



HAL
open science

ELECTROCHEMICAL STUDY OF POLYSULFIDE SOLUTIONS IN LIQUID AMMONIA

E. Levillain, C. Jehoulet, A. Demortier, J. Lelieur

► **To cite this version:**

E. Levillain, C. Jehoulet, A. Demortier, J. Lelieur. ELECTROCHEMICAL STUDY OF POLYSULFIDE SOLUTIONS IN LIQUID AMMONIA. Journal de Physique IV Proceedings, 1991, 01 (C5), pp.C5-237-C5-243. 10.1051/jp4:1991528 . jpa-00250652

HAL Id: jpa-00250652

<https://hal.science/jpa-00250652>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

ELECTROCHEMICAL STUDY OF POLYSULFIDE SOLUTIONS IN LIQUID AMMONIA

E. LEVILLAIN, C. JEHOULET, A. DEMORTIER and J.P. LELIEUR

URA 253 CNRS, HEI, 13 rue de Toul, F-59046 Lille cedex, France

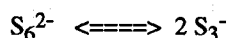
Résumé : Nous présentons les caractéristiques électrochimiques obtenues par voltampérométrie cyclique et par spectroscopie d'impédance pour les solutions de polysulfure de lithium et d'ammonium dans l'ammoniac liquide. Le comportement électrochimique dépend fortement du type de solution, conséquence de la dismutation de la plupart des ions polysulfures et du couplage des réactions de transfert d'électron avec des réactions chimiques en phase homogène.

Abstract : We present here the electrochemical characteristics obtained for cyclic voltammetry and impedance spectroscopy for lithium and ammonium polysulfide in liquid ammonia solutions. The observed electrochemical behaviour depends strongly on the type of solution, as a consequence of the disproportionation of most of the polysulfide ions and of the coupling of electron transfer reactions with homogeneous chemical reactions.

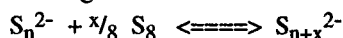
Introduction

In solution, solvent or molten salts, the polysulfide ions are possibly subjected to three types of reaction /1/ :

- an homolytic dissociation leading to radical ions; the typical example is the well known equilibrium :

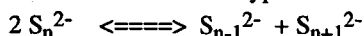


- a reaction of exchange of sulfur atoms :



This reaction has been used to prepare least reduced polysulfide from S^{2-} . In presence of an excess of sulfur, the reaction stops when the least reduced polysulfide in the solvent is obtained; the solution contains S_8 and S_{max}^{2-} .

- a disproportionation reaction of the type :



These polysulfides can also be partly or totally disproportionated; as a consequence, the stoichiometry of a disproportionation reaction of a given polysulfide ion can be complex and depend on the nature of the

solvent. An other consequence of this type of reaction : when a solvent is added to a solid of overall composition Li_2S_n , the resulting solution may usually contain, at equilibrium, several polysulfide ions.

In liquid ammonia, the following informations have been obtained by spectroscopic techniques /2,3/ :

- S_6^{2-} is the least reduced polysulfide. This ion is not disproportionated in neutral solutions and is always in equilibrium with S_3^-

- S_5^{2-} is strongly, if not totally, disproportionated.

- S_4^{2-} is only partially disproportionated. This has been shown by the observation of S_3^- (UV-visible, Raman, ESR) in the solutions. The reduced species cannot be identified by these techniques because the various polysulfides S_n^{2-} absorb at the same wavelengths (300 - 400 nm).

- The polysulfide ions are always more disproportionated in acidic (NH_4^+) solutions. This behavior is due to the displacement of the disproportionation reactions by the acid-base reaction



since it has been shown that HS^- is the only protonated sulfur species in liquid ammonia.

From a formal point of view, the oxidation number of a polysulfide ion S_n^{2-} is $-2/n$. The reactions of the polysulfides ions can be considered as redox reactions and studied by electrochemical techniques. In this communication, we present the contribution of electrochemistry to the knowledge of polysulfide ions solutions.

Experimental.

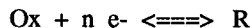
Li_2S_n and $(\text{NH}_4)_2\text{S}_n$ solutions are prepared by reduction of sulfur with Lithium or H_2S in stoichiometric amount. The details of this preparation have been described in detail elsewhere /4,5/.

The cyclic voltammetry have been performed with a potentiostat EGG 273 and a three electrodes cell. The auxiliary electrode was in gold or tungsten. The working electrode was a stationary gold disk electrode 2 mm in diameter. A gold or tungsten wire located near the working electrode was used as a pseudo-reference electrode. This is possible, because the various polysulfide ions are more or less disproportionated; the redox level of the solutions is always very well defined. Due to this set-up, the design of the cell was simple and temperature up to 10 °C can be attained. For the study of Li_2S_4 and $(\text{NH}_4)_2\text{S}_4$ solutions around the equilibrium potential, the addition of a supporting electrolyte was not necessary : the concentration of the electroactive species is very low compared to the concentration of Li^+ and S_4^{2-} ions. For other solutions and for the analysis at large overvoltages, LiNO_3 was used as the supporting electrolyte. For cyclic voltammetry experiments, the initial potential was the equilibrium potential (overvoltage = 0). From this value, the initial scan direction may be positive or negative.

The electrochemical impedance were measured between $10^{4.8}$ and 10^{-2} or 10^{-3} Hz (10 or 20 points per decade) with the Solartron 1250 frequency response analyzer and the Solartron 1286 electrochemical interface. When possible, the experiments where run on the same cells as the voltammetric experiments. For the purpose of clarity only 5 points per decade are displayed in the figures.

Li_2S_4 - NH_3 solutions at the equilibrium potential.

The experimental results obtained from cyclic voltammetry and electrochemical impedance for Li_2S_4 - NH_3 solutions give evidence of a simple electron transfer reaction in a solution containing both the oxidized and the reduced form of a redox couple :



The existence of a well defined equilibrium potential, the shape of the voltammograms (Fig 1), the influence of the initial scan direction and of the scan rate are in close agreement with the conclusions of a theoretical study of such a system /6/. The electrochemical impedance at the equilibrium potential in moderately concentrated solutions (Fig 2) confirms this conclusion. The small semi-circle observed at high frequency suggests a relatively fast electron transfer reaction and the Warburg line at low frequency is typical of the diffusion of the electroactive species.

We have shown /4/ that the coupling of the theory of cyclic voltammetry and electrochemical impedance with the experimental results with these techniques in a wide range of concentration and temperature gives, without any assumption, the number of electrons involved in the electrochemical reaction. Only a *one electron transfer reaction* can account for the experimental results.

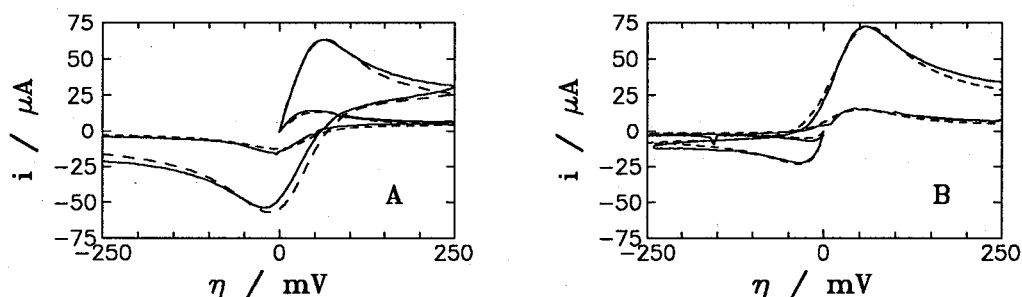


Fig 1. Cyclic voltammograms of a 0.36 M Li_2S_4 solution at 252 K; scan rates : 500 and 20 mV s^{-1} (A) positive initial scan direction; (B) negative initial scan direction.
(—————) experimental ; (- - - - -) theoretical

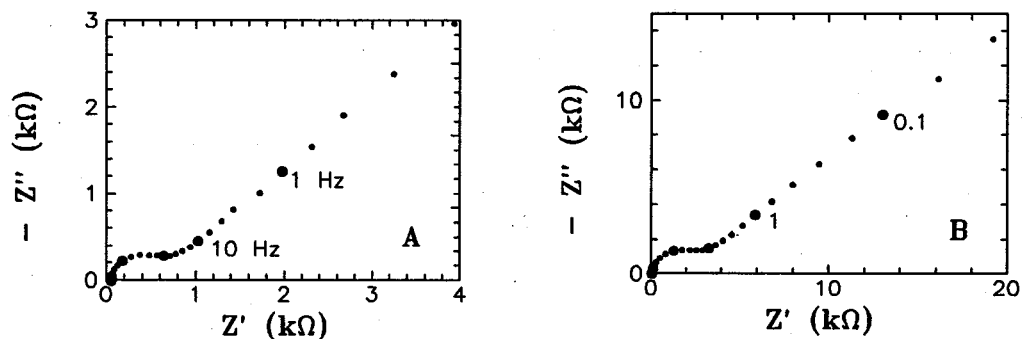
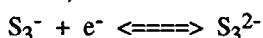


Fig 2. Impedance diagram of a 0.72 M Li_2S_4 solution on platinum (electrode area: 0.031 cm^2).
(A) 257 K; (B) 243 K.

The order of magnitude of the peak currents observed in cyclic voltammetry is weak. An estimate of the concentration of the electroactive species suggest that these concentrations are smaller by two orders of magnitude than the analytical concentration of the solutions and it can be concluded that the electroactive species are polysulfide ions resulting from the disproportionation of S_4^{2-} . The spectroscopic experiments have shown that S_6^{2-} and S_3^- are the only polysulfides more oxidized than S_4^{2-} and that the concentration of S_3^- increases with temperature. In $Li_2S_4-NH_3$ solutions, ESR experiments show that only one radical species, S_3^- , is present in solution /7/. This radical is the only singled charged species that can accept one electron. These arguments lead to the identification of S_3^- as the oxidized species of the redox couple. Therefore, the electrochemical reaction in the solution is :



This conclusion is supported by several experimental observations: *i* the variation of the cathodic peak currents with temperature, *ii* their variation, with the analytical concentration of the solution, which follows that of the ESR signal /4,7/, *iii* the variation of the shape of the voltammograms with the stoichiometry of the solution ($3.5 < n < 4.5$). It must be noted that S_3^{2-} cannot be identified by spectroscopy in Li_2S_4 solutions.

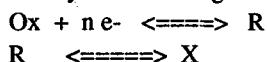
On the base of the conclusions derived above, the disproportionation reaction of S_4^{2-} may be written, as a first approximation, as :



This reaction is based on the assumption of the total disproportionation of S_5^{2-} ion in liquid ammonia. The experimental results show that the electrochemical properties are characteristic of a simple redox reaction and that the competition of homogeneous chemical reactions can be ignored. The chemical system can be considered as frozen on the time scale of the electrochemical experiments: the kinetics of the disproportionation reaction is rather slow. An estimate of the concentration of the electroactive species, based on an hypothesis for the diffusion coefficient, indicates that S_4^{2-} is only partly disproportionated: the concentrations of S_3^- and S_3^{2-} are always less than 1% of the analytical concentration.

$(NH_4)_2S_4 - NH_3$ solutions at the equilibrium potential.

The experimental data for $(NH_4)_2S_4 - NH_3$ solutions at the equilibrium potential appear to be very different from those found for Li_2S_4 . For cyclic voltammetry (Fig 3), when the initial scan direction is negative, a reduction peak current is observed; on the reverse scan, an anodic peak is displayed for the highest scan rates, which show that there is some reversibility of the electrochemical reaction. When the initial scan direction is positive, an anodic plateau almost independent of the scan rate is displayed. These observations are explained by the following model /4,6/ :



with Ox, R and X initially present in solution. The low intensity of the anodic plateau shows that the reaction is shifted strongly to the right. The observation, for high scan rates and low temperatures, of the reoxidation of R and of the anodic plateau independence from the scan rate show that the kinetics of the chemical reaction limit the oxidation current.

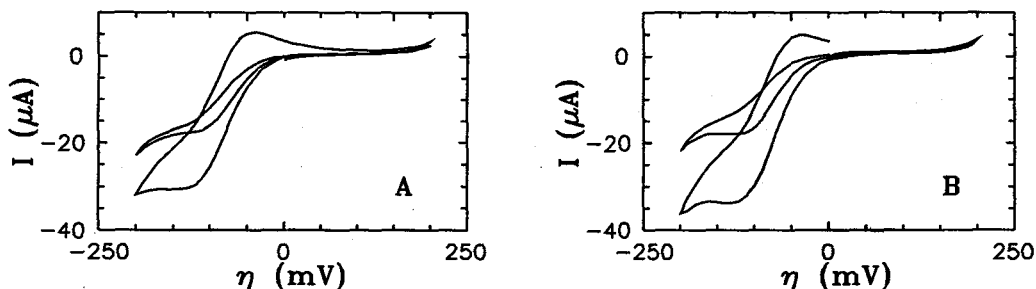


Fig 3. Cyclic voltammograms of a 0.24 M $(\text{NH}_4)_2\text{S}_4$ solution at 252 K; scan rate : 100 and 10 mV s^{-1} (A) negative initial scan direction; (B) positive initial scan direction.

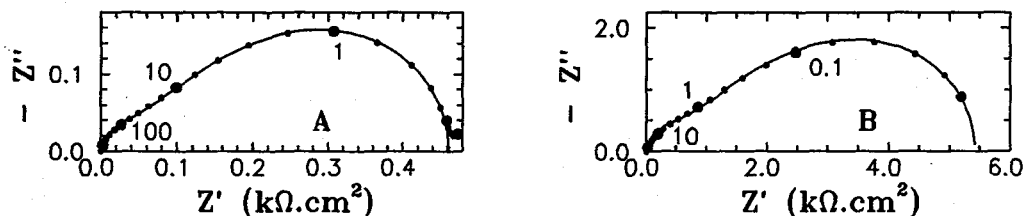


Fig 4. Impedance diagram of a 0.128 M $(\text{NH}_4)_2\text{S}_4$ solution on platinum. (A) 263.7 K; (B) 231.9 K. (●) experimental data; (—) best fit.

The shape of the impedance diagram (Fig 4) also suggests a Gerischer profile /8/ which is expected for the EC_R mechanism given above (electrochemical reaction, E, coupled with a reversible chemical reaction, C_R).

Since it has been shown by spectroscopic techniques that S_4^{2-} is also disproportionated in solutions of ammonium tetrasulfide in liquid ammonia, it is deduced that S_3^- and S_3^{2-} are present in solution. From the voltammograms it can be concluded that the reduced species, S_3^{2-} , is in equilibrium with another species. Since this phenomenon is not observed for $\text{Li}_2\text{S}_4\text{-NH}_3$ solutions, the chemical reaction must involve the NH_4^+ ions. The kinetic parameter of the chemical reaction can be obtained by a quantitative analysis of the impedance diagram. The variations of this parameter as a function of temperature and of the analytical concentration also suggest that the main factor is the ammonium ion concentration. It has been shown that HS^- is the only protonated sulfur species and that S_3^{2-} and S_2^{2-} are at least partly disproportionated in ammonium solutions. The equilibrium reaction is certainly more complex than a simple first order reaction and must proceed in several steps involving protonation and disproportionation reactions. Several reaction mechanisms can be written. This subject is under study by impedance spectroscopy for $(\text{NH}_4)_2\text{S}_n\text{-NH}_3$ solutions ($1 < n < 6$).

$\text{Li}_2\text{S}_n\text{-NH}_3$; large overvoltages.

The knowledge of the electrochemical properties of $\text{Li}_2\text{S}_n\text{-NH}_3$ solutions at the equilibrium potential has made possible the progress in the understanding of the behaviour of Li_2S_n solutions for large overvoltages. In this paper, we limit the discussion to the results obtained for one concentration ($C=0.036\text{ M}$) and one temperature ($0\text{ }^\circ\text{C}$) for the same scan rate ($0.2\text{ V}\cdot\text{s}^{-1}$).

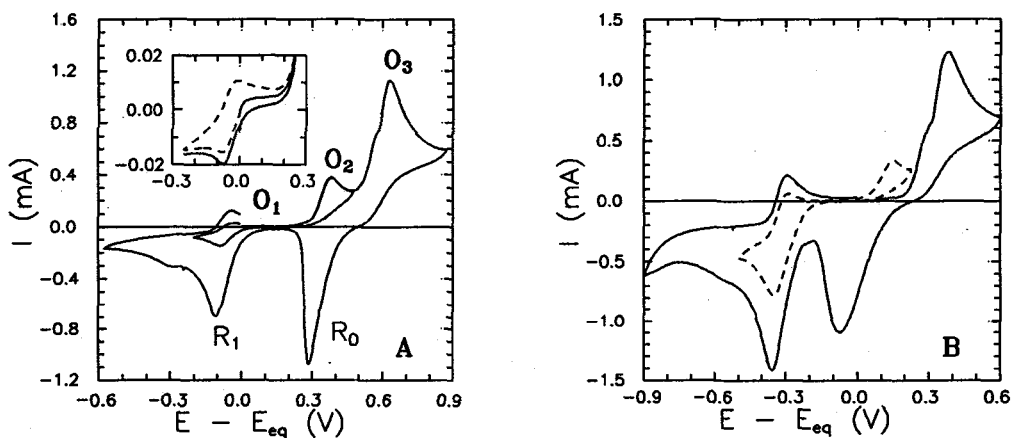


Fig 5 Cyclic voltammograms of $0.036\text{ Li}_2\text{S}_n$; $0.2\text{ V}\cdot\text{s}^{-1}$; 273 K . (A) Li_2S_4 ; (B) Li_2S_6
 (———) : positive initial scan direction; (- - - -) : negative initial scan direction.

Fig 5a displays the experimental data for a Li_2S_4 solution. The characteristics around the equilibrium potential, plotted in the insert, are similar to those of Fig 1; the reduction peak is noted R_1 and the oxidation peak, O_1 . When the initial scan direction is positive, an oxidation peak O_2 is observed. This peak is assigned to the oxidation of S_4^{2-} , the only species present in solution at high concentration. When the potential scan is switched immediately after O_2 , an increase in current for R_1 is observed: the irreversible oxidation of S_4^{2-} leads to the formation of $\text{S}_6^{2-} + \text{S}_3^-$. When the overvoltage is larger than the value related to O_2 , a large irreversible peak, O_3 , is observed. It will be shown later that this peak must be assigned to the oxidation of $\text{S}_6^{2-} + \text{S}_3^-$. The peak R_0 , observed on the reverse scan is due to the species formed during the oxidation O_3 . The shape of this peak is typical of an insoluble species precipitated on the electrode. By comparison with the cyclic voltammograms of solutions of S_8 in non aqueous solvents, DMSO /9,10/ and DMF /10/, we assign this peak to the reduction of insoluble S_8 deposited on the electrode. It must be noted that S_8 is highly soluble in liquid ammonia; however the dissolution is rather slow even at room temperature. An other confirmation of this assignment, is the large peak R_1 following R_0 : as in DMSO and DMF, the reduction of S_8 leads to the formation of $\text{S}_6^{2-} + \text{S}_3^-$.

The results for Li_2S_6 (Fig 5b) are coherent with these conclusions. When the scan direction is positive, the peak O_2 is not observed since the solution does not contain S_4^{2-} . The peak O_3 , the first oxidation process observed must be assigned to $\text{S}_6^{2-} + \text{S}_3^-$. When the scan direction is negative, as

expected, the peak current for R_1 is larger than in Li_2S_4 solutions. On the reverse scan, the oxidation peak O_2 , associated to S_4^{2-} , is observed. The reduction of S_3^- gives S_3^{2-} ; these two species react in the diffusion layer to produce S_4^{2-} ; this reaction, the opposite of the disproportionation reaction of S_4^{2-} is rather fast.

The experimental results for a solution of overall composition Li_2S_5 are consistent with these observations. Due to the absence of a "true" reference electrode, the peak potentials are function of the stoichiometry of the solutions. However, it is possible to reference all the potentials to the same origin: the potential of the peak R_1 . The same values (within the experimental errors) are obtained for O_1 , O_2 , O_3 and R_0 for all types of solutions, and also for sulfur and $(NH_4)_2S_n$ solutions. These values show that the peaks correspond to the same electrochemical phenomena in all types of solution.

Conclusion.

The electrochemical properties of Li_2S_n and $(NH_4)_2S_n$ solutions in liquid ammonia at the equilibrium potential give informations on the equilibrium state of these solutions. They confirm and complete the conclusions of the spectroscopic techniques.

The results presented in this paper for $Li_2S_n-NH_3$ solutions are preliminary and their interpretation is largely qualitative. They show that it will be possible to assign and understand the oxidation and reduction waves in Li_2S_n and $(NH_4)_2S_n$ solutions. With the exception of the system S_3^- / S_3^{2-} , the electrochemical systems are irreversible and may correspond to slow electron transfer reactions or/and to electron transfer coupled to irreversible homogeneous chemical reactions.

These results also show that the radical ion S_3^- plays a key role in the electron transfer reactions in these solutions.

Acknowledgements : The authors thank Professor G. Lepoutre for stimulating discussions. They express their gratitude to the CNRS, the Région Nord-Pas de Calais and the fondation Norbert Segard for fellowships to C.J. and E.L..

References

- /1/ Badoz-Lambling, J., Bonnaterre, R., Cauquis, G., Delamar, M., Demange, G., *Electrochim. Acta* **21** (1976) 119
- /2/ Dubois, P., Lelieur, J.P., Lepoutre, G., *Inorg. Chem.* **27** (1988) 73
- /3/ Dubois, P., Lelieur, J.P., Lepoutre, G., *Inorg. Chem.* **27** (1988) 1883
- /4/ Jehoulet, C., Demortier, A., Lelieur, J.P., *J. Electroanal. Chem.* **292** (1990) 153
- /5/ Jehoulet, C., Demortier, A., Lelieur, J.P., *J. Electroanal. Chem.* **296** (1990) 77
- /6/ Demortier, A., Jehoulet, C., *J. Electroanal. Chem.* **283** (1990) 15
- /7/ Pinon, V., Thèse Lille (1990)
- /8/ Gerischer, H., *Z. Phys. Chem.* **198** (1951) 286
- /9/ Martin, P., Doub, W.H., Roberts, J.L., Sawyer, D.T., *Inorg. Chem.* **12** (1973) 1921
- /10/ Levillain, E., Demortier, A., unpublished results