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RECENT DEVELOPMENTS IN THE UNDERSTANDING OF SOLUTIONS OF SULFUR IN LIQUID AMMONIA

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Résumé : La compréhension des solutions de soufre dans l'ammoniac a beaucoup progressé durant les dernières années. Ces progrès ont montré que le soufre est solubilisé dans l'ammoniac par un processus de dismutation Redox, mais des expériences ont montré que cette dismutation est très incomplète. Une fraction importante du soufre solubilisé reste au degré d'oxydation zéro, mais sous une forme différente de celle du cycle S_8 . Les différents résultats et hypothèses relatifs à cette espèce sont examinés. On indique brièvement les différents mécanismes proposés pour expliquer la solubilisation du soufre dans l'ammoniac liquide.

Abstract : The understanding of solutions of sulfur in liquid ammonia has been significantly improved during recent years. This progress gives evidence that sulfur is solubilized in liquid ammonia by a Redox disproportionation mechanism, but it has been shown more recently that this disproportionation is not complete. A large fraction of solubilized sulfur is in the zero oxidation state, but is not cyclic S_8 . Various results and hypothesis related to this species are reviewed. The proposed solubilization mechanisms of sulfur in liquid ammonia are also reviewed.

Introduction

The solubilization of sulfur in liquid ammonia to give highly colored solutions has been first observed by Gore in 1873 /1/. The first hypothesis related to the nature of chemical species in these solutions (SAS) was given by Ruff and Geisel in 1905 /2/. After addition of silver iodide to the solution, silver sulfide was precipitated and the evaporation of ammonia led to the observation of tetrasulfur tetranitride (S_4N_4). The equilibrium proposed by Ruff and Geisel was shown to be incorrect only 55 years later by Nelson and Lagowski /3/ and Zipp and Evers /4/. Nelson and Lagowski were the first to observe an influence of temperature on the absorption spectrum and they gave indication that two

chemical species are in a temperature dependent equilibrium. Other works at that time gave various hypotheses on the chemical species in SAS, and they showed the complexity of these solutions /5,6,7/.

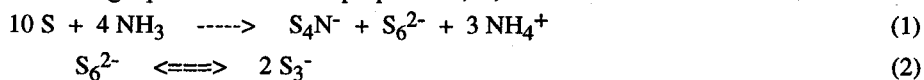
Starting point of the renewal of these studies

The starting point of the recent progress related to SAS is the identification in 1982 by Chivers and Lau /8/ of an oxidized form of sulfur (S_4N^-) and of a reduced form of sulfur (S_3^-). This unambiguous identification was performed by using Raman Spectroscopy. The presence of S_4N^- and of S_3^- in SAS was confirmed by Bernard et al. /9,10/ who showed that two points were rather critical to obtain valuable experimental data : they observed for the first time the photosensitivity of SAS, and they showed that this effect can strongly modify the absorption spectrum and the Raman spectrum of SAS ; they gave evidence that the equilibrium state of these solutions is reached very slowly. They also showed that SAS are very sensitive to traces of reducing agents.

At that time, experimental evidence had therefore been given that the solubilization of sulfur in ammonia is a Redox disproportionation mechanism. The unsolved problems could be formulated by the following questions : are other chemical species in SAS ? which are their absorption bands ? what are the concentrations of the chemical species ? which mechanisms lead to the equilibrium state ?

Chemical species in SAS

Extensive studies of the absorption spectrum of SAS versus temperature and concentration were made by Prestel and Schindewolf /11-14/, and by Dubois et al. /15,16/. The study of solutions of lithium polysulfide and ammonium polysulfide in liquid ammonia by Dubois et al. /17,18/ using spectrophotometry and Raman spectroscopy led to the identification of several polysulfides and to the conclusion that S_6^{2-} is the least reduced polysulfide in liquid ammonia and is in equilibrium with the radical S_3^- . The comparison of the absorption and Raman spectra for polysulfide solutions and for sulfur solutions showed that S_6^{2-} is also in equilibrium with S_3^- and those were the only observed polysulfides in SAS. The following equations were then proposed /9,10,15/ :



From this equation, the analysis of the absorption spectrum of SAS in the visible range gives a molar extinction coefficient of $7300 \text{ M}^{-1} \text{ cm}^{-1}$ for S_4N^- , while this quantity was found equal to $16000 \text{ M}^{-1} \text{ cm}^{-1}$ in acetonitrile by Chivers /19/. It was therefore concluded that the concentration of S_4N^- in SAS is lower than predicted from the above equation. This led us to investigate the influence of amide addition on the concentration of S_4N^- and of S_6^{2-} /20/. It was then shown (fig. 1) that the progressive addition of potassium amide in the solution increases the concentration of the oxidized species and of the reduced species. It was also observed that the oxidized species is gradually replaced by a more oxidized species and the reduced species by a more reduced species. It was concluded that a chemical species less oxidized than S_4N^- and less reduced than S_6^{2-} exists in SAS at the equilibrium state.

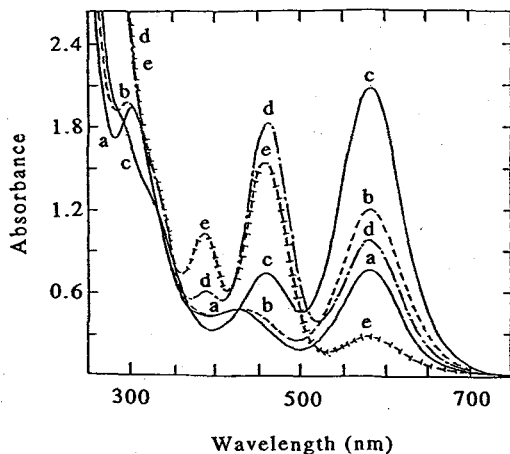


Figure 1. Absorption spectra of a sulfur-ammonia solution ($3.6 \times 10^{-2} M$) at room temperature. Optical path length = 0.5 mm. Spectra a - e have been recorded at equilibrium and are related to the following values of NH_2^-/S : (a) 0; (b) 0.25; (c) 0.44; (d) 0.6; (e) 0.75. In this experiment, the amide addition was performed in a very accurate manner. Each amide addition gave an increase of NH_2^-/S close to 0.07; only some of the equilibrium spectra are reported.

The strong increase of the concentration of S_4N^- after the first additions of potassium amide (fig. 2) shows that the disproportionation of sulfur in liquid ammonia is far from complete in the equilibrium state of these solutions. Since the studies related to polysulfide solutions had shown previously that S_6^{2-} is the least reduced polysulfide in ammonia, the oxidation number of sulfur in this species is between 0 and + 1/2. The possible species are therefore the sulfur imide S_7NH , the compounds $S_7N-S_x-S_7N$, and neutral sulfur or a species with sulfur in the zero oxidation state. The possible existence of $S_7N-S_x-S_7N$ will of course be related to formation of S_7N^- in solution.

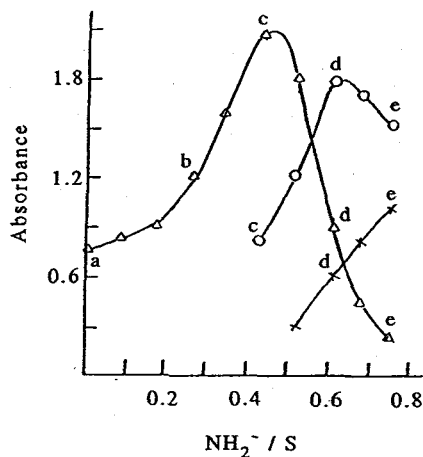


Figure 2. Variations of absorbance at 580 (Δ), 460 (o) and 390 nm (x) versus NH_2^-/S . These absorbances have been recorded at equilibrium, at room temperature. The absorption spectra (a to e) from Fig 1 are only a fraction of the spectra recorded at equilibrium. The absorption bands at 580 and 460 nm are assigned to S_4N^- and S_3N^- respectively. The absorption band at 390 nm has been tentatively assigned to $S_2N^- / 16,20/$

Consequently the study of solutions of S_7NH in ammonia was undertaken. The observation of S_4N^- (fig. 3) in either the absorption spectrum or the Raman spectrum of S_7NH-NH_3 solutions gives an unambiguous evidence of the disproportionation of S_7N^- . However, the main question was to determine if the disproportionation of S_7N^- in ammonia is complete or not. The concentration of S_4N^- in S_7NH-

NH_3 solutions was estimated through the absorption band of S_4N^- . We have found that the $\text{S}_7\text{NH-NH}_3$ solutions obey the Beer's law for the absorption band of S_4N^- at 580 nm up to a concentration at least equal to $2 \cdot 10^{-2} \text{ M}$; an extinction coefficient of $14000 \text{ M}^{-1} \text{ cm}^{-1}$ was obtained for S_4N^- , which is rather close to the value ($16000 \text{ M}^{-1} \text{ cm}^{-1}$) obtained by Chivers /19/ for solutions of $\text{PPN}^+\text{S}_4\text{N}^-$ in acetonitrile.

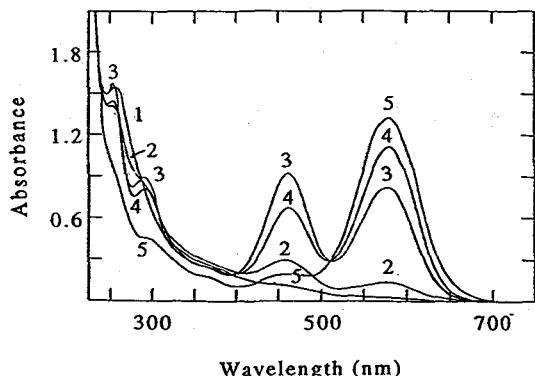


Figure 3. Absorption spectra of a $\text{S}_7\text{NH-NH}_3$ solution $8 \cdot 10^{-3} \text{ M}$ recorded during the solubilization process.

- (1) $T = -35^\circ\text{C}$ (after approximately 10 min at -35°C ; sample previously kept at -78°C);
- (2) $T = -35^\circ\text{C}$; after 2.5 h at -35°C ;
- (3) $T = -35^\circ\text{C}$; after 17 h at -35°C ;
- (4) $T = -35^\circ\text{C}$; after 63 h at -35°C ;
- (5) at equilibrium, at $T = 20^\circ\text{C}$.

Optical path length = 1 mm.

However in $\text{S}_7\text{NH-NH}_3$ solutions, two oxidized species are detected : S_4N^- (580 nm) and S_3N^- (460 nm) in low concentration. Consequently, the concentration of S_4N^- is necessarily lower than the concentration of S_7NH solubilized in ammonia, and the extinction coefficient of $14000 \text{ M}^{-1} \text{ cm}^{-1}$ for S_4N^- can only be an underestimated value. The influence of the addition of potassium amide on the absorption spectrum of $\text{S}_7\text{NH-NH}_3$ solutions was also investigated. It was observed that the first addition of potassium amide induces a decrease of the concentration of S_4N^- (fig. 4), which shows that the disproportionation of S_7N^- is complete in $\text{S}_7\text{NH-NH}_3$ solutions. Consequently, these experiments led to the conclusion that the disproportionation of S_7N^- is complete in ammonia. If the concentrations of S_3N^-

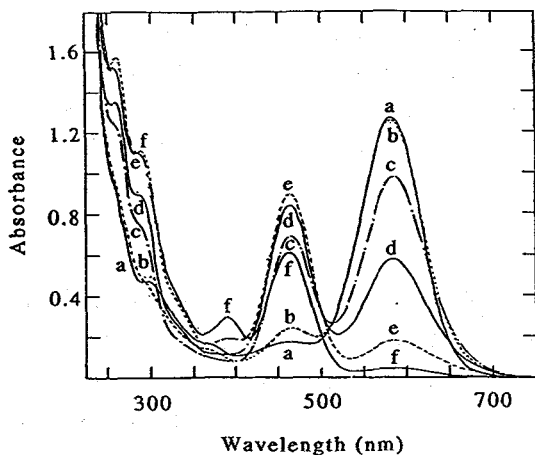


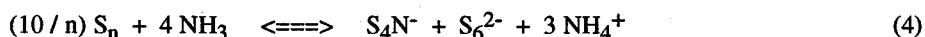
Figure 4. Absorption spectra of a $\text{S}_7\text{NH-NH}_3$ solution at 293 K; $c = 1.9 \cdot 10^{-4} \text{ M}$; optical path length = 1 mm.

- (a) at equilibrium; before the first addition of sodium amide
- (b) $\text{NH}_2^-/\text{S}_7\text{NH} = 0.3$
- (c) to (f) with increasing amount of amide

and S_3^- observed in these solutions are ignored, the disproportionation of S_7N^- can be written, as a first approximation, as :



where S_{am} is a neutral form of sulfur in ammonia. This analysis led to the conclusion that S_7N^- is not present in SAS and that S_{am} is present in these solutions. If the species S_{am} corresponds to only one species which is a chain of sulfur S_n , the disproportionation of sulfur in ammonia can be described by the equation :



From this equation a disproportionation constant K_n can be defined and calculated for several values of n . The disproportionation equation can be considered satisfactory if the equilibrium constant is effectively approximately constant in the range of dilute solutions. It was found /21/ that K_n increases with concentration for $n > 3$ and decreases for $n = 1$. For $n = 2$, K_2 is almost concentration independent. This suggests that the zero sulfur species at equilibrium involves two sulfur atoms. It is quite interesting to note that previous investigators had already suggested the presence of chemical species of the $S_{2,am}$ type in SAS. Kerouanton et al. /6/ have suggested the presence of S_2NH_3 in these solutions from cryoscopic studies. Sato et al. /22/ have suggested from organic syntheses using SAS that chemical species such as H_2NS^- and H_2NSS^- should be present in the solution.

Search for S_{am}

In a recent work Woolins et al. /23/ interpret their ^{14}N NMR work by the fact that S_7NH would account for 80 % of the S-N species in SAS solutions. More recently using ^{14}N and ^{15}N NMR Chivers et al. /24/ claim that S_7N^- accounts for ca. 80 % of the nitrogen containing anions in SAS. The conclusions of these authors are deduced from the comparison of the NMR study of S_7NH solutions with that of sulfur solutions. These conclusions cannot presently be reconciled with those deduced from UV-visible spectroscopy, because this latter technique led to the conclusion that S_7N^- is fully disproportionated in liquid ammonia /16,20/. The influence of amide addition on the absorption spectrum, as mentioned above, is a strong argument for the full disproportionation of S_7N^- in ammonia /20/. Obviously, it must be emphasized that the UV-visible experiments are run with dilute solutions (ca. 10^{-3} M) while NMR experiments are run with concentrated solutions (ca. 1 M). It does not seem possible to have an alternative suggestion for the assignment of the NMR data until more experiments are run, and they should be run at various concentrations of the S_7NH and sulfur solutions.

Schindewolf et al. /25,26,27/ succeeded recently to separate the components of SAS by anion exchange HPLC. They confirmed the presence of the anionic species with sulfur in oxidized and in reduced form. They also observed a chromatographic peak due to an anion with absorption bands at 300 and 420 nm. This anion in the separated form is unstable : its absorption spectrum changes with time to reach that of a SAS. They concluded that this anion contains sulfur in the zero oxidation state. They assigned this species as $S_xNH_2^-$ with $x = 4$. Their experiments reveal that $S_4NH_2^-$ is the primary species in the dissolution process which partly disproportionates to give mainly S_4N^- and S_3^- . They did not detect S_7N^- or uncharged species. These data are coherent with the results deduced from the influence

of the addition of potassium amide to SAS, but they cannot lead to the determination of the concentration of the various species in the solution. However, these data suggest that the overall effect of adding sulfur to ammonia is to increase the dissociation of this solvent.

A detailed quantitative analysis of the absorption spectra of SAS was recently done /28,29/. However such an analysis was only possible after the decomposition of the absorption spectra of $\text{Li}_2\text{S}_6\text{-NH}_3$ solutions /30/. It was then shown that between 220 and 800 nm, S_3^- and S_6^{2-} have 2 and 4 absorption bands, respectively. The extinction coefficient of these bands were determined /30/ and used in the decomposition of the absorption spectra of SAS. It was found that S_{am} has three absorption bands at 420, 300 and 250 nm. The decomposition of the absorption spectra of SAS allows the determination of the concentration of the various species. The variation of the concentration of the various species versus the concentration of the solution is plotted in Figure 5. It is seen that for rather concentrated solutions, most of the sulfur is solubilized under the form of S_{am} .

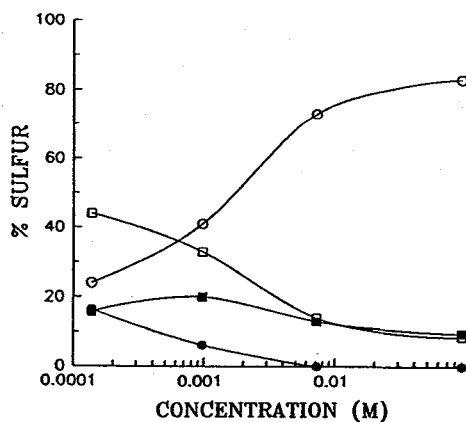


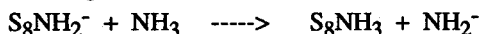
Figure 5. Proportion of the solubilized sulfur in the various species as a function of the concentration at $T = 290\text{K}$.

S_{am} (\circ) S_4N^- (\blacksquare)
 S_3N^- (\bullet) $\text{S}_6^{2-} + \text{S}_3^-$ (\square)

The highest concentration is 0.09 M.

On the solubilization mechanism of sulfur in liquid ammonia.

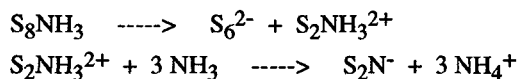
After their identification of S_4N^- and of S_3^- in SAS, Chivers and Lau /8/ proposed a reaction mechanism in which the first step would be the nucleophilic attack of cyclic sulfur, $c\text{-S}_8$, by the amide ion NH_2^- resulting from the self-dissociation of ammonia. According to Chivers and Lau, this nucleophilic attack would produce S_8NH_2^- that would disproportionate, giving first S_7N^- and H_2S , and subsequently S_4N^- and an ammonium polysulfide. Two arguments can be given against this model : the equilibrium concentration of NH_2^- is so small that the solubility of sulfur in ammonia could not be detectable ; when the solubilization of sulfur in ammonia is monitored by spectrophotometry, S_7N^- is not detected and these experiments show that S_4N^- is formed from the precursor species S_3N^- /16,17/. It has been suggested /21/ that, in the model of Chivers and Lau, amide could be regenerated by proton exchange, following



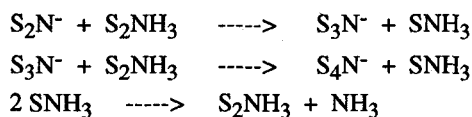
Obviously other S-S bonds in the S_8NH_3 species could undergo the same nucleophilic attack and yield smaller S_xNH_3 molecules such as S_2NH_3 according to



Meanwhile the same S_8NH_3 could undergo a disproportionation leading in the first step to the formation of S_6^{2-} and in the second step to the formation of S_2N^- :



The species S_2N^- produced in this reaction should be asymmetric with both sulfur atoms on the same side of the N atom ($S-S-N^-$) and different from the known symmetric species ($S-N-S^-$) ; it should be unstable and lead to S_3N^- and S_4N^- through reactions with S_2NH_3 such as :



Schindewolf et al. /27/ rule out the possibility that the solubilization would be initiated by the attack of NH_2^- on sulfur, because the equilibrium concentration of NH_2^- is so low in liquid ammonia. They suggest that the first step of the solubilization is the formation of $S_4NH_2^-$ by attack of ammonia on sulfur following



The disproportionation of $S_4NH_2^-$ would then lead to the formation of S_3^- and of S_3N^- . With such a model it is easy to realize that the disproportionation of $S_4NH_2^-$ would be strongly temperature dependent, but it is more difficult to understand that the reaction of S_8 with NH_3 is practically impossible at $-75^\circ C$, while it is much faster at, say, room temperature. This should mean that the disproportionation of $S_4NH_2^-$ is much easier when the temperature increases. It must also be noted that the above equation leads to an equilibrium concentration of NH_4^+ much larger than expected from Eq.(4). Consequently, the determination of the concentration of NH_4^+ could possibly confirm that S_{am} is indeed $S_4NH_2^-$.

The above equations are rather speculative, but it is hard to think that the solubilization process could be described very simply. These equations take into account the data from UV-visible spectroscopy : S_7N^- is not observed during the solubilization process and S_4N^- is formed from S_3N^- . The solubilization mechanism should also explain that the experimental process of solubilization is extremely slow and strongly temperature dependent. Obviously, a satisfactory model should be based on the spectroscopic identification of the yet unobserved intermediate species.

Conclusion

The understanding of solutions of sulfur in liquid ammonia has been much improved in less than 10 years. However the identification of the chemical species with the highest concentration, S_{am} , still requires further work and this is necessary to improve the description of the equilibrium state of these solutions. The identification of the transient species is also necessary in order to give a satisfactory interpretation of the reaction mechanism between sulfur and ammonia.

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