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Communication

ANION EXCHANGE WITH LIQUID AMMONIA: SEPARATION AND IDENTIFICATION OF THE MAIN COMPONENTS OF SULFUR-AMMONIA SOLUTIONS

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By anion exchange HPLC with NH_4NO_3 in liquid ammonia (0.0035 M) as mobile phase we succeeded to separate the main components of a solution of sulfur in liquid ammonia. By their absorption spectra we could identify the known anions S_4N^- and S_3N^- (sulfur in oxidized form) as well as S_3^- which is in equilibrium with $\text{S}_6^{=}$ (sulfur in reduced form). In addition we find an anionic compound which after separation decays to form a normal sulfur ammonia solution. It therefore must contain sulfur in zero oxidation state. We assign it tentatively the formula S_xNH_2^- —primarily formed by attack of ammonia on neutral sulfur.

Key words: Anion exchange; HPLC; liquid ammonia; sulfur; sulfur ammonia solution.

INTRODUCTION

In solutions of sulfur in ammonia^{1,2} (SAS; solubility about 0.65 kg S/kg NH_3) by disproportionation or redox reactions a series of light absorbing ions are formed as follows from the electrical conductivity and the UV/VIS-absorption spectra of the solutions.^{3–7} On evaporating off the solvent solid sulfur is recovered.^{1,2}

By comparison of the Raman and UV/VIS-absorption spectra of SAS with those of known compounds dissolved in ammonia the radical anion S_3^- in equilibrium with the hexasulfide anion $\text{S}_6^{=}$ (S in reduced form) and the tetrasulfurimide anion S_4N^- (S in oxidized form) could be identified beyond doubt.^{7–10} Cations in all cases are NH_4^+ -ions.

The equilibria depend on concentration and temperature, they are shifted by neutralization (addition of KNH_2)¹¹ or by addition of reducing or oxidizing agents as well as by the action of light,⁵ whereby other S- and SN-compounds are formed: e.g. $\text{S}^{=}$, S_7N^- , S_3N^- , S_3N_3^- , S_4N_4 etc. All these species also might be minority compounds in normal SAS. Because the spectra of the individual species overlap, their identification in SAS by spectroscopy alone is not possible. Separation, e.g. by chromatographic methods is necessary.

Chromatography on silicagel¹² leads to poor resolution only. But by anion exchange HPLC with a solution of NH_4NO_3 in ammonia the SAS can be

separated into its components which then can be identified by their absorption spectra.

EXPERIMENTAL

The experiments were carried out mainly at 25°C with a conventional HPLC pump (Waters, model 510) and an anion exchange column (Waters, IC-PAK Anion Column, 120 mm length and 2 mm diameter). A spectral photometer (Perkin Elmer Lambda 5; microcuvettes 6 mm optical path) served as detector, allowing to take the chromatograms at selected wave lengths or also to resolve the absorption spectra of the separated species.—SAS were obtained under exclusion of light, air and humidity at 25°C by dissolving high purity sulfur in liquid ammonia. Within 2 hours the final equilibrium in an 0.01 M SAS is established. Between 1 and 200 μ l of this solution were injected into the column. Elution was achieved with a 0.0035 M NH_4NO_3 liquid ammonia solution at a flow rate of 1 ml/min. To counteract the vapor pressure of ammonia (10 bar at 25°C) the system was pressured back with 10 bar nitrogen gas.

RESULTS AND DISCUSSION

Figure 1 shows three chromatograms taken at three different wave lengths; we observe three peaks *A*, *B* and *C* and a long tail. The spectra of Figure 2 were taken after interrupting the elution in the peaks or in the tail.

The first maximum of the chromatogram (*A* in Figure 1) has an absorption spectrum (full line in Figure 2) with a strong absorption band around 578 nm and increasing absorption below 300 nm. It matches that of a freshly prepared solution of $\text{PPN}^+\text{S}_4\text{N}^-$ in ammonia^{9,13} after exchange of the PPN^+ -ions ($[\text{N}(\text{PPh}_3)_2]^+$ = bis-triphenylphosphoranylidene iminium) with NH_4^+ -ions; peak *A* therefore is due to S_4N^- -ions.

The spectrum of the second, not well resolved chromatographic peak (*B* in Figure 1) is superimposed by the spectrum of the component of peak *C*. However in the chromatogram of an SAS which has been partially oxidized with S_4N_4 peak *B* is without change of retention time greatly enhanced at the expenses of peak *C*. The spectrum of peak *B* of this solution (dashed line in Figure 2) has

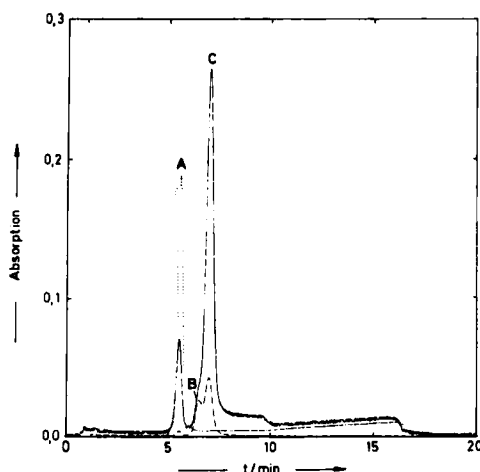


FIGURE 1 Anion exchange chromatograms of a SAS with photometric detection at 260 nm (—), 460 nm (---), and 610 nm (····). Experimental conditions see text. Absorption spectra were recorded when the peaks *A*, *B*, and *C* or the tail passed the detector.

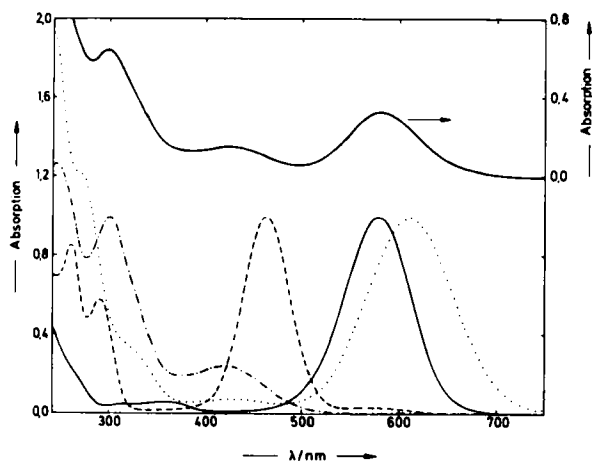


FIGURE 2 Normalized spectra of the identified components of a SAS at 25°C (left scale): S_4N^- (—), S_3N^- (---), $S_xNH_2^-$ (-·-·-), and S_3^- (···). For comparison the absorption spectrum of a 0.015 M SAS is given in the upper part of the figure (optical path 0.5 mm; right scale).

absorption maxima at 464, 290 and 260 nm which already could be recognized in the spectrum of peak B of the original SAS. This spectrum is identical to that of a freshly prepared solution of $PPN^+S_3N^-$ in ammonia^{9,14} after PPN^+/NH_4^+ exchange. Therefore peak B is due to S_3N^- -ions.

The absorption spectrum of peak C (dash-dotted line in Figure 2, maximum at 420 and 300 nm and further absorption increase below 280 nm) does not match the spectra of any other SN or S compound known to us. Peak C is reduced in intensity both by partial reduction and by partial oxidation of SAS with H_2S or S_4N_4 resp. Therefore the formal oxidation state of sulfur of the compound causing peak C must be close to zero (the sulfur oxidation state in S_4N^- , S_3N^- and S_6^- or S_3^- is 1/2, 2/3 and -1/3 resp.). Actually we assume it to be exactly zero,¹¹ for the spectrum of peak C changes with time and finally matches that of an unmodified normal equilibrium SAS. Although the unknown compound contains sulfur in the oxidation state zero it must be an anionic compound, because it passes the anion exchange column as a delayed sharp peak. We formulate it as $S_xNH_2^-$ formed by attack of ammonia on neutral sulfur ($S_x + 2NH_3 \rightleftharpoons S_xNH_2^- + NH_4^+$). A compound $S_xNH_2^-$ has been proposed already on the basis of mechanistic studies of SAS.¹⁵

Neutral or cationic components of SAS would pass the anion exchange without retention. We can not detect any absorption at the beginning of the chromatograms and therefore can state that light absorbing neutral or cationic sulfur components are not present or present only in very low concentrations.

Neither can we detect in our chromatograms the S_6^- -ion with its characteristic light absorption between 420 and 440 nm, which has been recognized as one of the majority components of SAS.^{8,10} As a divalent anion it is stronger absorbed on an anion exchange system and consequently eluted slower than univalent anions. However, S_6^- is in equilibrium with S_3^- ($S_6^- \rightleftharpoons 2S_3^-$) and this equilibrium is shifted to the right with decreasing concentration. Therefore we have to assume that on elution the absorbed S_6^- -ions steadily give off S_3^- -ions which are swept continuously through the column without forming a peak. Indeed in the long tail of Figure 1 S_3^- -ions can be identified by their absorption spectrum with a

maximum at 610 nm and increasing absorption below 400 nm (dotted line in Figure 2). A further proof of this assignment is that the chromatogram of a solution of $S_6^{=}$ (e.g. with NH_4^+ as cation) yields only that long tail.

CONCLUSIONS

By anion exchange HPLC with liquid ammonia and spectral photometric detection we have separated SAS into its components and have identified the oxidized species S_4N^- and S_3N^- , the reduced species S_3^- which is in equilibrium with $S_6^{=}$, and an anionic species with sulfur in zero oxidation state (described here as $S_xNH_2^-$). Other species are not present in SAS in detectable concentrations.

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