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ESR STUDY OF SOLUTIONS OF SULFUR AND POLYSULFIDES IN LIQUID AMMONIA

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Résumé : L'étude RPE des solutions de soufre et de polysulfures dans l'ammoniac liquide montre la présence d'une seule raie lorentzienne, située à $g = 2.0292$. Ce signal doit être attribué au radical anion S_3^- identifié dans ces solutions par spectrophotométrie et par spectroscopie Raman, et qui est donc la seule espèce radicalaire dans ces solutions. La concentration du radical S_3^- a été déduite des expériences RPE pour une large gamme de concentration des solutions. Pour les différentes solutions étudiées, la concentration de S_3^- augmente avec la concentration de la solution et passe par un maximum observé pour des solutions concentrées et attribué qualitativement à un appariement des spins des radicaux S_3^- .

Abstract : An ESR study of solutions of sulfur and polysulfides in liquid ammonia gives evidence of a simple Lorentzian line located at $g = 2.0292$. This signal must be assigned to the radical anion S_3^- identified in these solutions by spectrophotometry and Raman spectroscopy. It is shown that S_3^- is the only radical species in these solutions. The concentration of S_3^- has been determined from the ESR experiments for a wide concentration range of the solutions. For the various solutions, the concentration of S_3^- increases with the concentration of the solution and goes through a maximum, located in the concentrated range of solutions. This maximum is qualitatively interpreted by a spin pairing mechanism between the S_3^- radicals.

Introduction

A significant step in the understanding of the solutions of sulfur in liquid ammonia (SAS) was the identification in these solutions of S_4N^- and of the radical anion S_3^- by Chivers and Lau /1/ using Raman spectroscopy. However an ESR signal had not been previously observed in these solutions /2/. Chivers and Lau attributed the lack of an ESR signal in SAS to a possible dimerization of the S_3^- radical. The identification of S_3^- in SAS was confirmed by Bernard et al. /3,4/ using Raman spectroscopy and spectrophotometry. Dubois et al. /5,6/ showed that S_6^{2-} is the least reduced polysulfide in liquid

ammonia, and it is partly dissociated into S_3^- . The dissociation of S_6^{2-} is observed only for temperatures higher than ca. 200 K, and is strongly temperature dependent. Dubois et al. /5,6/ also observed that polysulfides are disproportionated in liquid ammonia, and that the disproportionation is higher for acidic solutions. In neutral solutions (Li_2S_n), the S_3^- radical has been observed from Raman spectroscopy and from spectrophotometry for $n > 3$. It is not observed for $Li_2S_3-NH_3$ solutions (for instance) because S_3^{2-} is not disproportionated in neutral solutions. However, in acidic solutions, $(NH_4)_2S_n$, the S_3^- radical has been observed for $n > 1$. Such differences result from the different disproportionation in neutral and acidic solutions.

The purpose of the present paper is to report the ESR identification of S_3^- in the various ammonia solutions in which this radical has been previously observed with other techniques : sulfur, lithium polysulfides and ammonium polysulfides. The purpose of these ESR experiments was also to check if S_3^- is the only radical in the investigated solutions, and also to determine the concentration of S_3^- in rather concentrated solutions, because for these highly colored solutions the concentration of S_3^- can only be deduced from the absorption spectra for dilute solutions.

Experimental

The lithium and ammonium polysulfide solutions are prepared by reducing sulfur with lithium and hydrogen sulfide respectively. The preparation of the solutions /5,6/, the ESR cells and the experimental conditions /13/ have been previously described.

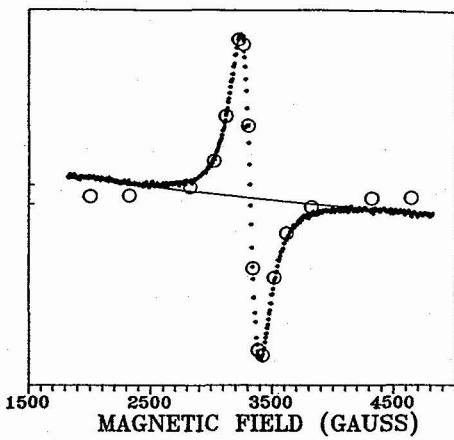


Figure 1. ESR signal of S_3^- at 290 K in a $Li_2S_6 - NH_3$ solution ($4 \times 10^{-3} M$). The experimental signal is fitted by the sum of a Lorentzian lineshape and a parabolic baseline.

..... : experimental data points.

oooo : Lorentzian lineshape

— : parabolic baseline

The sensitivity on the vertical scale is four times larger for the residuals than for the ESR signal.

The experimental signal is always rather weak and this leads to use high receiver gains. In these conditions a drift of the baseline is observed. The parameters of the ESR lineshape have been determined by fitting the experimental signal (Fig. 1) to the sum of a parabolic curve describing the drift of the baseline and of a Lorentzian signal following /7/ :

$$f(H) = \frac{16Y[2(H - H_0) / \Delta H_{pp}]}{\left[3 + \left[2(H - H_0) / \Delta H_{pp} \right]^2 \right]^2} + a(H - H_0)^2 + b(H - H_0) + c \quad (1)$$

where H_0 is the magnetic field at the center of the line, ΔH_{pp} the peak-to-peak linewidth of the derivative, Y the maximum of the derivative ; a, b and c are the parameters describing the parabolic shape of the baseline. The fit of $f(H)$ to the experimental signal using a non-linear least squares technique allows the determination of H_0 , ΔH_{pp} , Y, a, b and c. These parameters allow the calculation of the area A_s of the absorption signal using the classical formula /7/ relative to a Lorentzian lineshape :

$$A_s = \frac{2\pi}{\sqrt{3}} Y (\Delta H_{pp})^2 \quad (2)$$

The determination of the area A_s was found more accurate with the use of this fit procedure and Eq.(2) than with the numerical double integration technique available from the Bruker ESP 1600 computer program. The numerical double integration technique leads systematically to lower values for A_s by ca.5 %. This is assigned to the broad linewidth of the Lorentzian lineshape. On the wings of the signal, the signal is merged in the noise over a large magnetic field range.

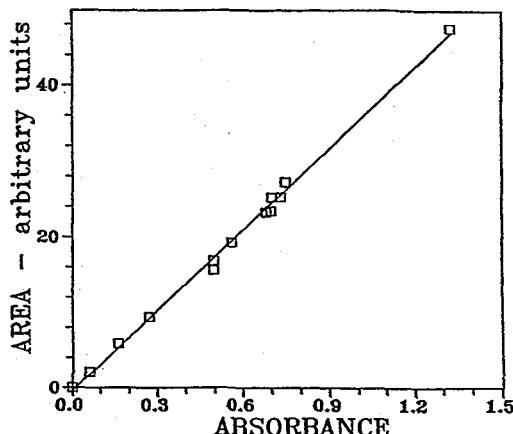


Figure 2. Plot of A_s versus A. The area A_s is given for an internal diameter of 1 mm and the absorbance A for an optical pathlength of 0.05 cm.

The conversion of the ESR signal of a given sample into the concentration of the paramagnetic species requires the calibration of the sensitivity of the spectrometer. For this purpose, we have demonstrated that the ESR signal of the S_3^- radical anion observed in solution of lithium hexasulfide (Li_2S_6) in liquid ammonia can be used as a standard /8/. It can easily be shown /8/ that the area A_s of the absorption signal is related to the absorbance A at 610 nm by :

$$A_s = \frac{V}{\beta \epsilon l} A \quad (3)$$

where ϵ is the extinction coefficient of S_3^- , l the optical path length, V the volume of sample undergoing the ESR resonance phenomenon, and β is a proportionality constant. Consequently, if for samples at a given temperature, or for a sample at various temperature, A_s is plotted versus the absorbance A at 610 nm, a linear variation must be obtained. Such a linear variation is found as shown in Fig. 2.

Results.

General aspects. For all the investigated samples (sulfur and polysulfides in ammonia) a single ESR line has been observed for temperatures higher than 200 K. All the recorded lines can be fitted to a Lorentzian lineshape. The position of the line ($g = 2.0292 \pm 0.0009$) is temperature and concentration independent. This ESR signal must be assigned to S_3^- because this radical has previously been identified in these solutions with Raman spectroscopy and visible spectrophotometry. For all the investigated samples, the area A_s of the ESR signal, *i.e.* the concentration of S_3^- , decreases when the temperature decreases and the ESR signal is not detectable at 200 K (Figs. 3a and 3b). These observations are in agreement with the variations of the concentration of S_3^- with temperature observed by spectrophotometry in dilute solutions of sulfur or polysulfides in liquid ammonia.

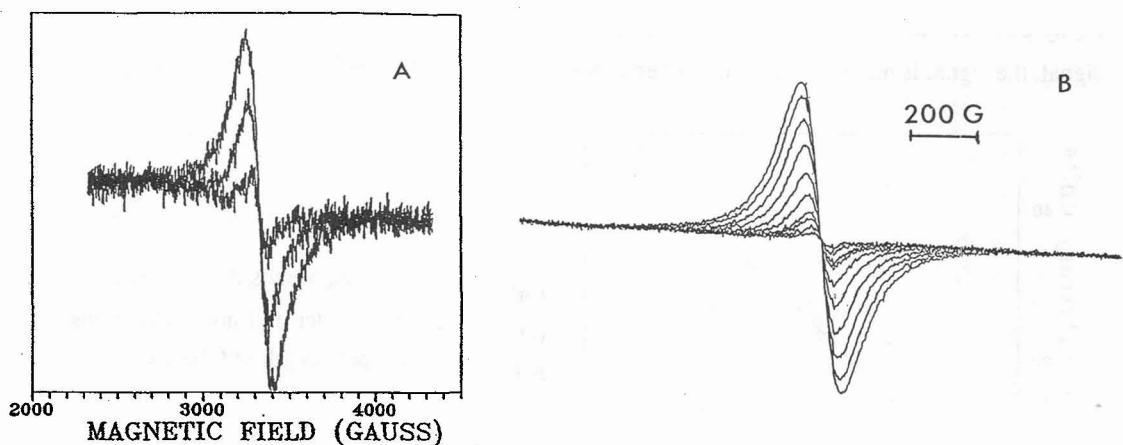


Figure 3. ESR signal of S_3^- ; A : in a $S - NH_3$ solution (0.1 M) ; $T = 286, 255, 225$ K. ; B : in a Li_2S_6 solution ($4 10^{-3}$ M) ; $T = 290, 280, 270, \dots 200$ K.

Solutions of sulfur in ammonia. The ESR signal has been detected in $S-NH_3$ in a large concentration range from about $1 10^{-3}$ M up to saturated solution (3.6 M) between 200 and 290 K. At a given temperature, the variation of the concentration of S_3^- with the concentration of the solution displays an unexpected behavior (Fig. 4). In the dilute range of concentration, the concentration of S_3^- increases slowly with the concentration of the solution : for a $2.5 10^{-3}$ M solution, the concentration of S_3^- is $3 10^{-4}$ M at room temperature. When the concentration of the solution is increased by a factor of one hundred (0.25 M), the concentration of S_3^- is increased by a factor of four and is close to $1.2 10^{-3}$ M.

These data confirm that the disproportionation of sulfur in ammonia is a chemical equilibrium, as it has been previously shown /11,12/, i.e. the disproportionation of sulfur is not complete. The unexpected aspect of these results is that the concentration of S_3^- goes through a maximum for concentrated solutions (ca. 1.5 M, i.e. for a mole ratio $NH_3/S \sim 24$) /13/. A similar behavior has been observed in solutions of polysulfides in ammonia, as indicated and discussed below.

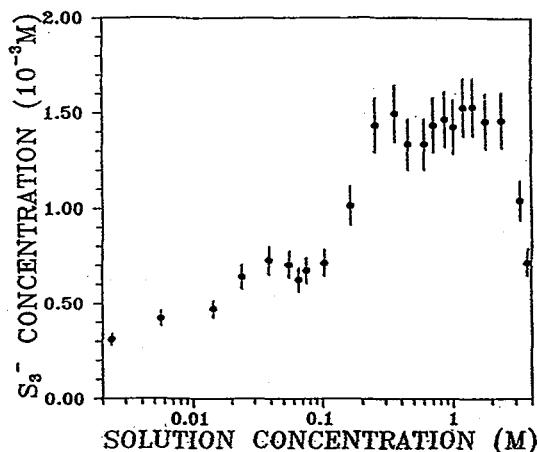


Figure 4. Variation of the S_3^- concentration versus the concentration of the $S-NH_3$ solution at 290 K.

Solutions of polysulfides in ammonia. For the comparison of the results obtained for polysulfide solutions with various stoichiometries (i.e. for various values of n), it was found useful to have a common concentration scale for all these solutions. This concentration scale is defined relatively to the number of sulfur atoms in the solution, whatever its oxidation state. On this scale, the "molar concentration" is given by $C_s = 36 n / R$. The concentration of S_3^- , deduced from the ESR signal for the various solutions at 290 K, is plotted versus the concentration of the solution on Fig. 5, where the concentration of the solution is given on the C_s scale. As expected from the absorption spectra /5,6/, the concentration of S_3^- is larger in $Li_2S_6-NH_3$ solutions than in $Li_2S_4-NH_3$ solutions and in $(NH_4)_2S_6-NH_3$ than in $(NH_4)_2S_4-NH_3$. The ESR results also confirm that the disproportionation of polysulfides ions is higher in acidic (NH_4^+) solutions than in neutral solutions. For $n = 6$, the concentration of S_3^- is higher in lithium than in ammonium solutions, because S_6^{2-} is disproportionated in ammonium solutions, as it has been shown from visible spectrophotometry /5,6/. For $n = 4$, S_4^{2-} is more disproportionated in acidic solutions and this leads to higher concentration of S_6^{2-} and therefore of S_3^- : the concentration of S_3^- is therefore higher in $(NH_4)_2S_4-NH_3$ solutions than in $Li_2S_4-NH_3$ solutions. These results previously shown from visible spectrophotometry for dilute solutions are here extended for all the concentrations.

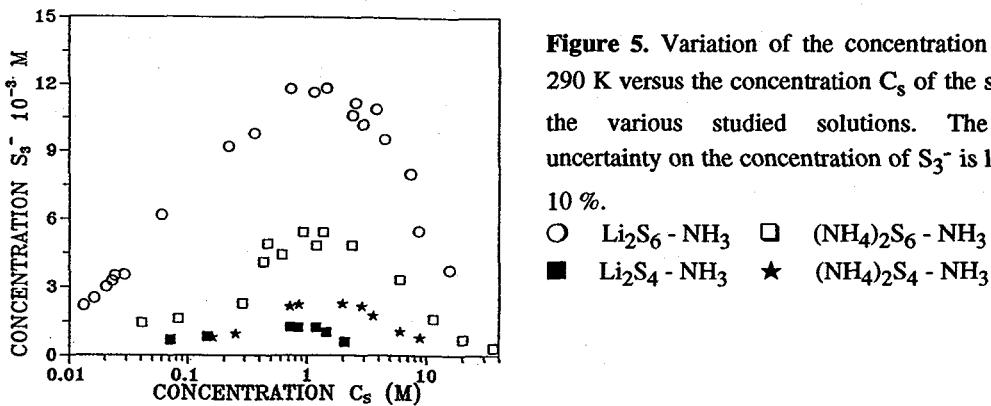


Figure 5. Variation of the concentration of S_3^- at 290 K versus the concentration C_s of the solution in the various studied solutions. The relative uncertainty on the concentration of S_3^- is lower than 10 %.

Figure 5 also shows that, for all types of solutions of polysulfide, the concentration of S_3^- increases with the concentration of the solution and goes through a maximum. This maximum is found for concentrated solutions. On the C_s scale, this maximum is located at the same concentration of the solution (*ca.* 1 M). It is found that the concentration of S_3^- at the maximum depends upon the studied solutions : at the maximum, the concentration of S_3^- is about five times larger for $Li_2S_6-NH_3$ solutions than for $Li_2S_4-NH_3$ solutions. Obviously, this maximum cannot be expected from the equilibrium constant given by eq. (3). It can be easily shown /9/ that the concentration $[S_3^-]$ can be expressed as a function of the dissociation equilibrium constant $K(T)$ of S_6^{2-} and the concentration C_o of S_6^{2-} at 200 K :

$$[S_3^-] = \frac{K(T)}{4} \left[\left(1 + \frac{16C_o}{K(T)} \right)^{1/2} - 1 \right] \quad (4)$$

From eq. (4) the concentration $[S_3^-]$ increases monotonically with C_o . Obviously, this equation is strictly valid only for dilute solutions when the activity coefficients can be ignored. Let us admit that eq (4) gives the theoretical concentration of S_3^- , i.e. $[S_3^-]_{th}$, while the ESR experiments give the experimental concentration $[S_3^-]_{exp}$. The difference between $[S_3^-]_{th}$ and $[S_3^-]_{exp}$ can be rationalized by plotting $\log([S_3^-]_{exp} / [S_3^-]_{th})$ versus $(C_s)^{1/2}$ (Fig. 6). A plateau is observed for dilute solutions, because the concentration of S_3^- is then correctly predicted by eq. (4). For moderately concentrated and concentrated solutions, a linear variation is observed versus $(C_s)^{1/2}$. This plot shows that the chemical process leading to the maximum of the concentration of S_3^- starts from the dilute range of concentration, and it suggests that the variations of the concentration of S_3^- result from the same chemical mechanism in all the concentration range, except for highly dilute solutions. The observed correlation between $\log([S_3^-]_{exp} / [S_3^-]_{th})$ and $(C_s)^{1/2}$ suggests that we are dealing with a mechanism controlled by ion-ion interactions. However, at the microscopic level, the decrease of the ratio $[S_3^-]_{exp} / [S_3^-]_{th}$ can be assigned to a spin pairing process between the S_3^- radicals. These radicals are submitted to two opposite forces : the long range coulombic repulsion force and the short range attractive magnetic force which is the driving force to the spin pairing process. When the concentration of the solution increases, the average distance between the S_3^- radicals decreases and the probability that two radicals could be paired increases. It is suggested that when two radicals are close enough to be paired, they form a transient

species in which each S_3^- keeps its structure. The same comparison between $[S_3^-]_{\text{exp}} / [S_3^-]_{\text{th}}$ and $(C_s)^{1/2}$ has been made for other types of polysulfide solutions in ammonia : $(\text{NH}_4)_2\text{S}_6$, $(\text{NH}_4)_2\text{S}_4$, Li_2S_4 . Similar variations to those observed for $\text{Li}_2\text{S}_6\text{-NH}_3$ solutions have been found, indicating that we are dealing with the same physical effect in all types of solutions /14/.

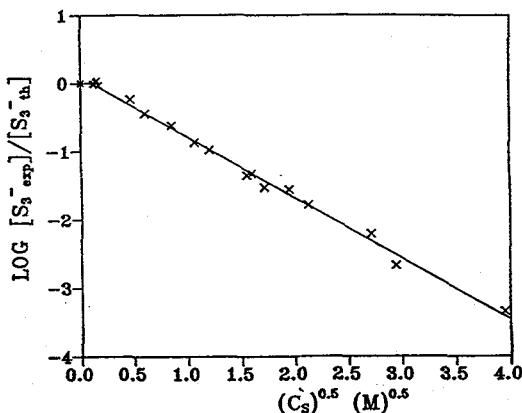


Figure 6. $\text{Log } ([S_3^-]_{\text{exp}} / [S_3^-]_{\text{th}})$ versus $C_s^{1/2}$.

The numerical equation of the linear part of the plot is : $-0.89 C_s^{1/2} + 0.114$

Variation of the concentration of S_3^- with temperature. It is well known that when the temperature decreases, the equilibrium between S_6^{2-} and S_3^- is shifted towards S_6^{2-} . The activation energy ΔH of this equilibrium has been determined for dilute solutions from spectrophotometry experiments and found to be equal to $49.1 \pm 1.0 \text{ kJ.mol}^{-1}$. If eq. (4) is considered, when $16 C_o \gg K(T)$ (i.e. $C_o \gg 3 \cdot 10^{-4} \text{ M}$ at room temperature), the concentration $[S_3^-]$ is approximatively given by :

$$[S_3^-] = (C_o K(T))^{1/2} \quad (5)$$

with $K(T) = K_o \exp(-\Delta H / RT)$. The activation energy can, therefore, be determined from the ESR experiments by plotting $\text{Log } [S_3^-]$ versus $1/T$. For dilute $\text{Li}_2\text{S}_6\text{-NH}_3$ solutions, ΔH is found equal to $49.0 \pm 1.0 \text{ kJ.mol}^{-1}$. However, for solutions more concentrated than 0.1 M , ΔH is found equal to ca. 60 kJ.mol^{-1} . The same values of ΔH are obtained for $(\text{NH}_4)_2\text{S}_6\text{-NH}_3$ solutions : about 50 kJ.mol^{-1} for dilute solutions and 60 kJ.mol^{-1} for concentrated solutions. The similarity of the results obtained for Li_2S_6 and $(\text{NH}_4)_2\text{S}_6$ solutions is an indication that the disproportionation of S_6^{2-} in the latter solutions is temperature independent.

Variation of the linewidth with concentration and temperature. The experimental values of ΔH_{pp} for the various investigated solutions give a well defined curve if the concentration scale C_s is used (Fig. 7). For dilute and moderately concentrated solutions, the linewidth is practically concentration independent. It is observed that the linewidth decreases sharply when the concentration of S_3^- decreases, i.e. for $C_s > 1 \text{ M}$. This correlation suggests that both variations could have the same origin.

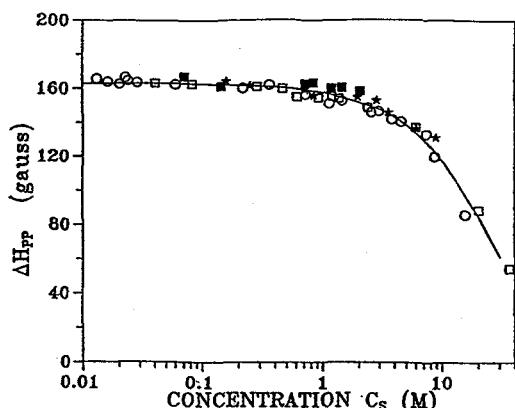


Figure 7. Variation of the linewidth ΔH_{pp} at 290 K versus the concentration C_s of the solution for all the investigated solutions.

○ $\text{Li}_2\text{S}_6 - \text{NH}_3$ □ $(\text{NH}_4)_2\text{S}_6 - \text{NH}_3$
 ■ $\text{Li}_2\text{S}_4 - \text{NH}_3$ ★ $(\text{NH}_4)_2\text{S}_4 - \text{NH}_3$

It has been found that the linewidth increases when the temperature increases : approximately 10 G. for every 10 degrees /14/. The variations of $\log \Delta H_{pp}$ are linear versus $1/T$, with a slope equal to $5.6 \pm 0.7 \text{ kJ.mol}^{-1}$. This slope is constant for dilute and moderately concentrated solutions. A close correlation is found between ΔH_{pp} and $\epsilon T / \eta$, where ϵ is the dielectric constant and η the viscosity of pure liquid ammonia. The slope of $\log (\epsilon T / \eta)$ is found equal to 5.3 kJ.mol^{-1} . The relaxation mechanisms will not be discussed in the present paper but it must be emphasized that the relaxation time is short ($\sim 1 \text{ ns}$) and that we are therefore dealing with a very fast relaxation mechanism.

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