

Electrochemical Reduction of Aromatic Sulfinic Acids in Dimethylsulfoxide

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ABSTRACT

The electrochemical reduction of benzenesulfinic, p-toluenesulfinic, and p-nitrobenzenesulfinic acids was studied in dimethylsulfoxide solutions. From cyclic voltammetry experiments, a chemical reaction following the first electron transfer was detected during the reduction process. A cyclic voltammetry technique using ultramicroelectrodes has provided kinetic parameters for the electron-transfer steps, from which it was possible to observe the influence of the ring substituent on the electrochemical reduction. The mechanism of the electroreduction of aromatic sulfinic acids in dimethylsulfoxide depends upon the nucleophilic attack of the radical anion produced on the starting compound during the reduction processes.

Introduction

Sulfinic acids are unstable organic sulfur compounds whose occurrence in nature is restricted to 2-aminoethanesulfinic acid, isolated from some mollusk species, and to cisteinosulfinic acid, which is an intermediate in the oxidation of cysteine.^{1,2} These compounds usually undergo disproportionation, producing the corresponding sulfonic acid and sulfonate ion. Sulfinic acids and their derivatives have been used as an analytical reagent for the determination of metallic ions,^{3,4} as precursors or reagents in polymerization processes,^{5,6} and even as an assimilating agent in medicine.⁷

In the literature there are several papers reporting the participation of sulfinic acids and their derivatives as intermediates in the electrochemical reactions of sulfur compounds. Simonet and Jeminet^{8,9} performed polarographic studies on aromatic sulfones in which the influence of the ring substituent was investigated. In aprotic medium a two-electron wave related to the cleavage of the C-S bond is observed. These authors observed the electrochemical inactivity of p-toluenesulfinic acid produced under these experimental conditions. In their aprotic medium, a well-defined one-electron polarographic wave was observed. Analysis of the electrolyzed solution by electron paramagnetic resonance (EPR) showed a signal attributed to the p-toluenesulfinic acid radical anion. The reported signal was only obtained if the solution was maintained at -20°C.

Gourcy *et al.*¹⁰ studied the electrochemical reduction of sulfonyl chlorides in dimethylformamide and acetonitrile solutions in the presence of alkyl halides as an electrophilic agent. These authors observed the production of ArSO_2^- and ArS^- species from the electrochemical reduction of the corresponding aromatic sulfonyl chlorides. The species produced reacted with the electrophilic agent pro-

ducing a sulfone or sulfide. The influence of the aprotic solvent was also investigated.

Jeminet *et al.*¹¹ reported results obtained from polarographic studies of sulfonyl chlorides. In dimethylformamide and dimethylsulfoxide solutions a two-electron reduction wave was observed plus an oxidation wave that was attributed to chloride ion. The authors pointed out the role of the acidic medium in the mechanism of the sulfonyl chlorides' electrochemical reduction.

Persson¹² studied the electrochemical behavior of methylbenzene sulfinates in buffered and dimethylformamide solutions. In dimethylformamide solutions, benzenesulfinate ion was reduced via a two-electron process. The observed electrolysis products were ArSO^- and ArSO_2^- . In another paper,¹³ the same author reported results obtained from electrochemical reduction studies performed with aromatic sulfonyl and sulfonyl chlorides on mercury and glassy carbon electrodes in acetonitrile solutions. It was reported that benzenesulfonyl chloride reduction, producing the corresponding benzenesulfinate and chloride ions, occurred by consuming 2 F/mol of the sulfonyl chloride.

Fleszar and Sanecki¹⁴ studied the electrochemical reduction of sulfinic acids and sulfonyl chlorides in strongly acidic ethanol and water solutions on a mercury electrode. These authors suggested that sulfinic acids are electroinactive under the experimental conditions used. They have related the occurrence of ArSO_2^- , ArSO_2SAr , ArSSAr , and ArSH products to the chemical reactions of sulfinic acids. In another paper¹⁵ these authors reported results for p-toluenesulfinic acid p-tolylester electrochemical reduction in the previously cited (strongly acidic ethanol and water) solutions, on a mercury electrode. The electrochemical reduction of the compound was described as a fusion mechanism of the sulfinic acid and sulfonyl chloride. Unfortunately, the acidic condition used probably catalyzed the chemical decomposition of the sulfinic acids.

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Recently, Mabon *et al.*¹⁶ reported results obtained from studies performed on the cathodic behavior of long chain aromatic sulfones in a low acidic medium. The compounds studied were reduced through C-S bond cleavage, producing the corresponding sulfinate ion and hydrocarbon.

As mentioned earlier, the sulfinic acids and their derivatives are frequently reported as intermediates and/or products of several reactions involving organic sulfur compounds. Despite that, there is no study of the electrochemical reduction of these compounds leading to the elucidation of the electrode processes of this class of compound. The aim of this paper is to provide base knowledge about the electrochemical reduction of aromatic sulfinic acids in an aprotic medium. This should help clarify the role of these compounds, and their derivatives, in other oxygenated sulfur organic compound processes.

Experimental

Benzenesulfinic (BS) and p-toluenesulfinic (TS) acids were obtained from aqueous solutions of the corresponding sodium benzenesulfinate (Aldrich) and sodium toluenesulfinate (Aldrich) by adding diluted hydrochloric acid solution (Merck). The p-nitrobenzenesulfinic acid (NBS) was obtained from the chemical reduction of p-nitrobenzenesulfonyl chloride (Merck).¹⁷ The products obtained were characterized by using melting point, nuclear magnetic resonance (NMR), and infrared spectrometry techniques. No detectable presence of impurities was observed.

The electrochemical experiments were performed in dimethylsulfoxide (DMSO, Merck) solutions using tetrabutylammonium tetrafluoroborate (Merck) as supporting electrolyte (Bu_4NBF_4). The solutions were deoxygenated by bubbling nitrogen gas before each experiment. A two-compartment glass cell was used in the cyclic voltammetry experiments, and a three-compartment cell was used in the potential-controlled electrolysis experiments. The counterelectrodes were a platinum ring for cyclic voltammetry and a platinum grid for electrolysis. A glassy carbon disk with an area of 0.07 cm^2 (Tokai Carbon Co.) was used as a working electrode for cyclic voltammetry, and a glassy carbon plate with an area of 9.2 cm^2 (CTA) was the working electrode in the electrolysis studies. All the potentials cited in this work are referred to an SCE, saturated calomel electrode (Analion).

Additionally, to obtain the kinetics data for the processes, cyclic voltammetric experiments using an ultramicroelectrode technique were performed.¹⁸ For these experiments a one-compartment Teflon cell with a two-electrode configuration, using a pretreated carbon wire ($4 \mu\text{m}$ diam) as a working electrode and an Ag/AgCl as a reference electrode was used.

An EG&G Princeton Applied Research Corp. Model 173 potentiostat-galvanostat coupled to an EG&G Model 175 universal programmer was used for the cyclic voltammetry and controlled potential electrolysis experiments. The data obtained were reported using a Houston Instruments Model RE0091 recorder. Alternatively, an IBM-compatible PC interfaced by an ADC card to the above-mentioned potentiostat was used to record cyclic voltammograms obtained at sweep rates higher than 0.5 V s^{-1} . In the ultramicroelectrode experiments, an EG&G Model 174 polarograph interfaced by an ADC to an IBM-compatible PC was used. All experiments were performed at 25°C .

To identify the species produced from the cathodic processes, an analysis of each solution was done after the electrolysis experiments. To do this a water volume three times greater than the electrolyzed solution volume was added to the electrolyte solution and any nonpolar compounds produced extracted by adding ethylether (Merck) or dichloromethane (Merck). The resulting extracts were injected into a Hewlett Packard Model 5890A gas chromatograph coupled to a Hewlett Packard Model 5970 mass detector. Alternatively, for NBS electrolysis products, the dichloromethane extracts were placed on a silica-gel column and eluted with ethyl alcohol. The solution obtained

was evaporated and the products dissolved in deuterated chloroform and identified by NMR.

Results and Discussion

Figure 1 shows the cyclic voltammograms obtained for the compounds studied. A cathodic current peak at a potential around -2.2 V is observed for the three compounds. These reduction processes do not have corresponding anodic peaks even for sweep rates as high as 30 V s^{-1} . This is indicative of the irreversible behavior of the cathodic processes. Additionally, NBS also had a cathodic process for which the current peak is observed at -1.0 V and the corresponding anodic process at -0.95 V . This electrochemical couple corresponds to an electron transfer via the nitro group from which the cathodic process produces a relatively stable radical anion.¹⁹ An anodic process at -0.74 V can be also observed which is only recorded when the sweep is reversed at potentials as high as -2.4 V , indicating it is due to the oxidation of the product of the electrochemical reduction of the NBS. The cyclic voltammetry parameters are displayed in Table I.

The irreversibility of the cathodic processes, attributed to the sulfinic function, can be the consequence of a slow electron transfer and/or a chemical reaction coupled to the faradaic processes. To obtain more information about these electrochemical reductions, we investigated the

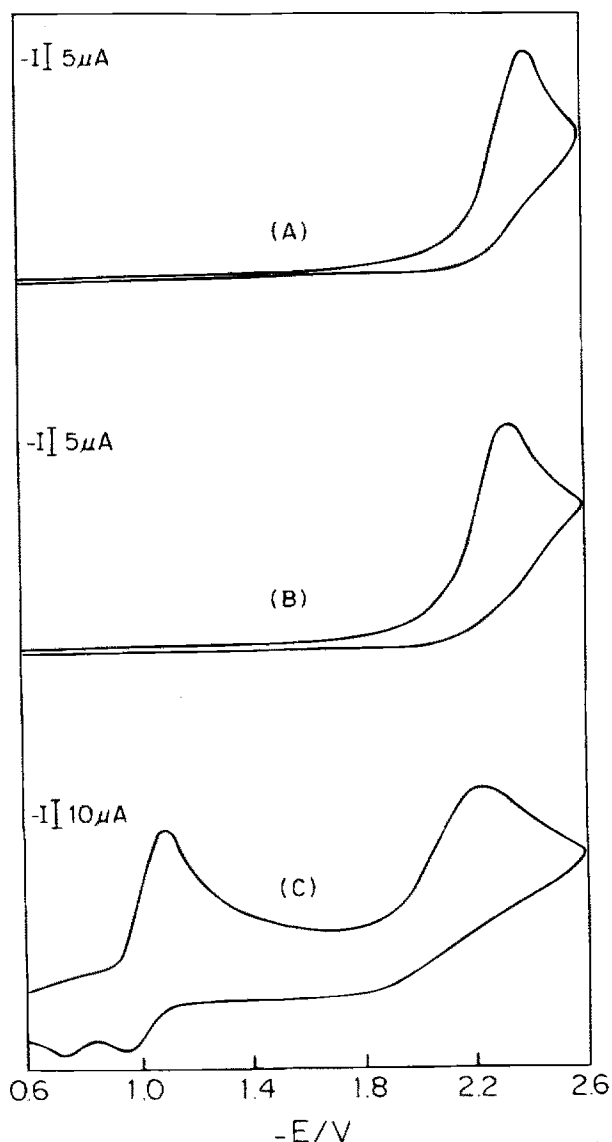


Fig. 1. Cyclic voltammograms for the compounds (a) BS, (b) TS, and (c) NBS in DMSO solutions at 25°C ($v = 0.10 \text{ V s}^{-1}$).

Table I. Cyclic voltammetry parameters for the compounds BS, TS, and NBS in DMSO solutions at 25°C ($\nu = 0.010 \text{ V s}^{-1}$).

Compound	$-E_p$ (V)	i_p/C (mA mM ⁻¹)	$ E_p - E_{p/2} $ (V)
BS	2.25	5.60	0.11
TS	2.35	4.70	0.11
NBS (1st peak)	1.00	8.90	0.10
NBS (2nd peak)	2.10	5.10	0.21

sweep rate dependence of the processes. It was noted that the $I_p/\nu^{1/2}$ values are independent of sweep rate for the cathodic processes of BS and TS, and there is a slight decrease in this parameter with increasing sweep rate for both cathodic processes of NBS.

On the other hand, we observed a shift in the cathodic peak potential with increasing sweep rate for all compounds studied. The corresponding E_p vs. $\log \nu$ plots (Fig. 2) show a $\delta E/\delta (\log \nu)$ value of 0.045 V for BS; 0.051 V for TS; and 0.030 and 0.051 V for the first and second cathodic processes of NBS, respectively. These results suggest the occurrence of a following coupled chemical reaction^{20,21} where the magnitude of the $\delta E/\delta (\log \nu)$ values are determined by the kinetic characteristic of the coupled chemical reaction.²¹ The similarity of the parameter values obtained from BS, TS, and from the second process of NBS indicates that the electron is transferred to the same kind of electroactive site, the sulfinic function, for each of the starting compounds.

The ultramicroelectrode (UME) allows the radial and perpendicular diffusion of the electroactive species to be separated by the choice of a proper sweep rate in a cyclic voltammetry experiment.²² This behavior can be used to mask the occurrence of the couple chemical reactions which follow the initial electron transfer. Any following chemical reactions, occurring at a moderate rate, should not show a significant influence on the UME current density. From this point of view, the cyclic voltammetry technique using an UME enables the acquisition of kinetic parameters during steady state.²³ The corresponding mathematical equation developed for the current-potential curve analysis is

$$E = E^* - 2.3 \left[\frac{RT}{(1-\alpha)nF} \right] \log \left[\frac{\{1 - (i/i_d)(1 + e^{-\theta})\}^{1.11}}{(i/i_d)} \right]$$

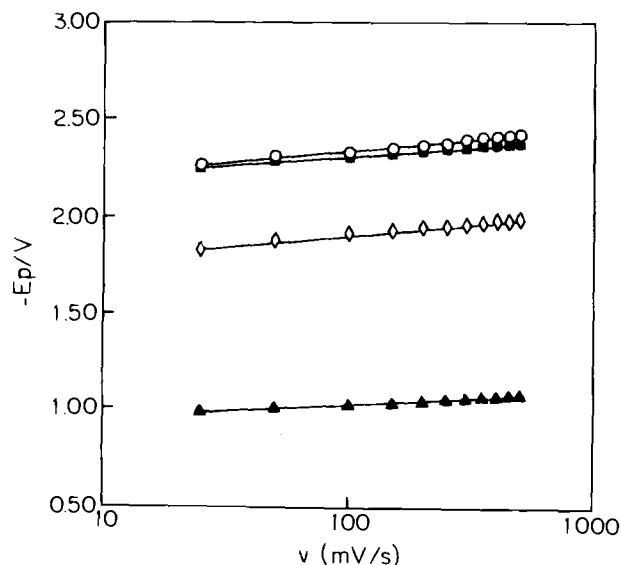


Fig. 2. Influence of the sweep rate on the peak potential for the compounds (■) BS, (○) TS, (▲) NBS (1st peak), and (◇) NBS (2nd peak).

where

$$E^* = E^{0'} - 2.3 \left[\frac{RT}{(1-\alpha)nF} \right] \log \left[\left(\frac{\pi}{4} \right) k^{0'} \frac{a}{D} \right]$$

and

$$\theta = \frac{nF}{RT} (E - E^{0'})$$

In these equations E is the electrode potential, α the electron-transfer coefficient, i the current density, i_d the limit current density, $E^{0'}$ the formal potential, $k^{0'}$ the electron-transfer rate constant, a the disk electrode diameter, and D the diffusion coefficient of the electroactive species. The remaining terms have the usual meanings.

Figure 3 shows the cyclic voltammograms obtained for BS, TS, and NBS on a carbon fiber UME. The steady-state voltammograms for BS and TS obtained had a small hysteresis between the cathodic and anodic sweeps. This hysteresis is probably due to the diffusion of the reduced species away from the electrode surface. The i_d values were calculated for each compound from the extrapolated background curve using the acquitted E , i data points. The cyclic voltammogram obtained for NBS showed an almost complete inhibition of the second step of the reduction process. Additionally, we observed a current peak at a potential corresponding to the first step of the reduction, which was unexpected for the experimental conditions used. This must be due to an unusual adsorption of the reduced species, but further experiments need to be performed to clarify the observed behavior.

From these cyclic voltammograms, the experimental data necessary to calculate the kinetics parameters were obtained.²³ The E'_s values were estimated from the steady-state curves in the potential region immediately before the increasing current due to the faradaic reaction. The very good curve fit obtained (Fig. 4) permitted the kinetics parameters to be calculated (Table II). It is observed that TS has the slowest electrochemical process due to the inductive effect of the $-\text{CH}_3$ substituent. Additionally, the values for the transfer coefficients calculated reflect the slow character of the faradaic step.

The results obtained from the controlled potential electrolysis experiments are summarized in Table III. The last column in the table shows the fractional number of electrons transferred for each compound. These might be different for various reasons, i.e., previous decomposition of the starting compound, a coupled chemical reaction and an electrochemically produced intermediate, or even a partially blocked electrode surface. From cyclic voltammograms obtained before and after each electrolysis experiment, no decomposition or partial blockage of the electrode surface, or the production of an electrochemically active species was observed. So, a following chemical reaction, as was proposed from the cyclic voltammetry studies, seems to be the best explanation for these observations. It must be noted that the radical anion produced from the electron transfer in a reductive process is an extremely reactive species. It is commonly found in aprotic media to react with the electrode surface, solvent, supporting electrolyte, or even with the starting compound.

From the mass and NMR spectra the dimers $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$ (mass/charge peaks = 218, 185, 154, 110, 84, 78), $\text{CH}_3\text{C}_6\text{H}_4\text{SSC}_6\text{H}_4\text{CH}_3$ (mass/charge peaks = 246, 214, 182, 124, 91), and $\text{NO}_2\text{C}_6\text{H}_4\text{SSC}_6\text{H}_4\text{NO}_2$ (quadruplet $\delta = 8.15$ ppm) were identified. These compounds should be electroactive under the experimental conditions used, but no electroactive compound was detected by cyclic voltammetry experiments performed after the electrolysis. The compound $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$ has an irreversible cathodic peak at -1.80 V for the same experimental conditions employed in this work.²⁴ In order to verify the origin of the identified dimers, we performed a potential-controlled electrolysis using BS. After this electrolysis, we recorded a cyclic voltammogram in the positive potential range where we observed an anodic current peak at 0.60 V (Fig. 5). A sub-

sequent electrolysis performed at that potential produced an electroactive specie that has a cyclic voltammogram with the same characteristics as the biphenyl disulfide. These results suggest that biphenyl disulfide is produced from the oxidation of the reduced products. The reduced

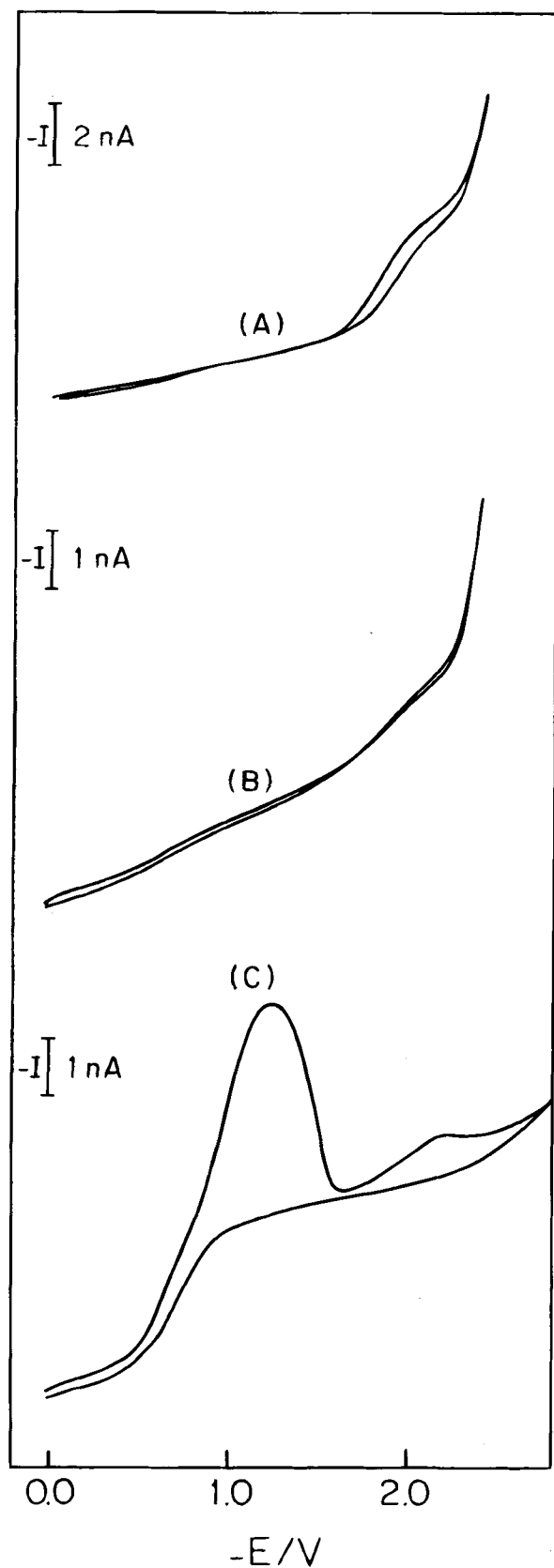


Fig. 3. Cyclic voltammograms for (a) BS, (b) TS, and (c) NBS on carbon UME in DMSO solutions at 25°C ($\nu = 0.010 \text{ V s}^{-1}$).

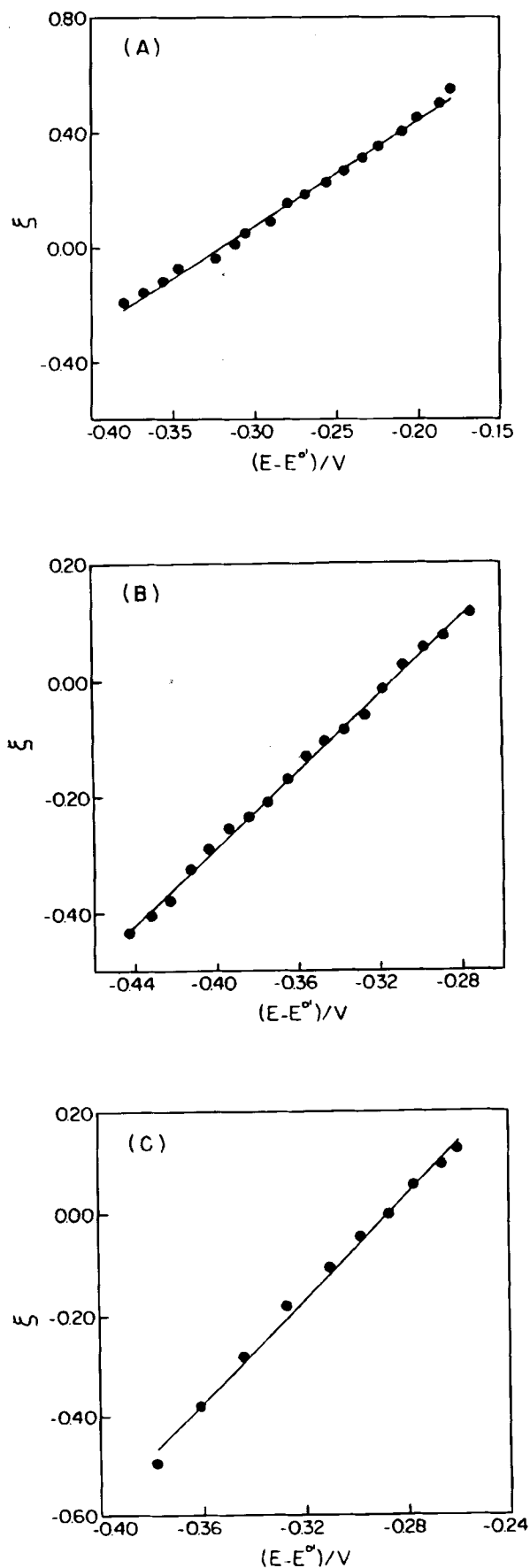


Fig. 4. Mathematical adjust²³ of the data obtained from cyclic voltammograms on UME: (a) BS, (b) TS, and (c) NBS. $\xi = \log \{1 - (i/i_d)[1 + \exp(-nF(E - E^\circ)/RT)]^{1.11}\} / i/i_d$.

Table II. Calculated kinetic parameters for BS, TS, and NBS in DMSO solution at 25°C.

Compound	α	k'_o (cm s ⁻¹)
BS	0.23	2.9×10^{-3}
TS	0.20	6.8×10^{-4}
NBS (1st peak)	0.31	2.4×10^{-3}

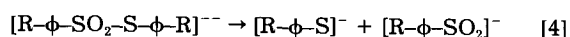
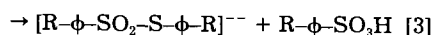
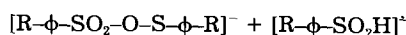
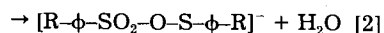
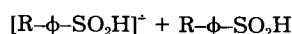
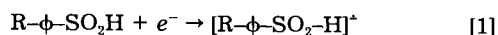
Table III. Potential-controlled electrolysis data for BS, TS, and NBS in DMSO solutions at 25°C.^a

Compound	$-E^*$ (V)	Q (C)	n_{app}
BS	2.40	8.4	0.5
TS	2.50	9.0	0.6
NBS (1st peak)	1.20	7.0	0.5
NBS (2nd peak)	2.40	20.6	0.7

^a E^* is the potential at which the electrolysis experiment, was performed. Q is the total charge applied, and n_{app} is the number of electrons transferred.

species is probably the corresponding phenyl sulfide ion, and the oxidation process occurred during the extraction step of the product analysis. The employed extraction procedure of the supporting electrolyte does not permit the identification of the sulfinic and sulfonic acids and other polar and ionic species which should remain in the aqueous phase.

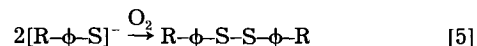
From all the information obtained, the following mechanism is proposed for the reduction of the compounds studied in DMSO solutions



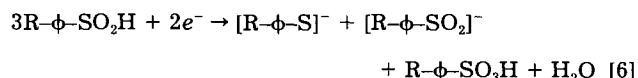
where $R = CH_3$ or H .

Step 1 is the electron-transfer reaction producing a radical anion that reacts with more of the starting compound (step 2). Steps 3 and 4 satisfy the observations of the following coupled chemical reaction. It must be remembered that the reported EPR signal for the anion radical^{7,8} was obtained at -20°C , which drastically decreased the rate of the chemical reactions. Additionally, steps 2 and 3 were characterized by Lazar and Vinkler from a detailed study performed with sulfinic acids in dimethylformamide solu-

tions.²⁵ The reactivity of the generated radical anion, and consequently the high rate of the chemical reaction involving that species could mask the expected effect on the $I_p/v^{1/2}$ values for the sweep rate range used in this work. The identified dimers were probably produced from the $R-\phi-S^-$ species generated by step 4 through a chemical oxidation that occurred during the extraction process in aqueous media

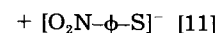
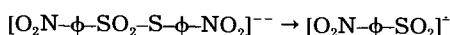
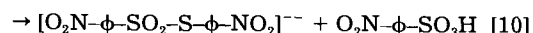
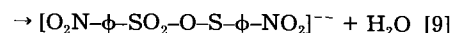
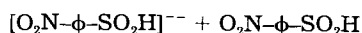
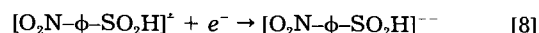


The overall reaction representing the electrochemical reduction is

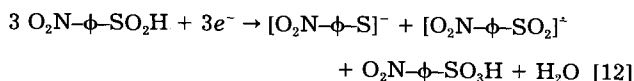


from which can be obtained the apparent number of electrons transferred, 0.67, which agrees very well with the number obtained from the electrolysis experiments. It is important to note that the proposed mechanism produces ionic and polar species already identified by other authors from the chemical reduction of sulfinic acids.²⁶

For NBS, it is proposed that an additional electrochemical step occurs involving an electron transfer through the nitro group, according to the following mechanism



where step 7 produces the radical anion $[O_2N-\phi-SO_2H]^-$ which has been shown to be stable from RPE studies performed in aprotic medium.¹⁹ This could account for the observed reversibility of the corresponding cathodic process and following chemical reaction that is slow compared to the BS and TS compounds. The identified dimer was probably produced from a chemical oxidation process similar to that already discussed for BS and TS. The overall reaction describing the electrochemical reaction is



from which is obtained the value of one electron transferred for each reduced substrate molecule. This satisfactorily agrees with the results obtained in the electrolysis experiments.

The results obtained show the dominant role of the coupled chemical reactions in the reduction mechanism. These chemical reactions occur as a nucleophilic attack of the radical anion and/or anionic species on the starting compound. The suggested electrochemical reduction mechanism agrees very well with the chemical one.²⁶

Acknowledgments

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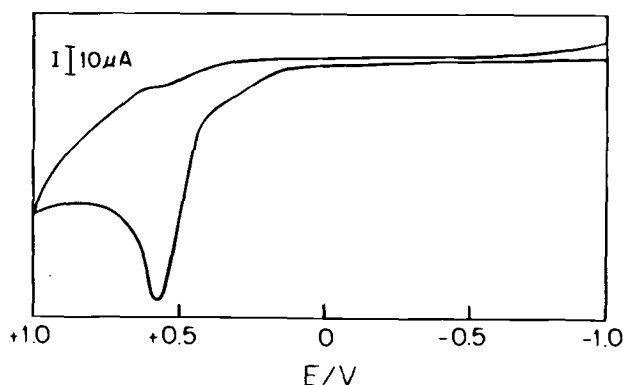


Fig. 5. Cyclic voltammograms obtained from an electrolyzed solution of compound BS in DMSO at 25°C ($v = 0.010 \text{ V s}^{-1}$).

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Competition Between the Plasticizer and Polymer on Associating with Li⁺ Ions in Polyacrylonitrile-Based Electrolytes

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ABSTRACT

The Raman and infrared spectra of the systems of plasticizer/LiClO₄ and plasticizer/polyacrylonitrile (PAN)/LiClO₄ have been recorded, where the plasticizer includes dimethylformamide (DMF) and propylene carbonate (PC). By comparing the spectra, it is found that the association of Li⁺ ion is more competitive with DMF than with PC in the liquid or gel electrolytes. Moreover, the addition of PAN into DMF/LiClO₄ solution has less influence on the Li⁺-solvent association than into PC/LiClO₄ solution. Although a strong interaction has been observed between Li⁺ ions and PAN in PC/LiClO₄/PAN electrolytes, no similar interaction is observed between Li⁺ ion and PAN in DMF/PAN/LiClO₄ system. However, after the plasticizer is removed from the gel electrolytes, apparent interaction is observed between Li⁺ ion and PAN. These phenomena lead to a conclusion that there is a competition between the plasticizer and the polymer for association with the Li⁺ ions in the PAN-based electrolytes. In addition, it is found that the multiple ion aggregates are formed without the appearance of the usual "solvent-shared ion aggregates" in the plasticizer-free electrolyte, which suggests that the Li⁺ ions may move both in the gel state and with the segmental chain of PAN while the ClO₄⁻ anion migrates mainly in the gel state in a practical PAN-based electrolyte.

Introduction

Polyacrylonitrile (PAN)-based electrolytes¹ are ionically conducting, plasticizer-dissolved salts in a polymer matrix. The polymer provides mechanical stability and the salt allows relatively high conductivity in the range of 10⁻³ S/cm at ambient temperature. These systems combine the desirable mechanical properties of polymers (e.g., low density, high flexibility, ease of fabrication, etc.) and the potential of high conductivity of liquid electrolytes. Since polymer electrolytes must function as both separator and electrolyte in a lithium or lithium-ion battery, a number of properties are critical for their successful use in the battery. From an electrochemical point of view, the electrolytes must satisfy a set of requirements, such as electrochemical stability over a certain voltage window, chemical and electrochemical compatibility with electrode materials and other components with which they may be

in contact, as well as good thermal stability, especially when in contact with the lithium electrode, and good mechanical properties. Huang² has synthesized several PAN-based solid electrolytes containing plasticizers, such as propylene carbonate (PC), ethylene carbonate (EC), dimethylformamide (DMF), dimethylsulfoxide (DMSO), sulfolane (SL), γ -butyrolactone (BL), etc., and their suitable combinations. It was found that these electrolytes have conductivities higher than 10⁻³ S/cm at room temperature and are quite compatible with metallic lithium. Moreover, the as-prepared polymer electrolytes showed good elasticity after storage in waterproof environments for a year. Of all the properties, the conductivity is one of the most important. Polymer electrolytes with conductivities higher than 10⁻³ S/cm at room temperature are suitable as electrolytes in lithium batteries used in many applications. The proposal³ to employ these materials as electrolytes in solid-state batteries has led to considerable interest in these materials from both applied and fundamental aspects.⁴⁻⁶

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