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Multiple internal reflection FTIR spectroscopic (MIRFTIRS) study of the redox process of poly(5-amino-1,4-naphthoquinone) film in aqueous and organic media

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Abstract

Poly(5-amino-1,4-naphthoquinone), PANQ, films are electroactive in both aqueous and organic solutions. The redox process of both the film and the quinone groups has been studied by MIRFTIRS and Probe Beam Deflection. The quinone system is very stable in acetonitrile and in aqueous solutions up to pH 11. Therefore, its redox properties suggest potential applications in diverse areas. © 1999 Elsevier Science Ltd. All rights reserved.

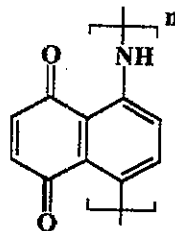
Keywords: Multiple internal reflection; Aqueous media; Organic media; Poly(5-amino-1,4-naphthoquinone)

1. Introduction

In a recent study [1], we have shown that the electrochemical oxidation of 5-amino-1,4-naphthoquinone (ANQ) in acetonitrile leads to conducting PANQ films. Data from an in situ Multiple Internal Reflection Fourier Transform Infrared Spectroscopy (MIRFTIRS) study and X-Ray photoelectron spectroscopy (XPS) analysis clearly showed that the electrooxidation was selective and that electropolymerization occurred via coupling para to the $-NH_2$ group. These results were confirmed by frontier orbital calculations [1]. The film structure is of the polyaniline type involving one quinone group per ANQ moiety (Scheme 1).

There was considerable interest in the insertion of quinoidal units into polymer films on modified electrodes for catalytic purposes [2–5]. PANQ films are also

expected to exchange cations upon oxidation and reduction of the quinone groups and are therefore interesting for applications in lithium ion batteries. In this paper, we present results concerning the electroactivity of the film and the underlying redox process as studied by in situ MIRFTIRS and Probe Beam Deflection.



Poly (5-amino-1,4-naphthoquinone)

PANQ

Scheme 1.

* Corresponding author.

2. Experimental

2.1. Materials

The electrolytes (LiClO_4 , NBu_4ClO_4) from Fluka were dried for 24 h under vacuum before use. Spectrophotometric grade acetonitrile (Aldrich) was handled under argon and the bottle was stored in argon atmosphere.

2.2. Polymer preparation

PANQ films were prepared on platinum or glassy carbon (GC) electrodes by potential cycling at 50 mV s^{-1} between 0.5 and 1.45 V vs SCE during 15 min. The medium was an acetonitrile solution containing 10^{-2} M ANQ and $10^{-1} \text{ M LiClO}_4$.

2.3. Electrochemical measurements

All electrochemical investigations were carried out in a one-compartment cell. The working electrodes were disks of GC (Tokai, 6 mm dia) or Pt (1.5 mm dia). They were polished with abrasive papers (Struers SiC paper 2000), rinsed in water, methanol with ultrasonic agitation, then air-dried before use. All experiments were carried out in argon atmosphere. The reference electrode was SCE.

2.4. MIRFTIRS study

For in-situ MIRFTIRS experiments in acetonitrile, the working electrode substrate was a germanium crystal coated with a thin layer of Pt deposited by sputtering (Balzers Model Sputron II). Details about MIRFTIRS experiments in organic medium have been described in a previous paper [6]. In acidic aqueous solutions, a ZnSe prism was used as the reflection element. A thick platinum layer was sputtered as a comb-like pattern so that the film could be grown on and between each Pt tooth. The reference electrode was a AgCl-covered silver wire dipping directly into the solution. MIRFTIRS spectra were recorded on a Nicolet SX 60 Fourier transform spectrometer.

In situ MIRFTIRS spectra at an indicated potential are transmittance difference spectra. For each spectrum, the reference spectrum is subtracted from that of the system at the indicated voltage.

2.5. PBD setup

The PBD setup arrangement has been described elsewhere [7–9]. An He–Ne laser (Uniphase Model 1103P) beam is aligned parallel to the electrode surface. The deflections induced by the formation of a

refractive index gradient in front of the electrode are measured with a position-sensitive detector. The PBD and current signals were recorded as functions of the applied electrode potential. A glassy carbon plate (1 cm wide) was used as working electrode. A $\text{Pd}(\text{H}_2)$ reference electrode was used in aqueous acid and a pseudo-reference Ag/AgCl was used for the organic solution.

Probe Beam Deflection is a technique that measures the concentration gradient in front of the electrode film by monitoring the refractive index gradient with a laser beam. The electrochemical oxidation–reduction process is accompanied by counterion exchange with the electrolyte solution to maintain film electroneutrality. The ion concentration in the solution changes, and a gradient of refractive index is created in a direction normal to the electrode surface. A beam travelling parallel to the surface suffers a deflection proportional to the concentration gradient, and therefore proportional to the extent and direction of ion flux. Positive deflection corresponds to insertion of ions into the film, while negative deflection implies release of ions into the solution. The PBD signal was monitored while the potential was scanned at constant rate (cyclic deflectometry).

3. Results and discussion

3.1. Electroactivity and stability

3.1.1. In organic medium

Cyclic voltammetry was performed in acetonitrile solution containing 0.1 M LiClO_4 or NBu_4ClO_4 as an electrolyte for both ANQ monomer and PANQ film. Fig. 1a shows the cyclic voltammogram recorded on a glassy carbon electrode with an acetonitrile solution containing $0.1 \text{ M NBu}_4\text{ClO}_4$ and $5 \cdot 10^{-4} \text{ M ANQ}$. Two well-defined redox couples are detected which correspond to the two systems of the quinone groups: Q/Q^- (couple I) and Q^-/Q^{2-} (couple II). With LiClO_4 as the electrolyte (Fig. 1b), only one asymmetric redox peak pair is observed at less negative potential. It is well established that in $\text{LiClO}_4/\text{acetonitrile}$ medium, very strong ion-pairing exists between Li^+ and the reduced dinegative quinone ions (Q^{2-}), while weaker association occurs with the semiquinone ions (Q^-) [10]. A shift to more positive potential occurs in LiClO_4 solution, indicating the formation of a “complex” between the reduced quinone anions and lithium cations. For the study of the PANQ film electroactivity we used

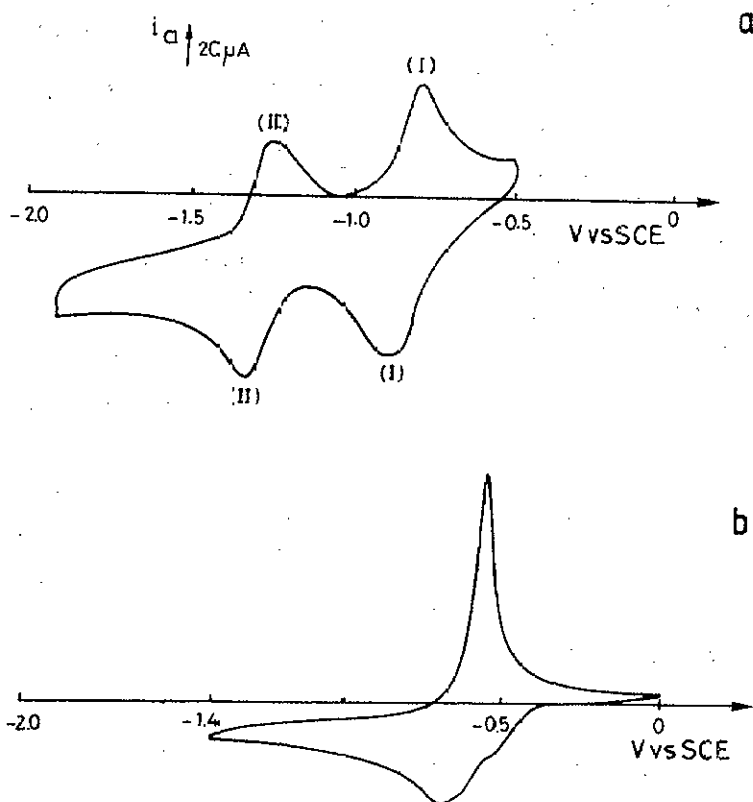


Fig. 1. Cyclic voltammetry at 50 mV s^{-1} with a glassy carbon (GC) electrode in: (a) $5.10^{-4} \text{ M ANQ} + 10^{-1} \text{ M NBu}_4\text{ClO}_4 + \text{CH}_3\text{CN}$; (b) $10^{-4} \text{ M ANQ} + 10^{-1} \text{ M LiClO}_4 + \text{CH}_3\text{CN}$.

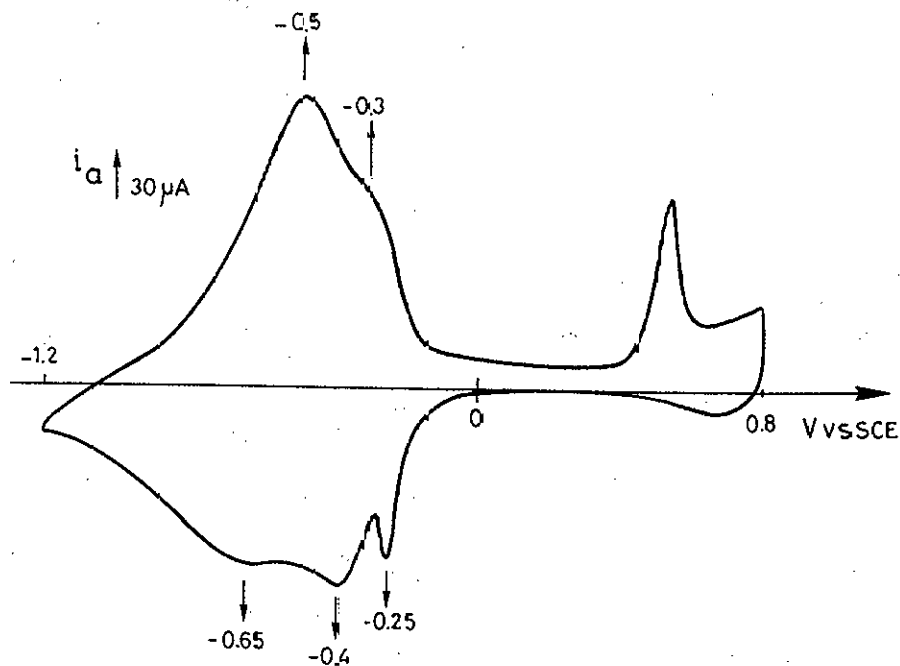


Fig. 2. Cyclic voltammogram of a PANQ-coated GC electrode at 20 mV s^{-1} in $0.1 \text{ M LiClO}_4 + \text{CH}_3\text{CN}$.

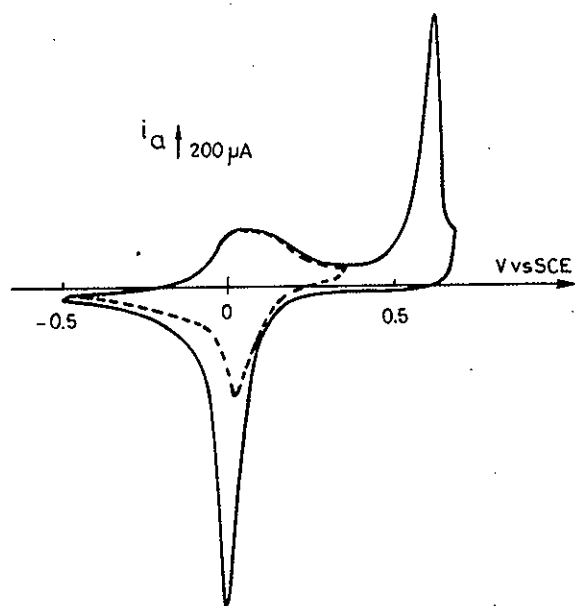


Fig. 3. Cyclic voltammogram of a PANQ-coated GC electrode at 50 mV s^{-1} in acidic aqueous solution of pH 1.1 (0.2 M $\text{NaClO}_4 + \text{HClO}_4$).

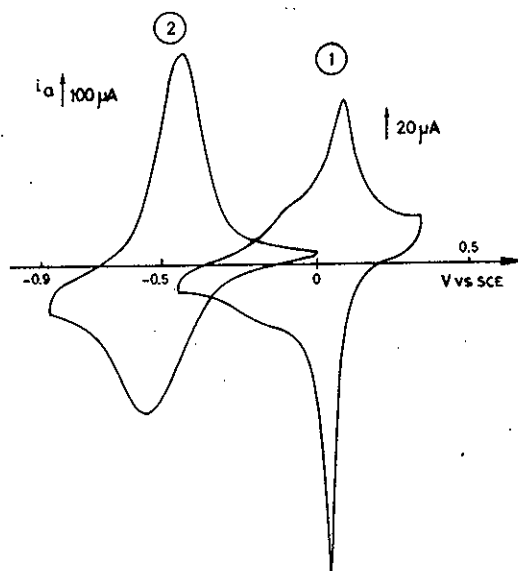


Fig. 4. Cyclic voltammograms of a PANQ-coated GC electrode at 50 mV s^{-1} (1) in pH 0.8; electrode surface = 0.07 cm^2 . (2) in pH 11; electrode surface: 0.28 cm^2 .

LiClO_4 , because this electrolyte was used during film formation.

The cyclic voltammogram of a PANQ-film-coated carbon electrode presented in Fig. 2 can be divided into two domains. In the negative domain, between 0 and -1.2 V , the two redox couples of the quinone groups are not well separated: $E_{\text{pc}} = -0.65$ and -0.4 V and $E_{\text{pa}} = -0.5$ and -0.35 V . The second domain, between -0.3 V and $+0.8 \text{ V}$, concerns the redox system of the polymer backbone. These attributions will be supported further by MIRFTIRS data.

The polymer film can be cycled between 0 V and -1.4 V without significant loss of activity. After 4 h of potentiodynamic cycling at 50 mV s^{-1} , 90% of film electroactivity remains.

From a cyclic voltammogram recorded at 5 mV s^{-1} , the specific charge for the quinone group of about 290 Ah/kg was estimated, which is rather high and equal to the theoretical value based on the quinone redox couple plus the necessary lithium ion. These data, along with the stability of the quinone group, are of interest for energy storage applications, in particular for batteries with PANQ cathode and lithium anode.

3.1.2. In aqueous medium

PANQ films are also electroactive in aqueous medium. Typical cyclic voltammograms for a PANQ-coated carbon electrode in pH 1.1 solution containing $0.2 \text{ M NaClO}_4 + \text{HClO}_4$ are shown in Fig. 3. Potential scans were performed, first in the negative direction, between $+0.35 \text{ V}$ and -0.5 V (dotted curve), then in the positive direction from -0.5 V to $+0.68 \text{ V}$; the same domain was maintained in the reverse scan (plain curve). In the region from $+0.35$ to -0.5 V , the redox couple of the quinone group is detected at $0.02/0.10 \text{ V}$. The full curve indicates that the polymer chain (polyaniline-like structure) is oxidized at 0.62 V and reduced at 0 V . The film reduction peak overlaps with the reduction peak of the quinone group. The film response is very stable during potential scanning. If the potential is scanned between 0.35 and -0.5 V , 75% of the film electroactivity remain after 1 h of scanning at 50 mV s^{-1} . The film response (couple $0 \text{ V}/0.62 \text{ V}$) is detected up to pH 8, while the redox couple of the quinone group is well defined up to pH 11. In Fig. 4, the voltammetric responses of the quinone group in the film at pH 0.8 and 11 are presented.

The dependence of $E_{1/2}$ on pH values between 0.8 and 11 is shown in Fig. 5a for the PANQ film. Between pH 0.8 and 3, a slope of -95 mV is found, while between pH 3 and 11 the slope is -62 mV .

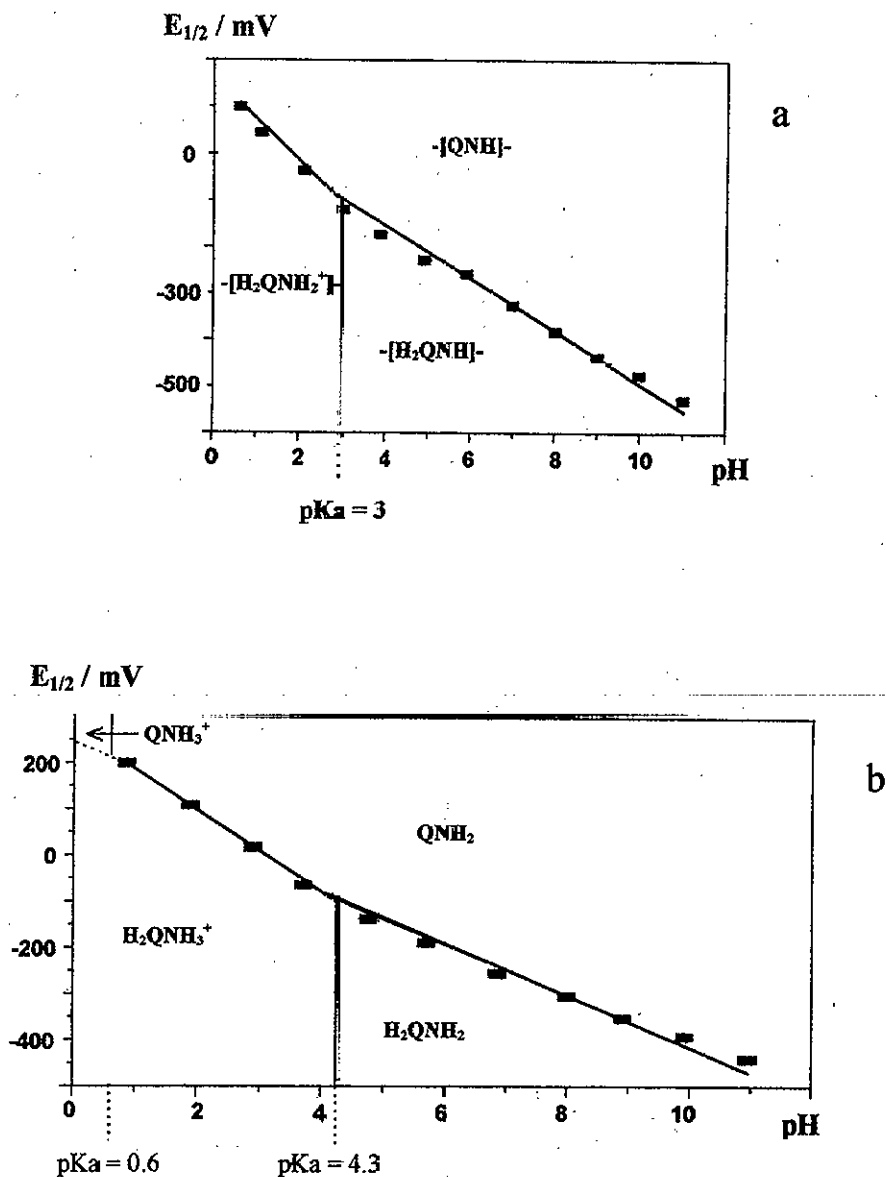
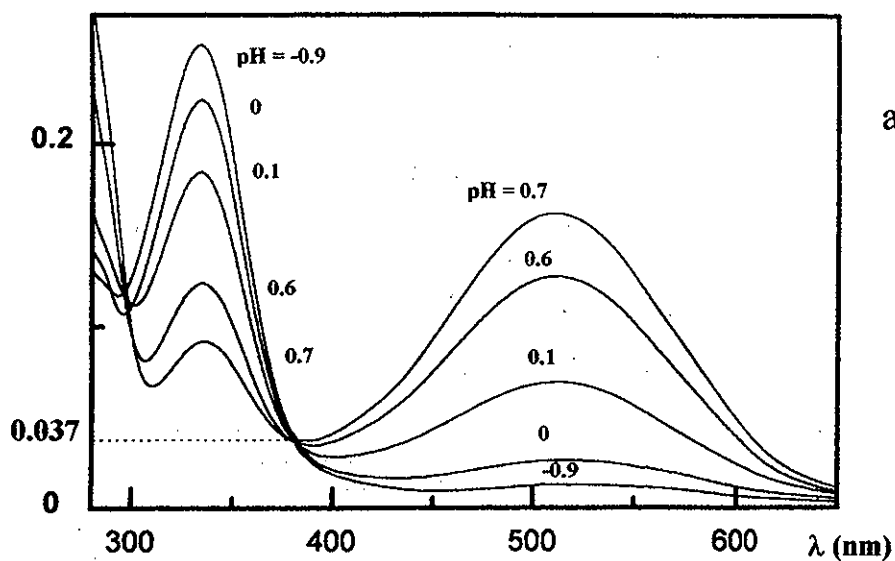


Fig. 5. Plot of $E_{1/2}$ vs pH for the redox couple of the quinone group in the case of: (a) PANQ-coated GC electrode in 0.5 M buffer solutions; (b) 5.10^{-4} M ANQ in buffer solutions + 0.3 M NaClO_4 .

Absorbance (a.u.)



Absorbance (a.u.)

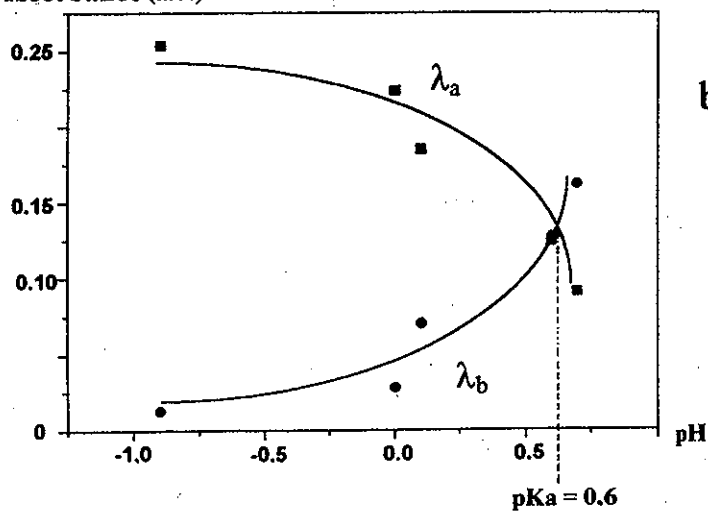
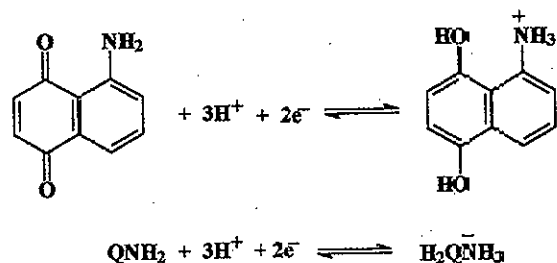


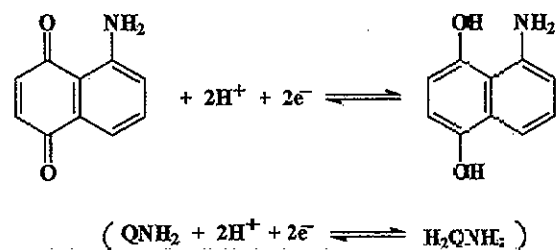
Fig. 6. (a) UV-Vis spectra at different pH of solutions containing 10^{-4} M 5-amino-1,4-naphthoquinone and H_2SO_4 adjusted to the desired pH. (b) Plot of absorbance values measured at λ_a and λ_b vs pH.

Similar slopes are obtained with the monomer 5-amino-1,4-naphthoquinone in the solution (Fig. 5b). For the monomer, the redox reactions corresponding to the two regions could be the following:

- between pH 0.6 and 4.3:

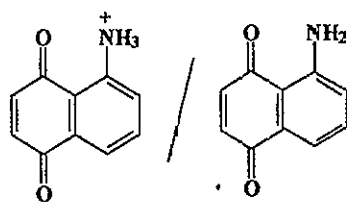


- between pH 4.3 and 11:



From Fig. 5b it can be deduced that the pK_a of the system $\text{H}_2\text{QNH}_3^+/\text{H}_2\text{QNH}_2$ is 4.3.

The pK_a value for the oxidized system

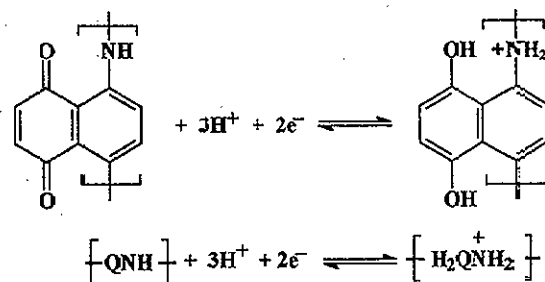


has been measured by UV-Vis spectroscopy. This technique allows the pK_a of an acid-base system to be determined by absorbance measurements, as two different forms exist at different pH. The absorbances were measured between pH of -0.9 and $+0.7$ with solutions containing 10^{-4} M of QNH_2 to which H_2SO_4 was added to attain the desired pH (Fig. 6a). An isobestic point is present ($\lambda_i = 381$ nm) indicating that we are dealing with a simple acid-base reaction. Two absorbance maxima are found at wavelengths of 333 nm (λ_a) and 509 nm (λ_b); they correspond to the acid and base form, respectively (Fig. 6a). In Fig. 5b, the absorbance measured at λ_a and λ_b vs pH is plotted, and the inter-

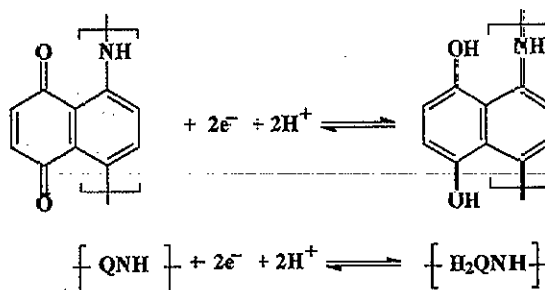
cept gives the pK_a value of the $(\text{QNH}_3^+/\text{QNH}_2)$ acid-base system which is 0.6 .

A comparison of the plots of $E_{1/2}$ vs pH for the polymer (Fig. 5a) and the monomer (Fig. 5b) leads us to propose the following redox reactions relative to the polymer film:

- between pH 0.8 and 3:



- between pH 3 and 11:



Consequently, the pK_a of the system $(\text{H}_2\text{QNH}_3^+)/(\text{H}_2\text{QNH})$ is 3 .

4. MIRFTIRS study

4.1. In organic solution

First, a potential step experiment between $+0.1$ V and -0.8 V vs Ag/AgCl was performed on a Ge/Pt electrode coated with PANQ film to analyse the redox process of the quinone group. Fig. 7 presents spectra S_{ox} recorded at $+0.1$ V and S_{red} at -0.8 V. The reference spectrum of the system before polarization was always subtracted.

In the spectrum S_{ox} of the oxidized film, the band intensity related to the $\text{C}=\text{O}$ stretching of the quinone group is strong (1628 cm^{-1}), but it is very weak in the spectrum S_{red} of the reduced film. A new weak band appears at 1540 cm^{-1} in the spectrum S_{red} , which can

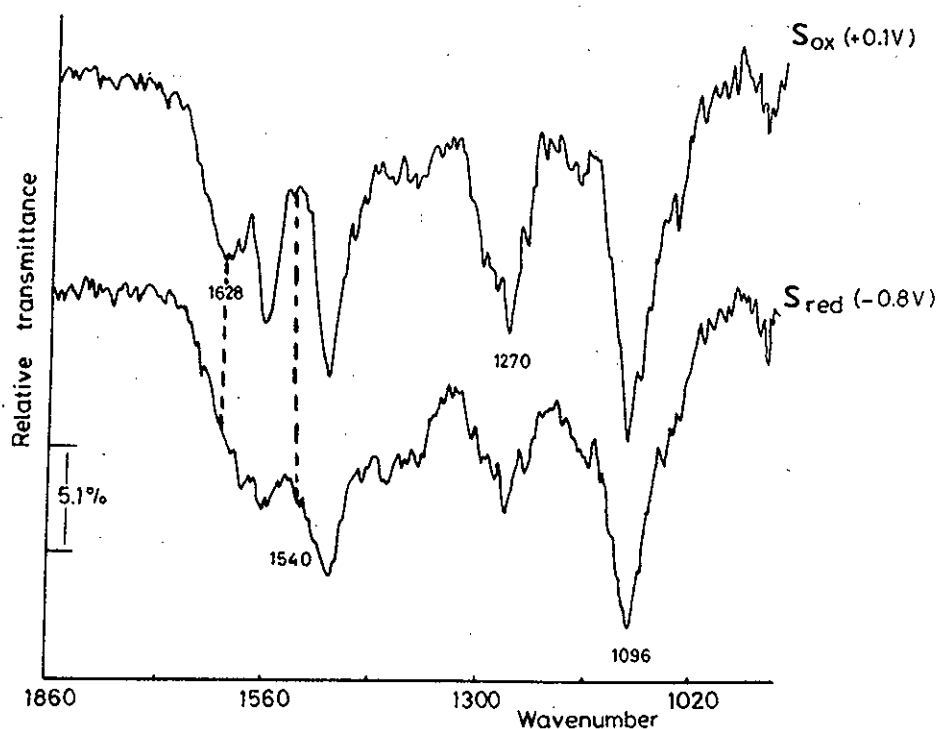


Fig. 7. In-situ MIRFTIRS spectra recorded at a potential step experiment between +0.1 V and -0.8 V vs Ag/AgCl in 0.1 M $LiClO_4 + CH_3CN$. The electrode is a Pt/Ge electrode coated with PANQ film. Spectra were recorded using 500 interferograms and the reference spectrum (obtained before polarization) was subtracted.

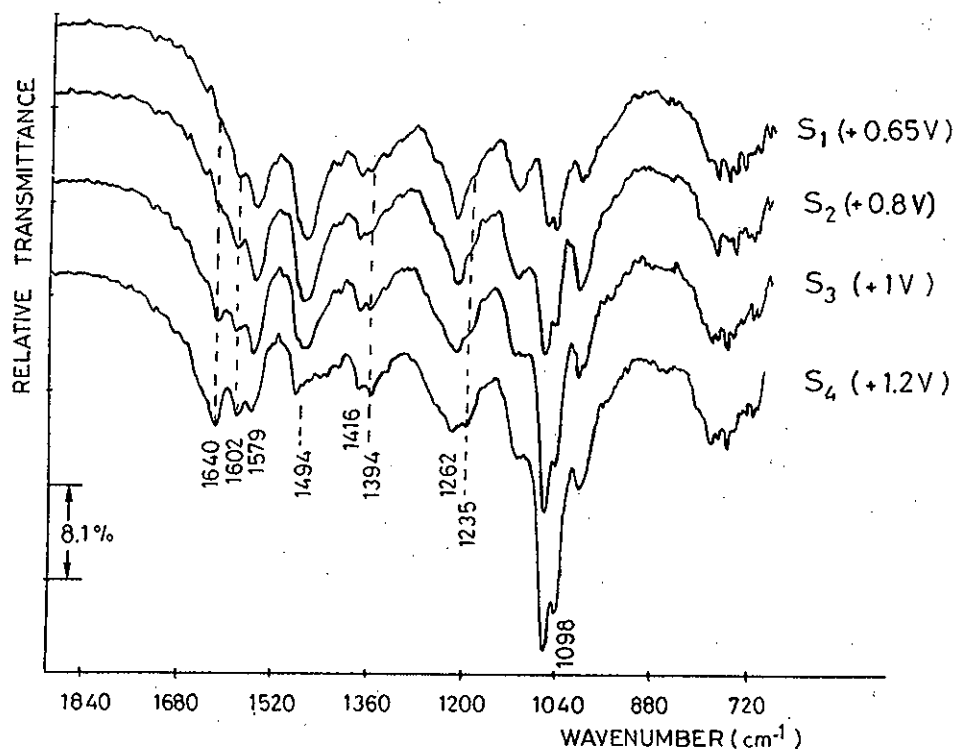


Fig. 8. In-situ MIRFTIRS spectra recorded with a Pt/Ge electrode coated with PANQ at +0.65, +0.8, +1, +1.2 V vs Ag/AgCl in 0.1 M $LiClO_4 + CH_3CN$. Spectra were recorded using 1000 interferograms and the reference spectra obtained at +0.4 V was subtracted.

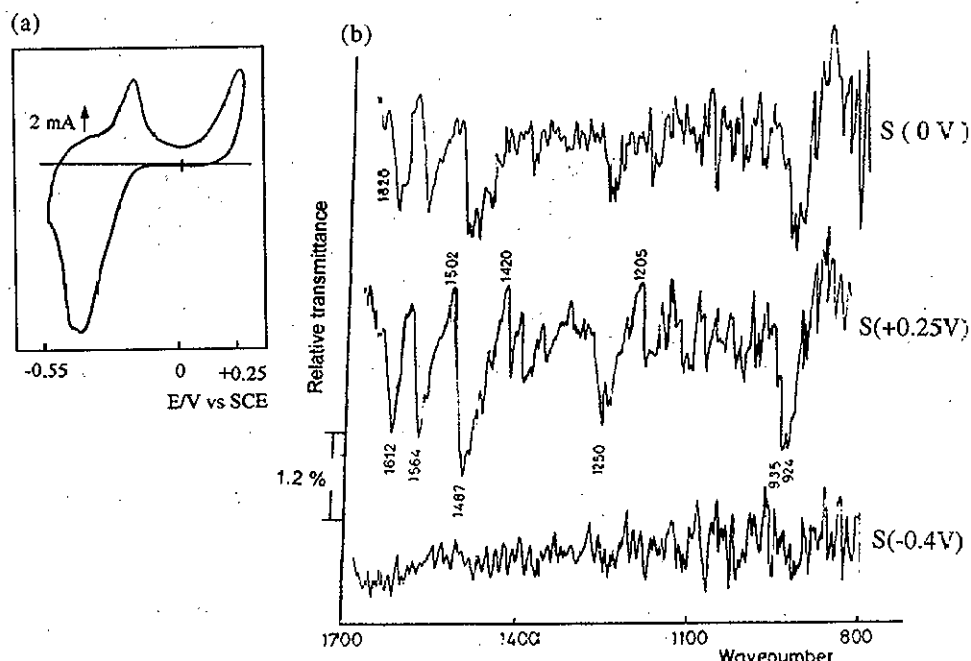


Fig. 9. (a) Cyclic voltammogram at 50 mV s^{-1} of a Pt/ZnSe electrode coated with PANQ in $0.1 \text{ M NaReO}_4/\text{HReO}_4$ (pH 2). (b) In-situ MIRFTIRS spectra recorded with a Pt/ZnSe electrode coated with PANQ at $+0 \text{ V}$ and $+0.25 \text{ V}$ vs Ag/AgCl. Spectra were accumulated with 1000 interferograms and the reference spectrum was that of the reduced form at -0.4 V .

be attributed to stretching vibrations of the complex $\text{U}-\text{U} \cdots \text{Li}^+$ [11].

Secondly, to study the redox process of the polymer chain, spectra were recorded at $+0.4$, $+0.65$, $+0.8$, $+1$ and $+1.2 \text{ V}$ vs Ag/AgCl. The spectrum obtained at $+0.4 \text{ V}$ was used as the reference and subtracted from the others. Thus, spectra $S_1 \rightarrow S_4$ presented in Fig. 8 are difference spectra and the bands indicate only the spectral changes occurring during oxidation of the polymer chain.

An increase in the intensity was detected for the band at 1640 cm^{-1} due to $\text{C}=\text{N}$ stretching vibrations of imine groups, for the band at 1602 cm^{-1} attributed to quinoid (Q) ring stretching vibrations, and for three other bands at 1416 , 1394 , and 1235 cm^{-1} attributed to semi-quinoid ring stretching vibrations.

A decrease in intensity was observed for two bands, at 1570 and 1494 cm^{-1} . The 1570 cm^{-1} band could be assigned to benzenoid (B) ring stretching vibrations and the 1494 cm^{-1} band is related to N–H deformation of secondary amine groups.

The band at ca 1096 cm^{-1} due to the anion dopant ClO_4^- increases during oxidation.

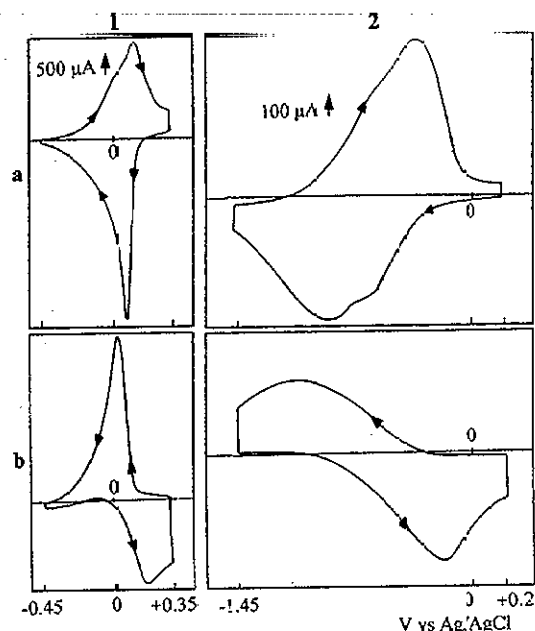


Fig. 10. Cyclic voltammograms (a) and cyclic deflectionograms (b) of a PANQ film in: (1) $0.5 \text{ M H}_2\text{SO}_4$; scan rate = 50 mV s^{-1} . (2) $0.1 \text{ M LiClO}_4 + \text{CH}_3\text{CN}$; scan rate = 20 mV s^{-1} .

4.2. In aqueous solution

In acidic aqueous solutions, the Ge/Pt system is not quite stable, hence the reflection element used was a ZnSe prism. The working electrode was a ZnSe element coated with a platinum minigrad. PANQ films were prepared in the spectroelectrochemical cell using an acetonitrile solution containing 10^{-2} M ANQ and 10^{-1} M LiClO_4 by potential scans at 50 mV s^{-1} during 10 min. The Pt/ZnSe electrode coated with PANQ was then studied in aqueous solution containing $0.1 \text{ M NaReO}_4/\text{HReO}_4$ at pH 2. The film response by cyclic voltammetry at 50 mV s^{-1} is shown in Fig. 9a.

Spectra were recorded at 0 V and +0.25 V (Fig. 9b). The spectrum of the fully reduced form at -0.4 V was taken as the background. In this way, only difference spectra are shown, describing the spectral changes occurring during the process. Bands pointing downward correspond to substances which are produced during the process, bands pointing upward indicate the consumption of substances.

In the spectra at 0 V and +0.25 V, a new band appears at 1620 cm^{-1} for the $\text{C}=\text{O}$ (quinone group) stretching vibrations. This band is detected as a shoulder because of an intense band at 1612 cm^{-1} . The latter band could be attributed to an $\text{N}=\text{ring}$ vibrational mode [12]. The other bands at 1564, 1487, and 1250 cm^{-1} could be assigned to the semi-quinoid ring [12–14].

In the spectrum at +0.25 V, upward-pointing bands appear at 1502, 1420 and 1205 cm^{-1} . These bands could be related to a benzenoid ring vibrational mode [13, 14]. These bands indicate a loss of benzenoid structure. The assignment of the different bands was based on data from numerous publications on FTIR studies of polyaniline [12–14].

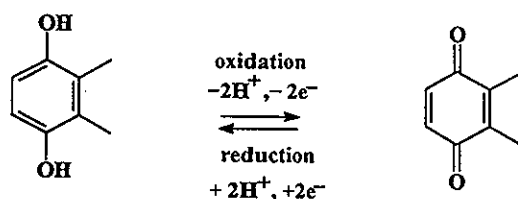
After recording the two spectra at 0 V and +0.25 V, we finally took the spectrum at -0.4 V . The fact that there is no band indicates that the spectrum recorded at -0.4 V at the beginning of the experiment to be used as the reference spectrum is the same as that recorded at the end at the same potential. This proves that the redox process is reversible and the film does not deteriorate.

5. Probe beam deflection study

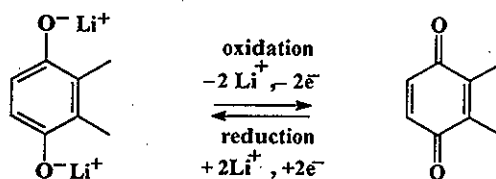
Probe Beam Deflection analysis has been performed during the redox process of the quinone group in both aqueous and organic media.

In Fig. 10, curves a-1 and a-2 are cyclic voltammograms obtained with a PANQ film-coated GC electrode in $0.5 \text{ M H}_2\text{SO}_4$ (a-1) and in $0.1 \text{ M LiClO}_4 + \text{CH}_3\text{CN}$ (a-2). Curves b are the cyclic deflectionograms recorded simultaneously during cyclic voltammetry. In both cases, negative deflections are detected on oxidation, which implies release of ions into the solution. On reduction, positive deflections are observed, which implies insertion of ions into the film. The exchange of cations occurs in both cases, i.e., exchange of protons in aqueous acid and exchange of Li^+ ions in anhydrous acetonitrile. These data corroborate the MIRFTIRS results obtained in acetonitrile solution. The redox processes of the quinone groups are then confirmed as follows:

In aqueous acid



In anhydrous acetonitrile



The exchange of Li^+ ions in organic solution meets the requirements for application in lithium batteries.

6. Film redox process

From the above data, a tentative redox mechanism is proposed for the PANQ film:

In acidic aqueous solutions, the dominant species used for charge compensation is the proton, but at the beginning a few anions move into the polymer film during oxidation. The protonated salt is oxidized to form a cationic radical. Relaxation and delocalisation of the electrons lead to a so-called polaron lattice, exhibiting semiquinoid character. In a further step of oxidation, two electrons and two protons are involved to oxidize the four moieties of the polyaniline chain.

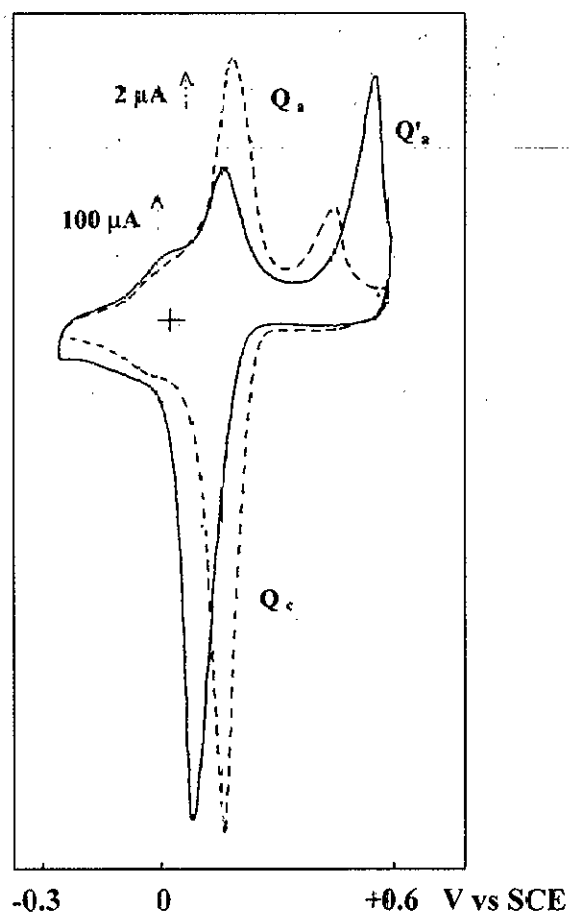
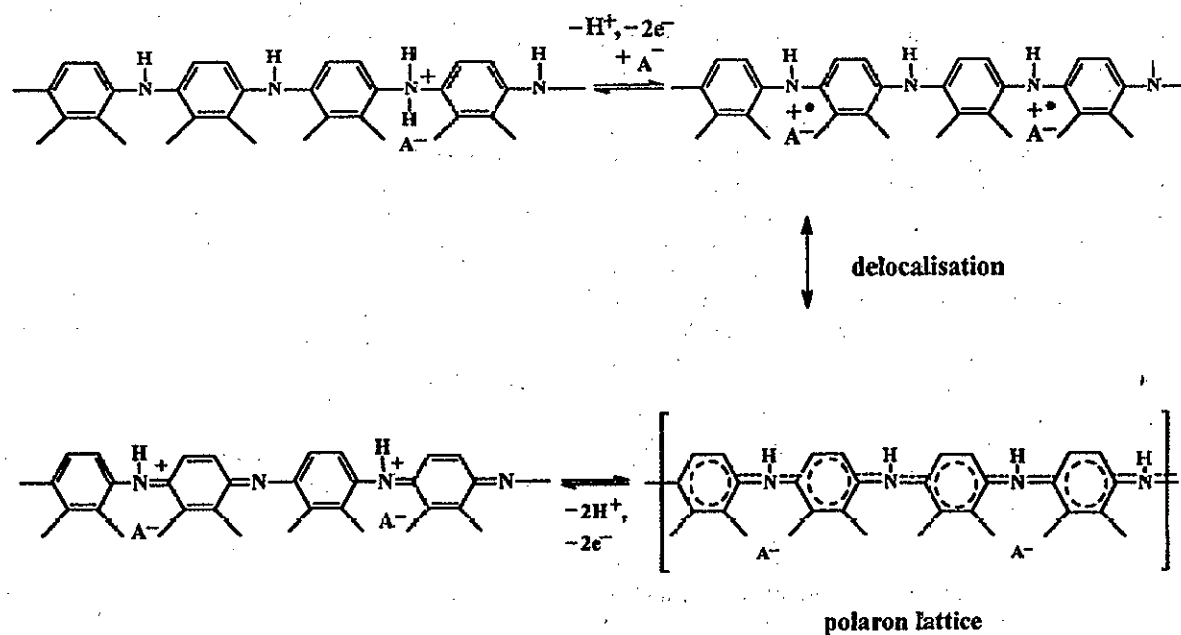


Fig. 11. Cyclic voltammograms recorded with a PANQ-coated carbon electrode in 0.5 M H_2SO_4 : at 50 mV s^{-1} (solid line); at 1 mV s^{-1} (dotted line).

In parallel with this redox process, interactions probably exist between the quinone and the polyaniline redox system. In a recent work, similar interactions between polyaniline and quinone moieties have been revealed [15].

Fig. 11 shows the cyclic voltammograms recorded with a PANQ-coated carbon electrode in 0.5 M H_2SO_4 . The cyclic voltammogram recorded at a high scan rate (50 mV s^{-1}) is presented as a solid line, that recorded at a low scan rate (1 mV s^{-1}) is shown as a dotted line. At the high rate the anodic charge Q_a from the first oxidation peak is small, whilst Q_a for the second oxidation peak is rather high. At the low scan rate, most of the film can be oxidized at the potential of the quinone redox couple. This behavior seems to indicate that at high rates a part of the reduced quinone is only oxidized when the polyaniline moieties start to conduct electrons.

In other words, at the first scan rate a part of the film cannot be oxidized. This is because the conductivity of the film in the potential interval between the oxidized quinone and the beginning of the polyaniline oxidation is very low. As soon as the polyaniline moieties are oxidized, the film becomes conducting again and the remaining reduced quinone moieties can be oxidized.

The cathodic reduction of the film seems to be faster. The charge of the cathodic peak is independent of the scan rate, which means that the redox reaction of the whole film is complete at the scan rates investigated.

7. Conclusion

PANQ films are electroactive in both aqueous and organic solutions. The stability and the high specific charge, 290 Ah/kg, of this polymer are interesting for applications in rechargeable batteries. Besides, the elec-

troactivity of the quinone group in almost all the pH range with a remarkable stability opens the way to potential applications in electrocatalysis and in sensor devices.

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