NH_2^- on sulfur as stated before,[5] because due to the small dissociation constant of ammonia (6×10^{-35} at $-35°C$[12]), the equilibrium concentration of NH_2^- is so small that the dissolution of sulfur in ammonia never could be observed. This of course does not exclude that in amide solution the dissolution of sulfur is accelerated.[4,9]

$S_4NH_2^-$ disproportionates leading to S_3^- and S_3N^-

$$9\,S_4NH_2^- \rightleftharpoons 4\,S_3N^- + 8\,S_3^- + 2\,NH_3 + 3\,NH_4^+ \qquad \text{(b)}$$

which in turn with increasing NH_4^+ and S_3^- concentration is reduced to S_4N^-

$$10\,S_3N^- + 2\,S_3^- + 3\,NH_4^+ \rightleftharpoons 9\,S_4N^- + 4\,NH_3 \qquad \text{(c)}$$

Of course S_4N^- also can be formed directly from $S_4NH_2^-$

$$5\,S_4NH_2^- \rightleftharpoons 2\,S_4N^- + 4\,S_3^- + 2\,NH_3 + NH_4^+ \qquad \text{(d)}$$

Finally we have to include the dimerization of S_3^-

$$S_6^{2-} \rightleftharpoons 2\,S_3^- \qquad \text{(e)}$$

With these equilibrium reactions we can understand the changes of the relative concentrations of species listed in Table I. On dilution the equilibria (b), (d) and (e) in which the number of particles are increased are shifted to the right thus leading to a decrease of the relative concentration of $S_4NH_2^-$ and an increase of that of S_3^- and S_4N^-: vice versa reaction (c) is shifted to the left leading to an increase of the relative concentration of S_3N^-. This reaction sequence also explains that on neutralization with NH_2^- the concentration of $S_4NH_2^-$ decreases and those of S_4N^-, S_3^- and S_3N^- increase.[4,9] We will report on this and other modifications of SAS by chemical and photochemical means in due time.

ACKNOWLEDGEMENT

We are grateful for financial support to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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