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In situ multiple internal reflection Fourier transform infrared spectroscopic (MIRFTIRS) study of the electrochemical immobilization of heteropolyanions in poly(1-naphthol) coated electrodes*

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Immobilization of a Dawson-type heteropolyanion, $P_2W_{18}O_{62}^{6-}$ in a poly(NAP-1) film is performed by electropolymerization of 1-naphthol in the presence of an electrolyte and the corresponding heteropolyacid. *In-situ* i.r. analysis reveals a heterogeneous distribution of the heteropolyanion (HPA) in the polymer matrix with a larger amount at the metal–film interface. The electrochemical properties of the poly(NAP-1)/P_2W_{18} film were studied in aqueous and organic solvents. In acidic medium, cyclic voltammetry shows three bielectronic waves from the HPA; in acetonitrile, the same transfers are observed in addition to the redox system of the polymer. *In-situ* MIRFTIRS spectra indicate that the electrochemical oxidation-reduction process of poly(NAP-1)/P_2W_{18} occurs with the same structural change as for poly(NAP-1) without HPA.

1. Introduction

The synthesis of electrodes modified by heteropolyanions (HPA) entrapped in polymer films has recently attracted the attention of electrochemists [1–7]. The polymeric matrices used were polyvinylpyridine [1, 2], polyaniline [3, 4], polypyrrole [5], poly(3-methylthiophene) [6] or polyacetylene and poly(alkylthiophene) [7]. The favoured strategy was the electrostatic incorporation of HPA in a polymer already fixed on an electrode surface [1–5, 7]; the immobilization of HPA during the electrochemical synthesis of polymer films is less frequently used [6].

Such modified electrodes have good potential for application in electrocatalysis. It is of interest to investigate the distribution of HPA inside the polymer matrix and the electrochemical properties of the resulting films.

In this paper, we present results concerning the immobilization of HPA during the electropolymerization procedure. The polymer matrix is a new electroactive and conducting film, poly(1-naphthol), which we have recently synthesized [8]. The film structure, characterized by a MIRFTIRS study, comprises alternate naphthylene and furan rings [8]. A Dawson type heteropolyacid ($P_2W_{18}O_{62}H_6$), nH_2O can be incorporated in poly(1-naphthol) films when added to the electrolytic medium during electropolymerization of 1-naphthol. The film growth with HPA distribution in the polymer matrix and the electrochemical oxidation-reduction of the resulting film were studied *in-situ* using the MIRFTIRS method.

2. Experimental details

The heteropolyacid used was $P_2W_{18}O_{62}H_6$, nH_2O (denoted P_2W_{18} for simplification); 1-naphthol supplied by Aldrich was sublimed before used.

The films were usually synthesized using potential cycling between 0.4 and 1.5 V against Ag/AgCl in an acetonitrile solution containing 0.1 M 1-naphthol, 0.1 M $LiAsF_6$ and 10^{-3} M P_2W_{18}.

For electrochemical experiments, a two-compartment cell was used, the working electrode being a glassy carbon or a platinum disk. For *in-situ* MIRFTIRS study, the working electrode was a germanium prism coated with a thin layer of platinum or gold.

The spectroelectrochemical cell was described in previous papers [9–10].

3. Results and discussion

3.1. *Electrochemical synthesis*

Polymer films were deposited onto Pt, or glassy carbon disc electrodes by potential cycling between 0.4 and 1.5 V against Ag/Ag Cl (Fig. 1). The solution used was 0.1 M 1-Naphthol + 0.1 M $LiAsF_6$ + 10^{-3} M P_2W_{18} + Acetonitrile. The infrared study described in §3.2 demonstrates that P_2W_{18} is incorporated in the poly(NAP-1) film.

Scanning electron micrographs (SEM) reveal that the film morphology is different for poly(NAP-1) with or without entrapped HPA. Figure 2a shows the

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* This paper is dedicated to Professor Dr Fritz Beck on the occasion of his 60th birthday.

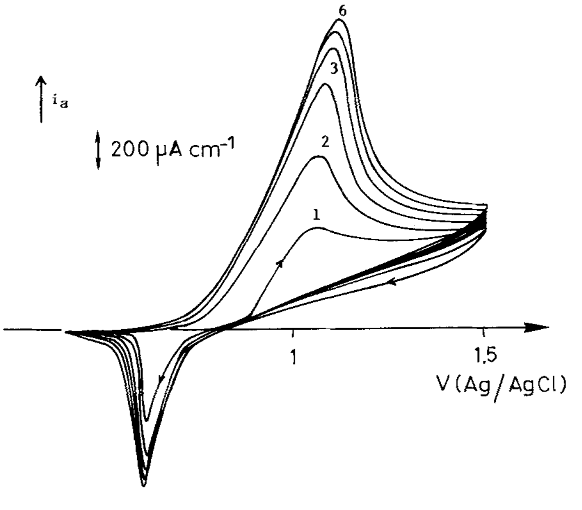

Fig. 1. Cyclic voltammograms of poly(NAP-1)/P_2W_{18} during film growth. Medium: 0.1 M 1-naphthol + 0.1 M $LiAsF_6$ + 10^{-3} M P_2W_{18} + acetonitrile. The electrode is a platinum disc with a surface of 0.196 cm^2, scan rate 50 mV s^{-1}.

topology of a Pt electrode coated with a poly(NAP-1) film obtained by 10 potential scans between 0.2 and 1.3 V at a scan rate of 50 mV s^{-1}. The film appears to have a globular structure with sections of globules packed together. The globule diameters of 0.8 µm are typical. The poly(NAP-1)/P_2W_{18} synthesized in similar conditions (Fig. 2b) shows several differences from Fig. 2a. The structure is always globular but much more compact and the globule diameters increase to a mean value of 5.3 µm. SEM was also used to measure films thickness at the cross-section of a polymer film when a strip of polymer was scratched out. The poly(NAP-1) film in Fig. 2a has a thickness of ~1.5 µm while for poly(NAP-1)/P_2W_{18} in Fig. 2b the thickness is ~4.5 µm.

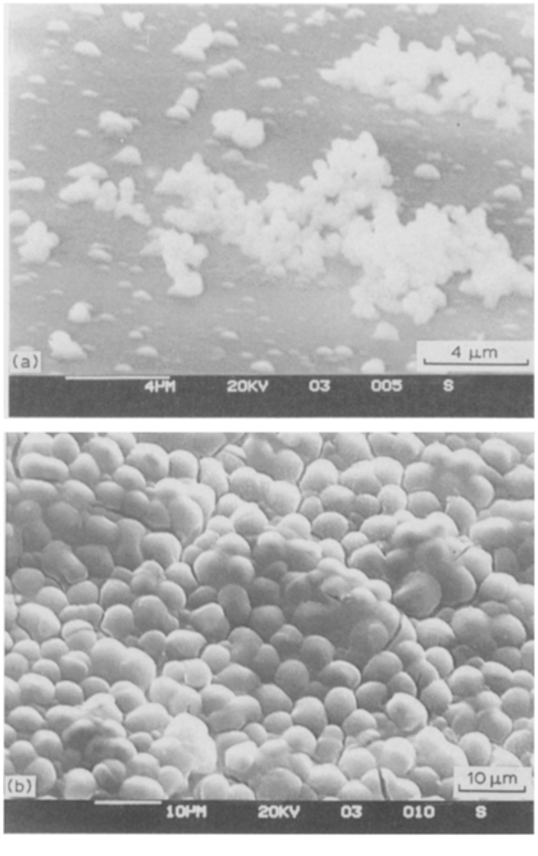

Fig. 2. SEMs for films on Pt. (a) poly(NAP-1) films: the film was formed by 10 scans between 0.2 and 1.3 V at 50 mV s^{-1} in 0.1 M 1-naphthol + 0.1 M $LiAsF_6$ + CH_3CN. (b) Poly(NAP-1)/P_2W_{18} films: the film was formed by 10 scans between 0.2 and 1.3 V at 50 mV s^{-1} in 0.1 M 1-naphthol + 0.1 M $LiAsF_6$ + 10^{-3} M P_2W_{18} + CH_3CN.

3.2. *An in-situ i.r. study of the film growth*

3.2.1. Film formation by a potential sweep at slow scan rate. A MIRFTIRS study was performed to analyse the polymer structure and the film growth. Spectra are recorded during the formation of poly(NAP-1)/P_2W_{18} by a single potential cycle between 0.2 and 1.3 V at a slow scan rate of 2 mV s^{-1}.

Figure 3 represents the reference spectrum which is that of the system (Ge/Au electrode in an acetonitrile solution containing 10^{-1} M 1-naphthol + 10^{-1} M $LiAsF_6$ + 10^{-3} M P_2W_{18}) before polarization.

The spectra of $P_2W_{18}O_{62}^{6-}$ in the solid state have been reported and discussed [11]. The structure of this HPA has been determined by Dawson [12] and refined by d'Amour [13]. It comprises two PO_4 tetrahedra connected by octahedra of W and O atoms.

The PO_4 stretching vibrations were observed at 1090 and 1022 cm^{-1}. Three bands at 960, 912 and 780 cm^{-1} were assigned to the asymmetric stretching vibrations of the W–$O_{terminal}$ bonds, the "inter" W–O–W bridges and the "intra" W–O–W bridges [11], respectively.

Returning to the reference spectrum (Fig. 3), it shows approximately the same bands for P_2W_{18} in the solution studied. PO_4 vibrations are seen at 1084 and 1038 cm^{-1}. Bands of W–O are observed at 960 and 918 cm^{-1}. The third band at 780 cm^{-1} should overlap with the 778 cm^{-1} band of the monomer. It will be seen later that when the film is formed, the monomer band at 778 cm^{-1} disappears and a broad band appears at ~800 cm^{-1} which is related to the stretch of W–O–W bridges (Fig. 3).

A strong band related to the AsF_6^- ions in solution is visible at 703 cm^{-1} and the C≡N stretch of acetonitrile at 2251 cm^{-1} (i) and 2290 cm (w).

For the monomer, the presence of bands at 750 and 798 cm^{-1} are noted due to the C–H out of plane vibrations of three adjacent aromatic hydrogen atoms in polynuclear aromatic compounds [14] and a band at 778 cm^{-1}, which is due to C–H vibrations of the four adjacent aromatic hydrogen atoms [14].

Considering now the *in situ* MIRFTIRS spectra recorded during the potential scan between 0.2 and 1.3 V (Fig. 4). When the electrode attains an average potential of 0.85 V, many bands related to the poly(NAP-1)/P_2W_{18} film are detected. Band intensities increase up to spectrum S_4 corresponding to ~1.2 V. Spectra recorded during the reverse scan $S_5 \rightarrow S_7$ show bands with band intensity remaining steady, S_6 and S_7, are then not presented. This fact can be explained in the following way. In the domain studied in our experimental conditions, the penetration depth

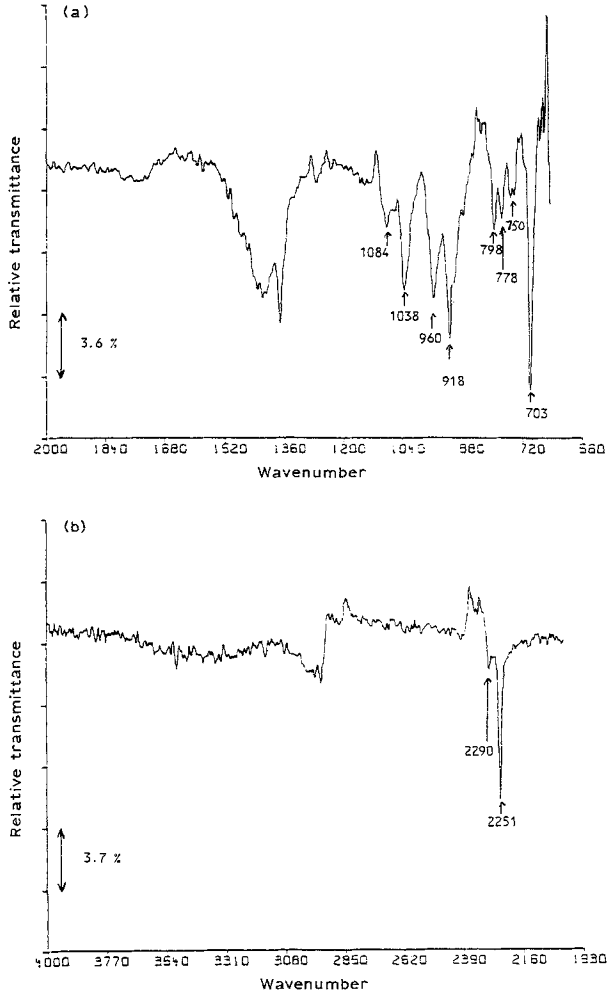

Fig. 3. The reference spectrum of the system (Ge/Au electrode in 10^{-1} M naphthol + 10^{-1} M $LiAsF_6$ + 10^{-3} M P_2W_{18} + acetonitrile) before polarization.

of the evanescent wave varies between ~340 nm (at the wavenumber of 2000 cm^{-1}) and 850 nm (at the wavenumber of 800 cm^{-1}) [15, 16]. We have measured in the dry state the thickness of a film synthesized in the same conditions (potential scan between 0.2 and 1.3 V) on platinum. This thickness by SEM was ~2.5 μm. During the *in situ* MIRFTIRS experiment, the film is in solution and not in the dry state, but the thickness should not be smaller than 2.5 μm. So the MIRFTIRS spectra explores only the inner film layers with thickness $\leqslant$ 850 nm. This explains why the band intensity remains steady after spectrum S_4.

The MIRFTIRS spectra show that the film formed has the structure of poly(NAP-1) with P_2W_{18} entrapped in the film (Fig. 4). Poly(NAP-1) is composed of alternating naphthylene and furan moieties [8]. The coupling in the polymer chain occurs at the nucleus containing the -OH group and does not affect the second nucleus of the ring because the two bands related to the three adjacent H atoms at 750 and 798 cm^{-1}, visible in the reference spectrum, now disappear; only one very strong band at 765 cm^{-1} is present which is due to C–H vibrations of the four adjacent aromatic hydrogen atoms [14].

The aromatic $C{=}C_{ar}$ stretch is seen at 1587 cm^{-1}, for the furan ring, the C=C band of furan is at 1570 cm^{-1}. The asymmetric vibration of the C–O–C linkage of furan rings is detected at 1289 cm^{-1}. It is accompanied by a band at 1081–1061 (shoulder) cm^{-1} due to symmetric vibration of the same bond [17–19]. In this case, the 1081 cm^{-1} should be overlapped with the 1090 cm^{-1} band due to P_2W_{18}. A strong band at 1217 cm^{-1} has been attributed to $C{=}\overset{+}{O}{=}C$ stretch of the film in the oxized form [8]. The poly(NAP)^+ film should be associated with AsF_6^- ions, detected at 708 cm^{-1} and P_2W_{18} ions. The PO_4 stretching vibrations are visible at 1090 cm^{-1}. The W–O bands are seen at 968 cm^{-1}, 900 cm^{-1} and a broad band at ~800 cm^{-1}.

A spectrum was also recorded in the same film in the dry state after formation by external reflection spectroscopy (Fig. 5). Approximately the same bands are found for poly(NAP-1)/P_2W_{18}. Nevertheless, the comparison of the *in situ* spectra (Fig. 4) which give information concerning the inner film layers (thickness $\leqslant$ 0.85 μm) and the *ex situ* spectra (Fig. 5) related to the outer film layers, show that the quantity of P_2W_{18} is much more important near the metal-film interface. In the *in situ* spectra, the ratio of P_2W_{18}/AsF_6 is great while it is smaller in the *ex situ* spectra. Poly(NAP-1) is obtained in a partially oxidized form, the positive charge of the oxidized polymer should be compensated by P_2W_{18} and AsF_6^- anions. In the inner layers P_2W_{18} is predominant while the opposite is true for the outer layers.

In order to gain deeper insight in to the film growth during the electropolymerization, attempts were made with a MIRFTIRS study during film formation by performing successive potential scans at a higher scan rate.

3.2.2. Film growth during successive potential sweeps at high scan rate. A MIRFTIRS study was performed with a Ge/Au electrode in an acetonitrile solution containing 10^{-1} M 1-naphthol + 10^{-1} M $LiAsF_6$ + 10^{-3} M P_2W_{18}. Four successive potential sweeps between 0.4 and 1.5 V at a scan rate of 20 mV s^{-1} were applied to the electrode. Spectra were recorded at the end of each sweep. S_1^{ox}, S_3^{ox}, S_5^{ox}, S_7^{ox} are spectra obtained at the end of the positive scans 0.4 V → 1.5 V and S_2^r, S_4^r, S_6^r, S_8^r, those obtained at the end of the negative scans 1.5 V → 0.4 V. All spectra are presented in Fig. 6.

After the first positive scan 0.4 V → 1.5 V, spectrum S_1^{ox} presents all the bands related to poly(NAP-1) film structure at 1589, 1571, 1483, 1290, 1221 and 766 cm^{-1} as well as bands due to P_2W_{18} entrapped in the film at 1090, 970, 903 and at ~822 cm^{-1}. AsF_6^- ions are seen at 702 cm^{-1}. As in the preceding case (§3.2.1), poly-(NAP-1) was obtained in the oxidized form as indicated by the $C{=}\overset{+}{O}{=}C$ band at 1221 cm^{-1} which is associated with bands due to AsF_6^- and P_2W_{18}. In the first film layers, the amount of P_2W_{18} is greater than that of AsF_6^- ions. At the end of the first negative scan 1.5 V → 0.4 V, P_2W_{18} was entrapped in significant

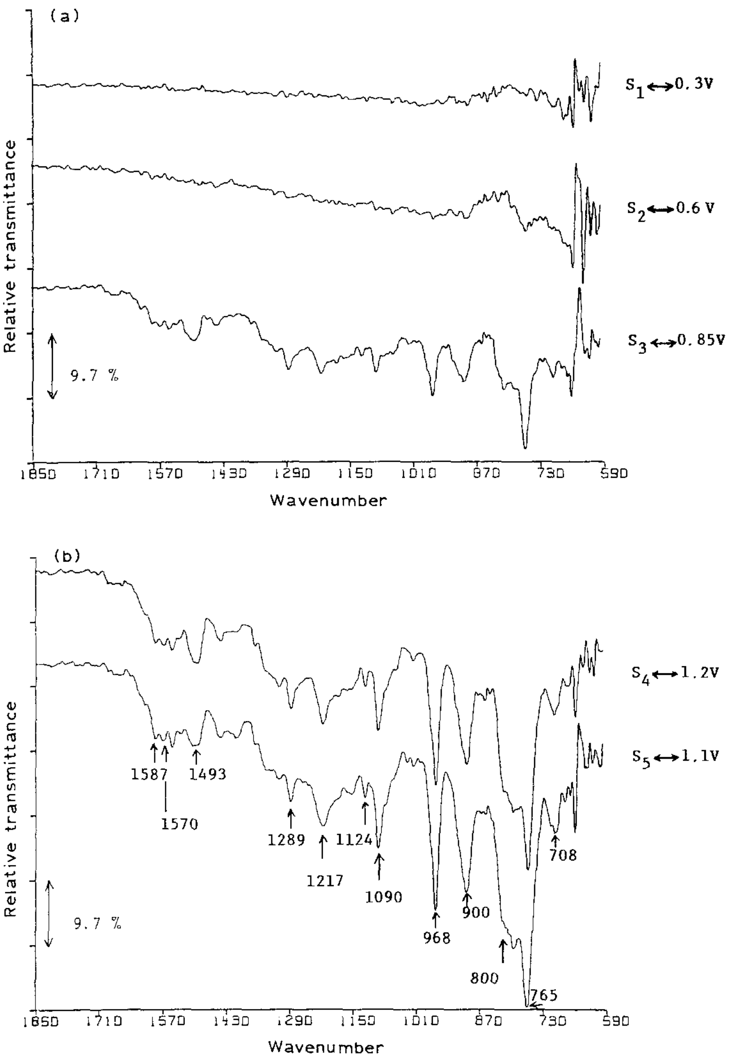

Fig. 4. *In situ* MIRFTIRS spectra recorded during a potential scan between 0.2 and 1.3 V at 2 mV s^{-1}. Medium: 0.1 M 1-naphthol + 0.1 M $LiAsF_6$ + 10^{-3} M P_2W_{18} + acetonitrile. Each spectrum was obtained using 500 interferometer scans (about 130 s). Spectra normalized with respect to reference spectrum in Fig. 3.

quantity. Spectrum S_2^r shows strong bands related to P_2W_{18}.

For the second sweep, in the oxidation scan (S_3^{ox}), the AsF_6^- band is more important and the band with a shoulder at 1090 cm^{-1} (in S_1^{ox}–S_2^r) is now deconvoluted into two bands, the one at 1097 cm^{-1} can be assigned to P_2W_{18} and the second at 1079 cm^{-1} is due to the symmetric C–O–C bond of the furan ring in the film. From S_4^r and S_8^r, bands related to the film remain likely steady. In contrast, an increase in intensity is observed for bands due to P_2W_{18} and AsF_6^- in S_4^r. The same findings are observed for the next two scans. In the oxidation process 0.4 V → 1.5 V (spectra S_5^{ox}, S_7^{ox}), P_2W_{18} bands and AsF_6^- band diminish, in the reduction 1.5 V → 0.4 V (spectra S_6^r, S_8^r), those bands increase. A tentative explanation could be that as P_2W_{18} can be reduced in this medium, (the first cathodic peak is situated at 0.16 V), it diffuses more easily to the electrode during the negative scan and is entrapped in the polymer matrix in great quantity. The increase in intensity of the AsF_6^- band may show that $LiAsF_6$ is diffusing into the polymer matrix, Li^+ ions compensate the excess of negative charge from P_2W_{18}; probably AsF_6^- replaces that part of the P_2W_{18} which was associated with the oxidized polymer in the inner layers.

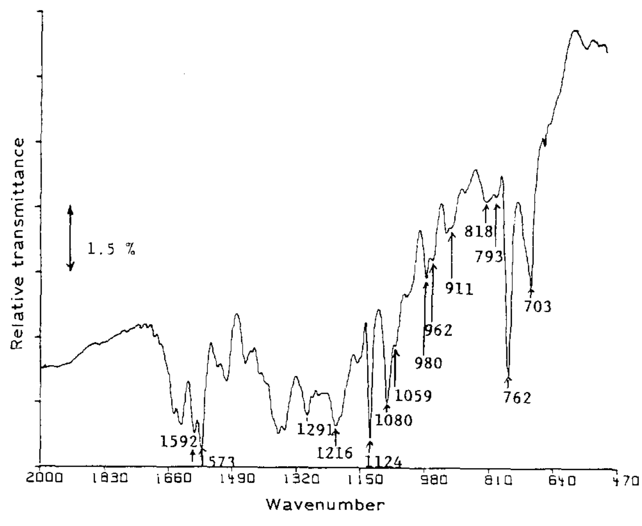

Fig. 5. *Ex situ* external reflection i.r. spectrum of the poly(NAP-1)/P_2W_{18} after formation. Film as obtained in Fig. 4.

The findings observed in this experiment lead to the conclusion that independently of film formation conditions, the distribution of P_2W_{18} inside the polymer matrix is the same: P_2W_{18} is more concentrated in the inner layers than in the outer layers.

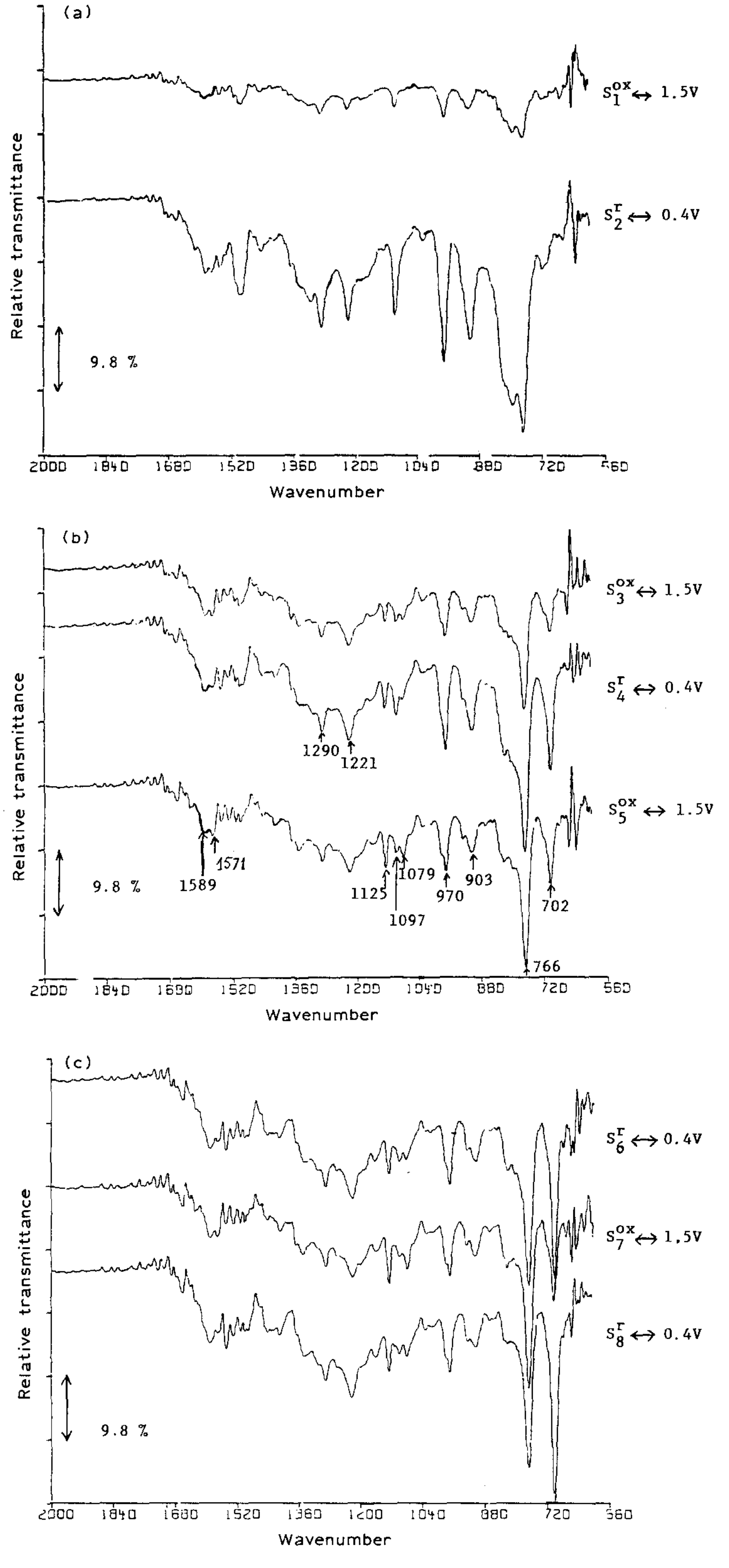

Fig. 6. *In situ* MIRFTIRS spectra recorded during poly(NAP-1)/P_2W_{18} films growth by four successive potential scans between 0.4 and 1.5 V at 20 mV s^{-1}. Medium: 0.1 M 1-naphthol + 0.1 M $LiAsF_6$ + 10^{-3} M P_2W_{18} + acetonitrile. Each spectrum obtained using 200 interferometer scans (duration: 52 s).

3.3. *Electrochemical properties of poly(NAP-1)/P_2W_{18})*

3.3.1. Study in aqueous medium: 0.1 M *H_2SO_4*. Cyclic voltammograms obtained with a poly(NAP-1)/P_2W_8 coated carbon electrode in an aqueous solution containing 0.1 M H_2SO_4 at different scan rates are presented in Fig. 7a. For comparison, the corresponding cyclic voltammograms obtained with a freshly polished carbon electrode in the presence of 10^{-3} M P_2W_{18} in the same electrolyte are shown in Fig. 7b.

In solution, the first two waves (Fig. 7b) have been shown to rise from one electron each [20]. In the poly(NAP-1)/P_2W_{18}, the first wave merges with the second. Otherwise, the formal potentials, $E^{0\prime}$, are approximately the same for P_2W_{18} in solution or confined in the film. Considering the intensity of the third wave, the peak current varies linearly with scan rate up

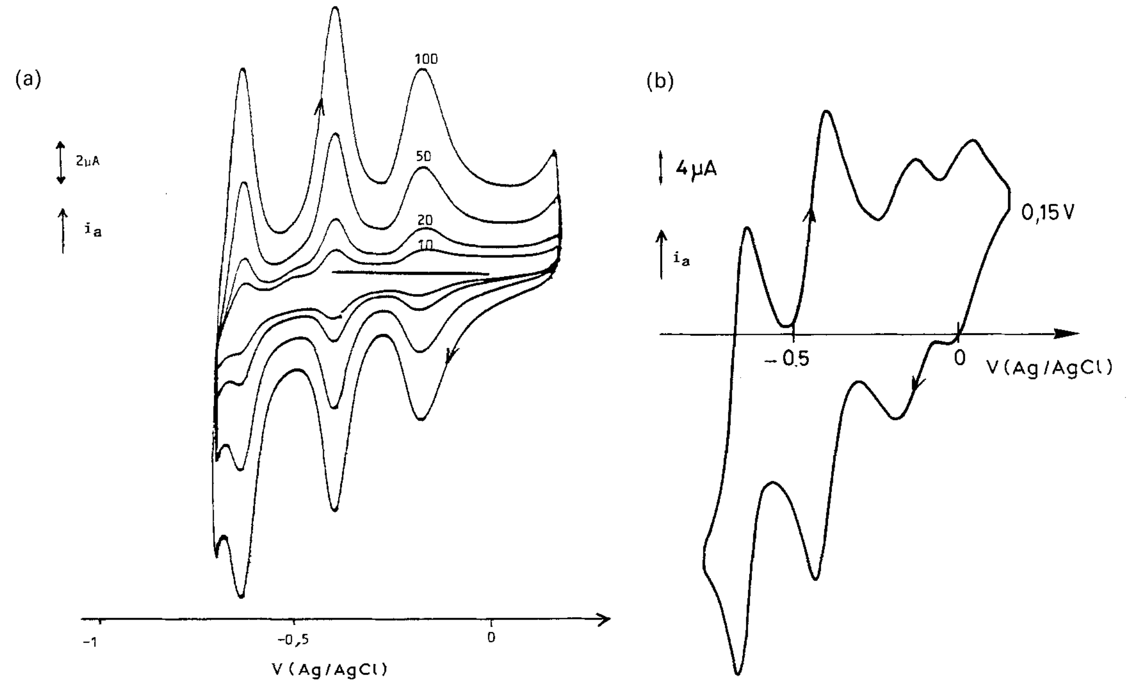

Fig. 7. (a) Cyclic voltammograms obtained with a poly(NAP-1)/P_2W_{18} coated carbon electrode in 0.1 M H_2SO_4; The scan rates are in $mV s^{-1}$; electrode surface area = 0.28 cm^2. (b) Cyclic voltammograms obtained with a carbon electrode in a solution of 10^{-3} M P_2W_{18} + 0.1 M H_2SO_4. Scan rate: 100 $mV s^{-1}$; electrode surface: 0.07 cm^2.

to 100 $mV s^{-1}$. The surface concentration calculated at 50 $mV s^{-1}$ gives a value of 1.9×10^{-10} mol cm^{-2}.

3.3.2. Study in organic solvent: 0.5 M $HClO_4$ + CH_3CN. Cyclic voltammetry of a poly(NAP-1)/P_2W_{18} modified electrode was also performed in acetonitrile solution containing as electrolyte $HClO_4$ (0.5 M) (Fig. 8a).

Curve 1 shows the cyclic voltammetric pattern obtained in the domain 1.15 V at −0.35 V/SCE. The main redox system corresponding to the poly(NAP-1) film is well defined at 0.8 V (E_{pc}) and 1.05 V (E_{pa}). The three waves related to P_2W_{18} entrapped in the film are also well visible by increasing the intensity sensitivity (Curve 2). The cathodic peak potentials (E_{pc}) are situated at −0.28 V, −0.02 V, +0.19 V and the anodic peak potentials E_{pa} at −0.24 V, 0 V and +0.16 V.

Cyclic voltammetry of P_2W_{18} in a solution of 0.5 M $HClO_4$ + acetonitrile with a carbon electrode shows also three redox waves at approximately the same

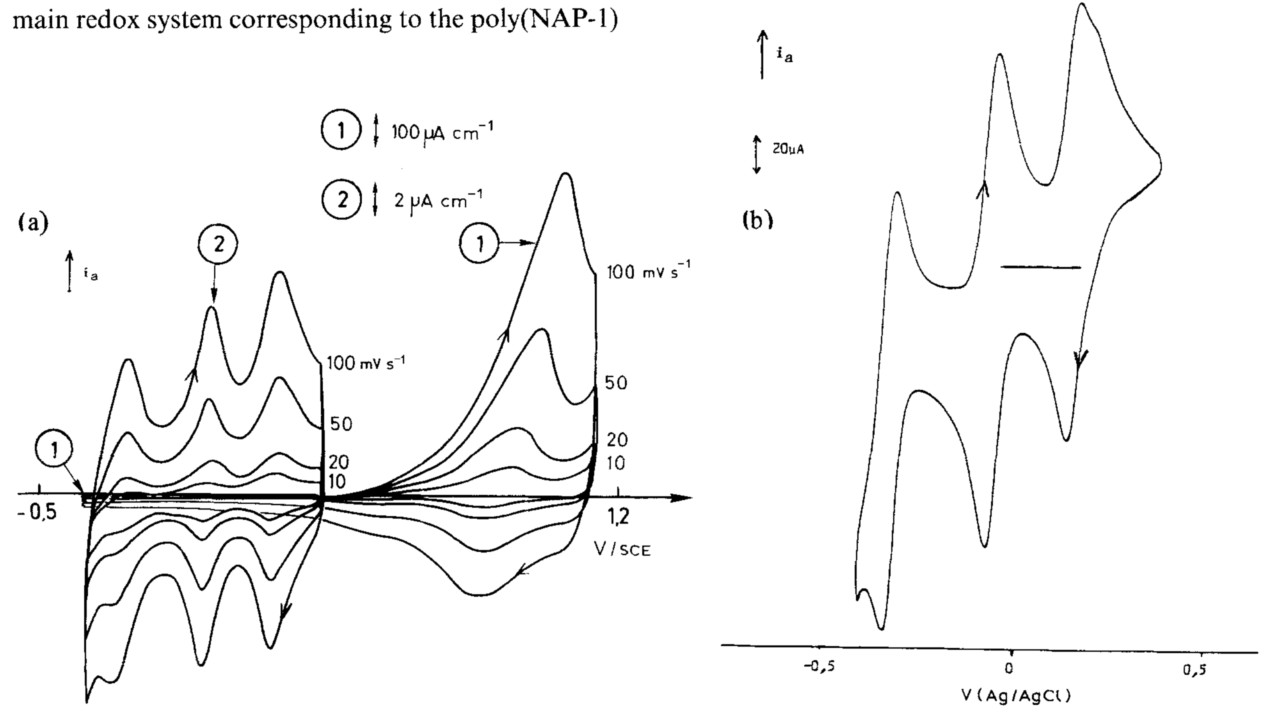

Fig. 8. (a) Cyclic voltammogram obtained with a poly(NAP-1)/P_2W_{18} coated carbon electrode in 0.5 M $HClO_4$ + acetonitrile. Electrode surface: 0.07 cm^2; scan rates as indicated. Curve 1: potential scan between −0.35 and +1.15 V; curve 2: potential scan between −0.35 and +0.35 V. (b) Cyclic voltammogram obtained with carbon electrode in a solution of 10^{-3} M P_2W_{18} + 0.5 M $HClO_4$ + acetonitrile. Scan rate: 50 $mV s^{-1}$, electrode surface: 0.28 cm^2.

potentials (E_{pc} at -0.33 V, -0.07 V and $+0.14$ V, Fig. 8b).

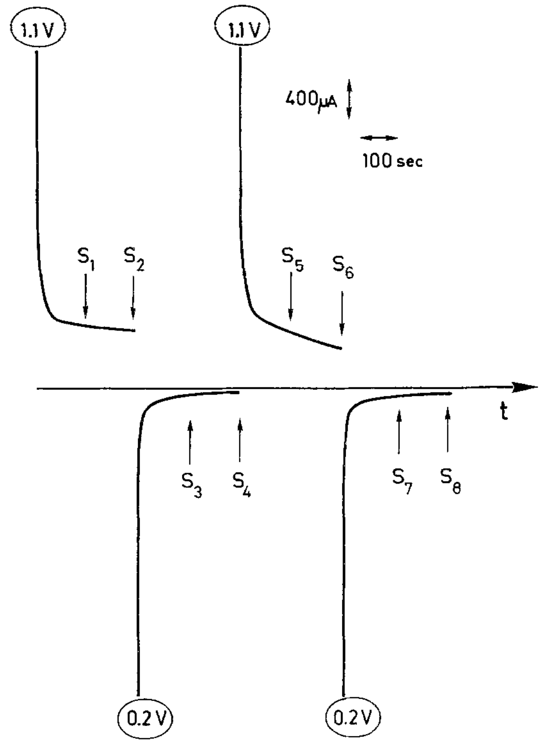

Fig. 9. Double potential step experiment between 1.1 and 0.2 V against Ag/AgCl with a poly(NAP-1)/P_2W_{18} gold coated electrode in 0.1 M $LiAsF_6$ + CH_3CN solution. The spectrum numbers indicate the time at which spectra were recorded. Time between two spectra is ~130 s which is necessary to accumulate 500 interferometric scans.

3.4. *In situ MIRFTIRS study of the electrochemical oxidation-reduction process of poly(NAP-1)/P_2W_{18} film*

A double-potential step between 1.1 and 0.2 V was performed on a gold electrode coated with poly(NAP-1)/P_2W_{18} (Fig. 9). The film was synthesized as in §3.2.1. by a single potential cycling between 0.2 and 1.3 V at 2 mV s^{-1} with $LiAsF_6$ as electrolyte (thickness ~2.5 μm in dry state).

In situ MIRFTIRS spectra were recorded during this experiment (Fig. 10). Each spectrum results from accumulation of 500 interferometer scans (~130 s). Spectra were successively recorded. S_1^{ox}, S_2^{ox} are spectra of the system when polarized at 1.1 V. S_3^r, S_4^r those recorded when stepping to 0.2 V. For the second step, S_5^{ox}, S_6^{ox} were obtained at 1.1 V and S_7^r, S_8^r at 0.2 V. All data in these spectra concern only the inner part of film with thickness $\leqslant 0.85$ μm. On oxidation at 1.1 V (S_1^{ox}, S_2^{ox}), AsF_6^- diffuses into the polymer; on reduction at 0.2 V (S_3^r, S_4^r), this band at 699 cm^{-1} decreases.

During the second step at 1.1 V (S_5^{ox}, S_6^{ox}), the AsF_6^- band increases. This suggests that diffusion of AsF_6^- in the polymer matrix is slow and progressive. As all the bands become more intense from S_6^{ox}, the probable meaning is that the swelling of the film has changed its optical properties, followed by an increase in the penetration depth of the evanescent wave.

The structural change of the poly(NAP-1)/P_2W_{18} film during the oxidation-reduction process occurs in the same manner than for the poly(NAP-1) film without entrapped P_2W_{18} [21]. Spectra S_6^{ox} corresponding to the oxidized form and S_7^r to the reduced form are presented in Fig. 10c in a restricted domain 1800–970 cm^{-1}.

In the oxidation process at 1.1 V (S_6^{ox}), bands at 1547 cm^{-1} for inter-ring C=C stretch and at 1221 cm^{-1} for $C{=}\overset{+}{O}{=}C$ stretch are intense while in the reduction process at 0.2 V (S_7^r), the latter bands diminish and are replaced by a strong band at 1120 cm^{-1} related to inter-ring C–C stretch [21].

4. Conclusion

The results presented in this paper show that poly(NAP-1) seems to be a good support for the immobilization of heteropolyacids. The distribution of HPA inside the polymer matrix is not homogeneous as demonstrated by *in-situ* IR analysis.

The electrochemical oxidation-reduction process of the poly(NAP-1)/P_2W_{18} film occurs as for the poly(NAP-1) film alone with similar change in the polymer structure.

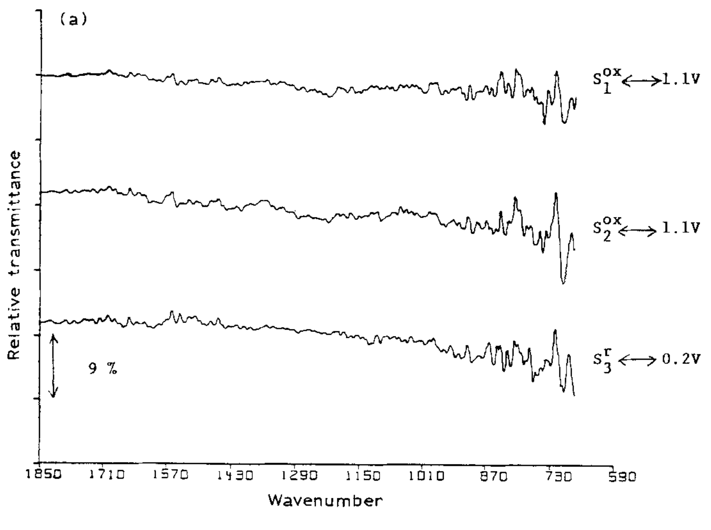

Fig. 10. (a) and (b) *In situ* MIRFTIRS spectra recorded during the experiment in Fig. 9 for $S_1 \to S_8$. (c) Spectra S_6^{ox} at 1.1 V (oxidation state) and S_7^r at 0.2 V (reduction state) in a restricted domain 1800–970 cm^{-1}.

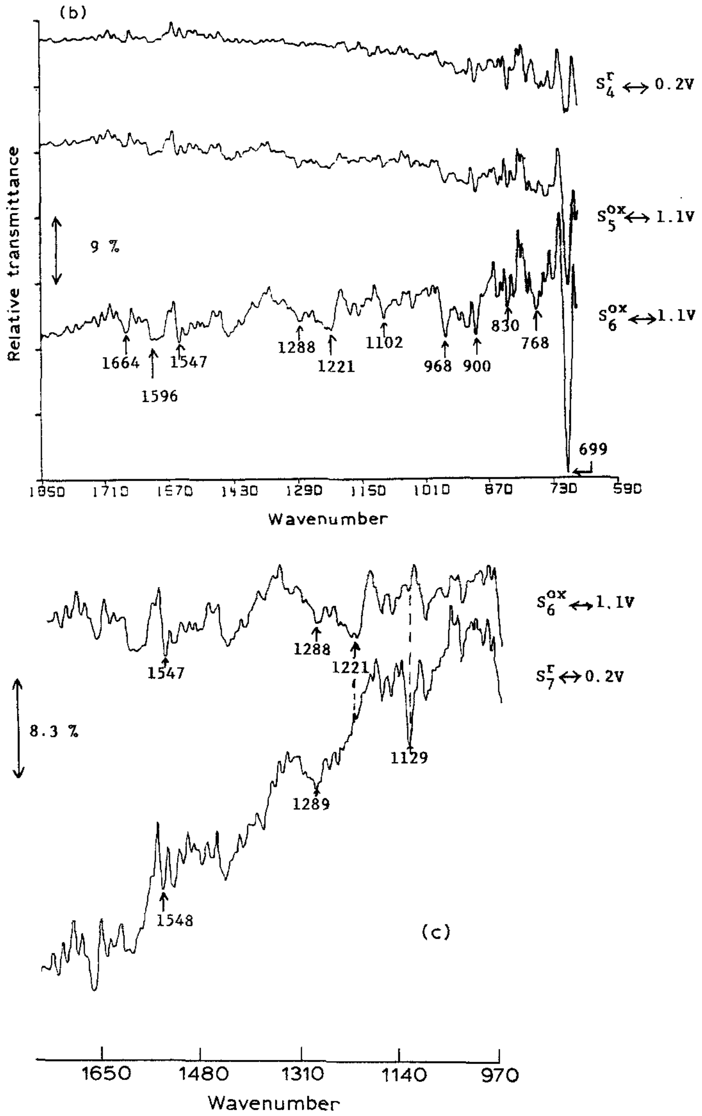

Fig. 10. Continued.

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