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Properties of polyaniline formed at tin dioxide electrodes in weak acid solution: effect of the counterion

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Polyaniline films have been formed at tin dioxide electrodes in aqueous 0.4 M acetate buffer solutions of pH between 3.5 and 5.5 with added nitrate, perchlorate or halide electrolyte, in order to study the effect of the counterion on the structure and electrochemical properties of the polyaniline film. The films were characterized electrochemically by cyclic voltammetry and by impedance, and morphologically by scanning electron microscopy. Marked differences between the films are found, the highest conductivity and electrochemical response being with nitrate counterion. The films formed are generally flat and porous, with evidence of some small irregular growths. These results are compared to those obtained in sulphuric acid solution.

1. Introduction

A considerable amount of research has been undertaken into the properties of polyaniline (PANI) films formed on electrode substrates, and has been recently summarized [1]. PANI exhibits the general characteristic of conducting polymers of switching between insulating and conducting states according to the applied potential. Whereas the conducting form corresponds to the half-oxidized state, application of higher potentials leads to another insulating form and possible polymer degradation. The oxidation state changes are associated with a change in colour, i.e. an electrochromic reaction [2, 3]. An important difference between PANI and most other conducting polymers is that it can be easily prepared in aqueous solution, which can bring advantages in terms of ease of experimental procedure in the preparation stage, and can be exploited in terms of incorporation of substances such as enzymes that need an aqueous environment. The incorporation of enzymes within a thin conducting polymer layer during electropolymerization, if achievable, should reduce the activity loss normally associated with enzyme immobilization. It was previously found that electrochemically prepared PANI in powder form could be used as a support for enzymes, with a good immobilization yield [4].

The conductivity of PANI is significantly reduced as the pH of the solution is increased; however, this decrease can be offset by incorporation of electrolyte anions during electropolymerization in order to achieve electroneutrality [5–8]. Anions have been shown to play an important role in the electropolymerization mechanism in acid solution [9] and in the properties of electrochemically doped PANI films [10, 11]. Additionally, anion sensors for flow injection analysis have been constructed using polyaniline electrodes and based on the doping/undoping phenomenon [12].

In order to incorporate enzymes, a pH value of greater than 4 must be employed. There have been reports of success in this type of immobilization [13, 14]. Nevertheless a detailed examination of the properties and morphology of the films formed under these conditions has not been carried out. This is important in elucidating the range of possibilities for use of PANI in aqueous electrolytes.

In this paper a study of polyaniline films formed at pH values between 3.5 and 5.5 in acetate buffer, in the presence of different electrolyte anions, at semitransparent tin dioxide electrodes is presented. Cyclic voltammetry, impedance spectroscopy and scanning electron microscopy are used to characterize the films and the results are compared with those for films formed at low pH.

2. Experimental details

2.1. *Electropolymerization*

Aniline (Merck *pro analysi*) was distilled under reduced pressure, kept in the dark and used within one week. Polyaniline thin films were formed at semitransparent tin dioxide electrodes on a glass substrate of area 4 cm^2 (Phosphor Products Ltd) by electropolymerization of 0.1 M aniline in aqueous electrolyte solutions containing 0.4 M acetate buffer plus nitrate, perchlorate or halide salts of potassium or sodium of 0.4 M concentration. Tridistilled water was used to make all solutions, and the pH value was varied between 3.5 and 5.5. A platinum foil counter electrode and Radiometer K401 saturated calomel reference

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electrode were employed. Experiments were carried out at 25 ± 0.5 °C.

In electropolymerization studies in acid solution, carried out for comparative purposes, the electrolyte described above was replaced by 0.5 M sulphuric acid or 1.2 M hydrochloric acid.

A potentiostat with triangular wave generator constructed in this laboratory was employed. The potential was swept between -0.2 and $+0.8\,V_{SCE}$ for 10 min. The coated electrodes were then transferred to a solution of the same composition, but without aniline, for characterization.

2.2. *Film characterization*

Cyclic voltammetry was carried out with the same potentiostat used in electropolymerization. Impedance spectra were recorded with a Solartron 1250 frequency response analyser coupled to a Solartron 1286 electrochemical interface and controlled by a HP9816 microcomputer. Absorption spectra were recorded with a Hitachi 220S u.v.-visible spectrophotometer. Scanning electron microscopy (SEM) was performed with a Jeol T330 scanning electron microscope fitted with a Tracor energy dispersive X-ray microanalysis (EDX) accessory. Electrodes were sputter-coated with a thin gold film before SEM was undertaken (magnification × 7500 at 20 kV).

3. Results and discussion

The films obtained on tin dioxide electrodes were characterized as detailed below. Comparison is made with films formed in strong acid media.

3.1. *Cyclic voltammetry*

Cyclic voltammograms of films formed in the presence of nitrate anions are shown in Fig. 1 for various pH values. In this particular case, it is seen that an increase in pH causes an increase in peak current up to pH ~ 5.3. The first oxidation peak is shifted to positive potentials with respect to acid solution and is pH dependent. A graph of peak potential against pH is approximately linear with slope 160 mV dec^{-1}. For comparison, Fig. 2 shows the results obtained for electropolymerization in 0.5 M H_2SO_4. The maximum currents for nitrate are about 10% of the corresponding maximum values in acid solution. This does not always happen with other counter ions. Figure 3 shows cyclic voltammograms obtained with different counter ions at the pH corresponding to maximum peak current, and Fig. 4 plots the peak currents obtained from cyclic voltammetry, conducted under the same conditions for various anions, as a function of pH. Several observations can be made:

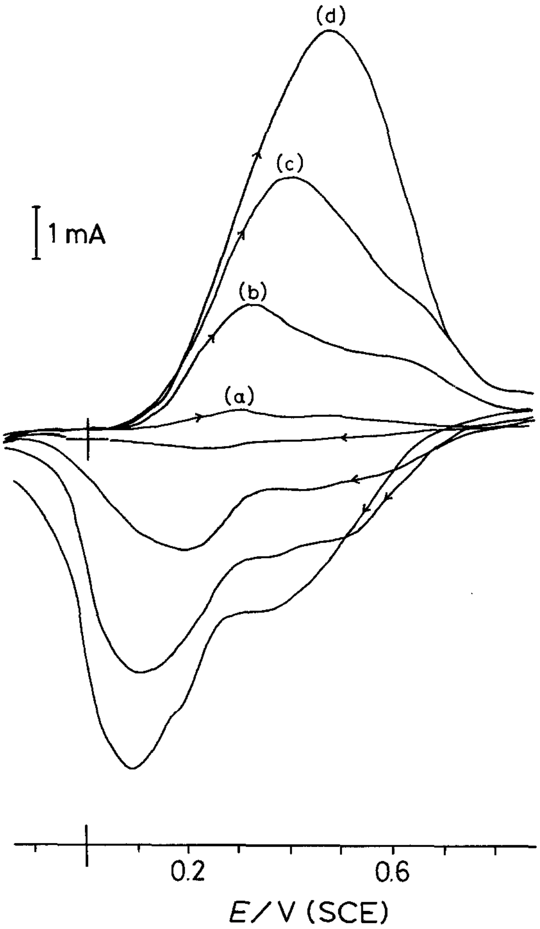


Fig. 1. Cyclic voltammograms of PANI films in 0.4 M acetate buffer with 0.4 M KNO_3 at pH: (a) 4.0, (b) 4.5, (c) 5.0, (d) 5.5. v = 50 mV s^{-1}.

(i) The two oxyanions NO_3^- and ClO_4^- lead to higher currents than those for halide ions; bromide leads to higher currents than chloride. These results correlate well with previous studies on detection of these anions at polyaniline electrodes in flow injection analysis [12].

(ii) There is a small effect of the cation, as manifested in the differences in the voltammograms corresponding to electrolytes containing NaCl and KCl. This can probably be ascribed to cation size.

(iii) A maximum appears at pH 5.3 for all anions (except for Cl^- with Na^+). Interestingly for perchlorate there is a second maximum at pH 4.5. This profile was checked to ensure that it was correct and reproducible. A specific interaction between the polyaniline chain and the perchlorate anion is thus indicated.

It has been affirmed that for pH > 2, oxidation probably corresponds to counterion injection compensating electron removal (half an electron per monomer unit) [15], assuming that the reduced form of PANI is not protonated. With the data from Fig. 4, this deduction may be questioned, at least for films formed in acetate buffer. The existence of an acid dissociation constant at pH ~ 5.3 would help in explaining the higher currents obtained, and below this pH, there may be partial protonation. Although there are many possibilities for electroactive groups in PANI, the conducting form almost certainly contains $-NH^+$ groups [2]. These can be electroneutralized by electrolyte anions in the film through schemes

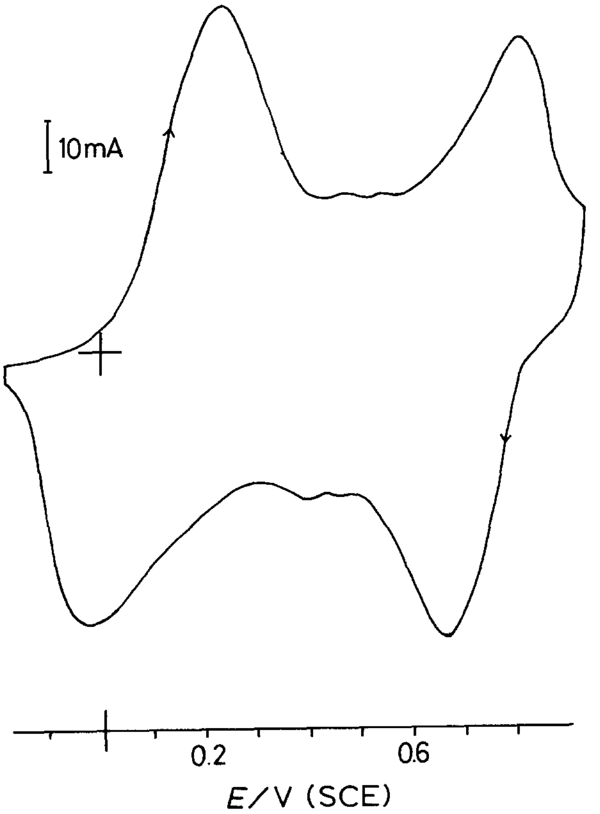


Fig. 2. Cyclic voltammogram of PANI film in 0.5 M H_2SO_4. $v = 50 \mathrm{mV\,s^{-1}}$.

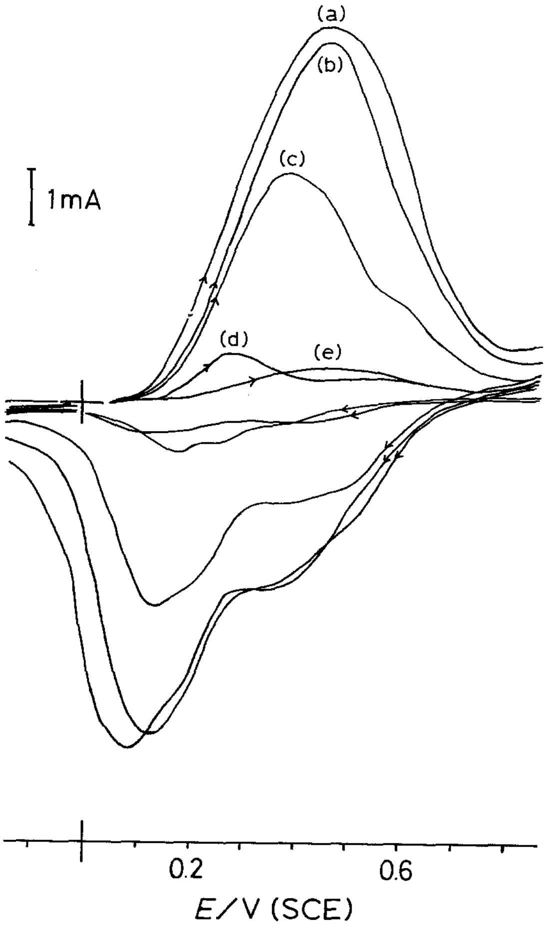
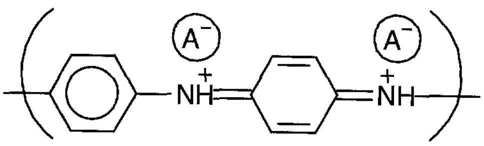


Fig. 3. Cyclic voltammograms of PANI in 0.4 M acetate buffer at pH of maximum peak current for oxidation with different anions (0.4 M) added as: (a) KNO_3 (pH 5.3), (b) $NaClO_4$ (pH 4.5), (c) NaBr (pH 5.3), (d) KCl (pH 5.2), (e) NaCl (pH 5.1).

such as:



It is thus not surprising that the stabilization afforded by different counterions could lead to different pK_a's for protonation, as occurs with perchlorate. The ease of incorporation of counterions during electropolymerization is of obvious importance.

It has also been stated that the lower the film conductivity, the greater the hydrophobicity of the film surface [16]. A simple test of spraying water on the coated electrode showed that the films formed in halide media, and particularly at high pH, (brown and colourless films, see later) showed a marked ability to repel water. This hydrophobic character correlates with cyclic voltammetry results that showed very small currents for films formed at higher pH.

3.2. *Impedance*

Previous studies of PANI in strong acid solution [17, 18] have shown that the impedance can be described to a good approximation by a Randles-type circuit. Thus, in the reduced and fully oxidized insulating states corresponding to negative and to high positive applied potentials, a semicircle of high charge transfer resistance together with Warburg diffusion is seen. At intermediate potentials corresponding to the conducting half-oxidized form, the current is purely capacitive and leads to a vertical line in the complex plane impedance plot. To these general considerations we have to add the effect of surface roughness, clear from electron micrographs, which reduces the phase angles obtained [19]. This roughness can be corrected for. Such impedance spectra were obtained in this laboratory in sulphuric and hydrochloric acid solution at tin dioxide electrodes [4].

The forms of impedance spectra described above are obtained in the media of higher conductivity. However, heterogeneities in the films, which occur particularly in films of lower conductivity, may result in different parallel pathways through which charge transfer can occur. Thus it is reasonable to expect various charge transfer processes with different time constants to appear in the spectra and there to be no clearly defined potential range where purely capacitive currents exist. It has been noted previously [5] that the zone of potential where no oxidation occurs narrows progressively as the pH is increased, and that the inclusion of anions in the film reduces this purely capacitive potential window.

Figures 5 and 6 show typical spectra in nitrate medium and pechlorate medium respectively, at three potentials corresponding to the reduced state (− 0.1 V), the conducting half-oxidized state (+ 0.6 V) and the fully oxidized state (+ 1.0 V). The spectra were

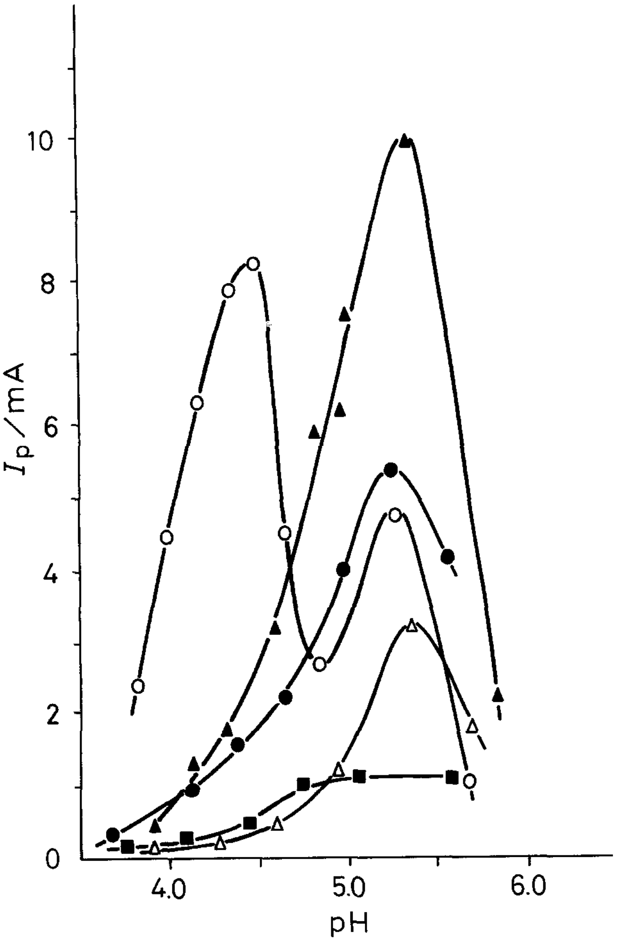


Fig. 4. Plot of oxidation peak current with pH for different electrolytes (0.4 M): (▲) KNO_3, (○) $NaClO_4$, (●) NaBr, (△) KCl, (■) NaCl.

recorded in this order to avoid any effects from film degradation at high potential.

A quantitative evaluation of the shape of the impedance plots is difficult. However, there is a higher resistive component than for films formed at low pH and, for perchlorate, the existence of more than one charge transfer process. Indeed, as discussed above, the variation of cyclic voltammetric peak current with pH in Fig. 4 shows two peaks, suggesting two types of interaction between perchlorate and the polymer chain.

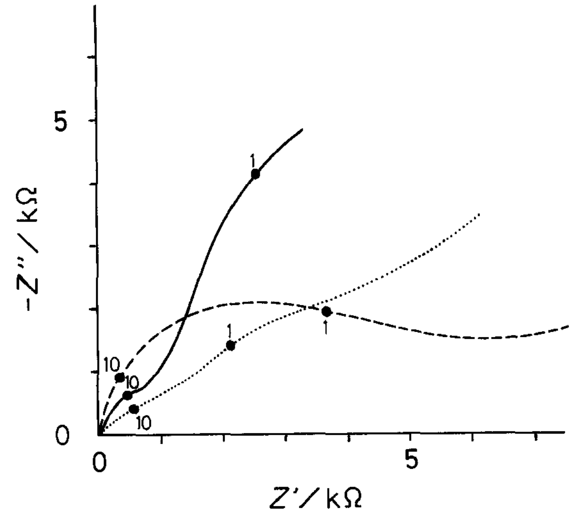


Fig. 5. Impedance plots of PANI coated tin dioxide electrodes in 0.4 M acetate buffer + 0.4 M KNO_3 at pH 5.2. (····) −0.1 V, (——) +0.6 V, (– – –) +1.0 V.

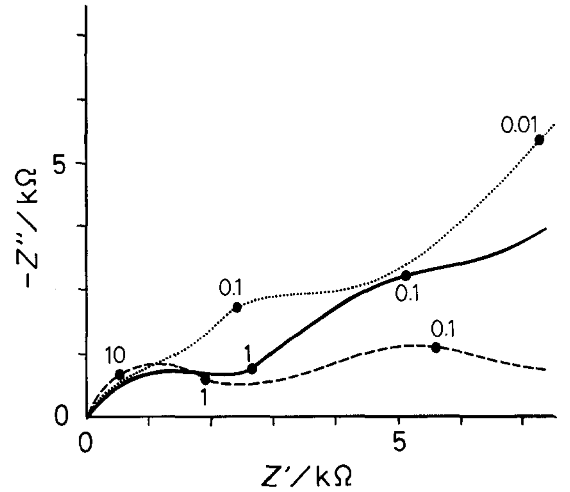


Fig. 6. Impedance plots of PANI coated tin dioxide electrodes in 0.4 M acetate buffer + 0.4 M $NaClO_4$ at pH 5.0. (····) −0.1 V, (——) +0.6 V, (– – –) +1.0 V.

3.3. *Chromatic properties of PANI films*

The visual aspect of the as-formed films, and during recording of cyclic voltammograms, was noted. Differences in colour with applied potential were slight. The information is summarized in Table 1. Conducting PANI is associated with a green/blue coloration at low pH i.e. protonated species, and the colour varies with applied potential according to the oxidation state; red/brown is for nonprotonated species [2, 3].

Table 1 shows that green/blue coloration is obtained primarily with nitrate and perchlorate counter ions, corroborating the cyclic voltammetry and impedance results. A typical absorbance spectrum is shown in Fig. 7, and compared with that of films formed in 0.5 M H_2SO_4. Differences can be ascribed to different film thicknesses, as films grow very fast in sulphuric acid media.

3.4. *Morphology*

PANI formed in sulphuric acid solution is characterized by a duplex film: a thin, compact layer of polymer attached to the substrate, covered by a fibrous structure, reflecting the rapid growth of the film at certain sites to give a dendrite-like appearance [20, 21]. In hydrochloric acid solution [22], where film growth is slower, the film is smoother and there is little crosslinking. These observations were confirmed on tin dioxide electrodes.

At higher values of pH, the film is less conducting and grows much more slowly. Thus relatively smooth films are predicted. In acetate buffer alone, the individual nucleation sites can be seen, Fig. 8(a). However, in the presence of counter ions growth is faster and the polyaniline nuclei begin to coalesce. The detailed morphology of the films obtained thus depends on the counter ion identity, illustrated in Fig. 8(b)–(e), in order of decreasing electrochemical

Table 1. Colour of PANI-coated tin dioxide electrodes formed in 0.4 M acetate buffer plus 0.4 M salt at $E = 0.5\ V_{SCE}$ for various pH values

Electrolyte (0.4 M) added to acetate buffer (0.4 M)	*pH*		
	3.5	*4.5*	*5.5*
None	NC	NC	NC
KNO_3	Dark green-blue	Dark green-blue	Dark green-blue
$NaClO_4$	Green-blue	Dark green-blue	Brownish blue
NaBr	NC	Bluish	Brownish green
NaCl	NC	Greenish yellow	Reddish brown
KCl	NC	NC	Brown
K_2SO_4	NC	NC	NC

NC signifies no colouration.

response. Sometimes isolated spherical or tree-like growths appear on an otherwise fairly flat surface, as in Fig. 8(c) in the presence of perchlorate. Microanalysis of these growths and of the flat part of the films indicates the presence of the relevant counter ion (except in the case of nitrate, because EDX is unable to respond to N or O). However, by analogy with the other anions, it is to be expected that the counterion is present.

These results clearly show the importance, in the electropolymerization process, of pH and of counter ion identity, which are important factors affecting film growth, and thence film morphology and thickness.

3.5. *Final remarks*

It has been demonstrated that the choice of the electrolyte anion as well as the pH can significantly influence the conductivity and electrochemical properties of PANI films formed and characterized at pH values between 3.5 and 5.5. The oxyanions tested give the highest response, the order in current response being

$$NO_3^- > ClO_4^- > Br^- > Cl^-$$

There is a small effect from the cation identity.

Evidence was also found in this work for rapid doping/undoping in the PANI films. Films formed in acetate buffer with counterion present and then placed in sulphuric acid solution began very quickly, after one minute, to give the same qualitative electrochemical response as those formed in strong acid. However, the currents never reached the same magnitude, which is probably a reflection of the films being thinner. In a similar way, films formed in sulphuric acid, see Fig. 2, and subsequently placed in acetate buffer rapidly lost their high conductivity and the electrochemical behaviour became similar to that of films formed in acetate media. Thus, although the morphology of the films formed in acetate buffer and in

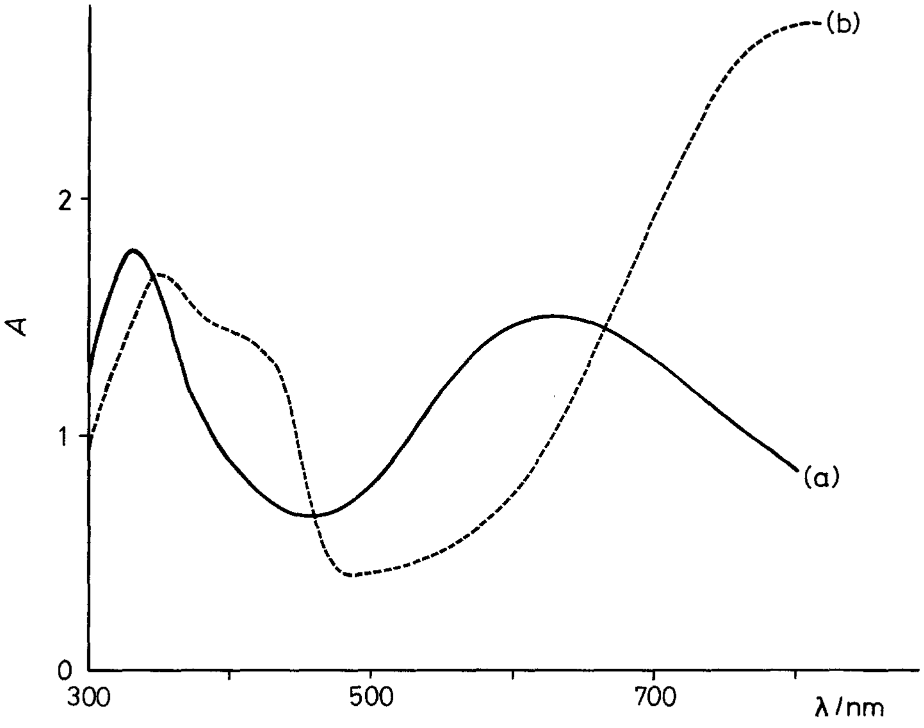


Fig. 7. Visible absorption spectra of PANI films formed in (a) acetate buffer with nitrate counterion (pH 5.0), (b) sulphuric acid (pH 0.2).

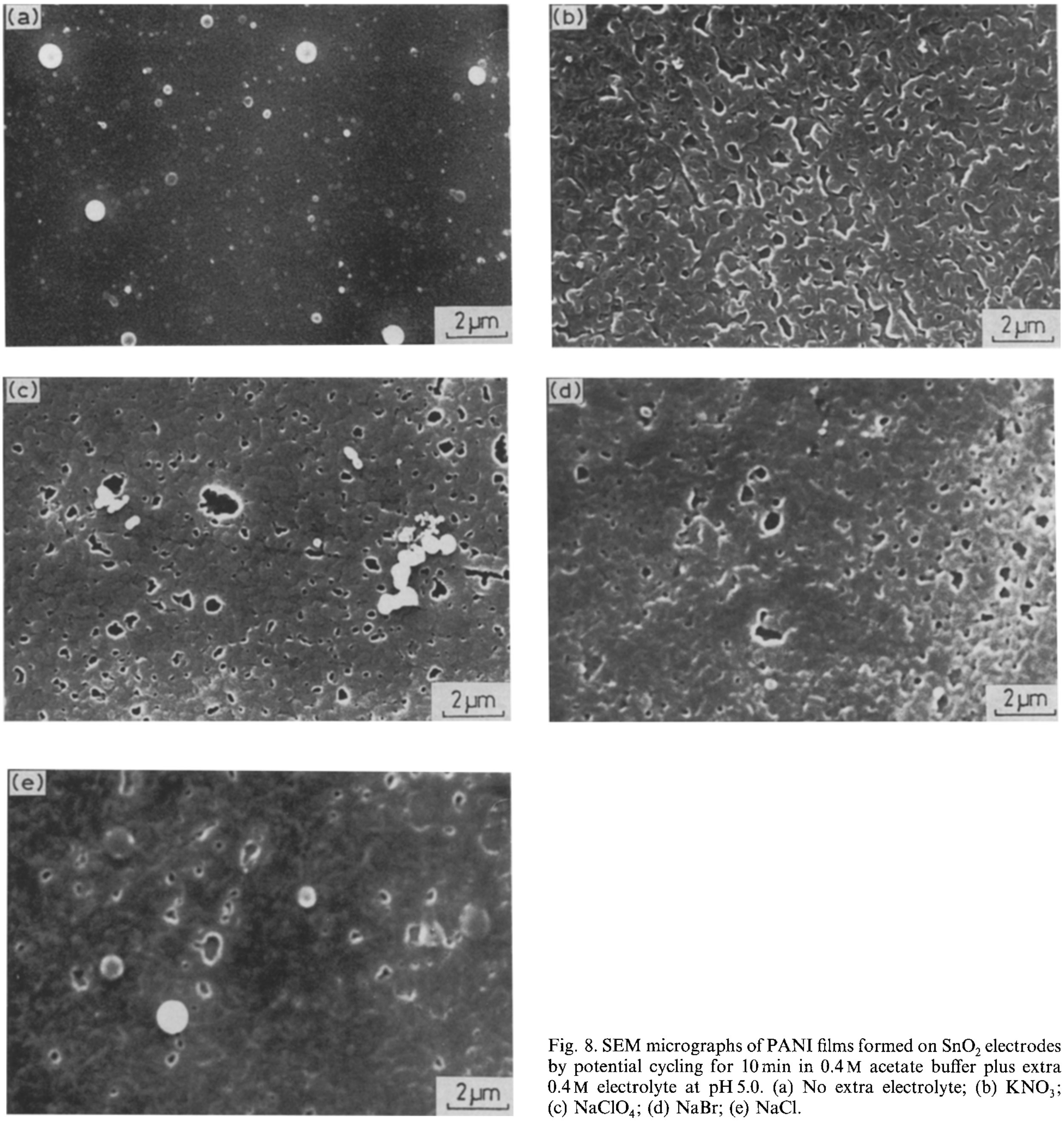


Fig. 8. SEM micrographs of PANI films formed on SnO_2 electrodes by potential cycling for 10 min in 0.4 M acetate buffer plus extra 0.4 M electrolyte at pH 5.0. (a) No extra electrolyte; (b) KNO_3; (c) $NaClO_4$; (d) NaBr; (e) NaCl.

strong acid solution is very different, this does not affect the electrochemical properties to a significant extent. These are principally dependent on the pH of the environment.

It is also necessary to consider the effect of the electrode substrate. Most work conducted on PANI has employed platinum substrates [1]. The identity of the substrate is particularly important in the formation and rate of formation of the first layers of polymer. Tin dioxide electrodes were employed in this work in order to study the morphology and chromatic properties of the polyaniline films. Data obtained on tin dioxide electrodes, for experimental conditions where comparison is possible, are similar to those at platinum electrodes [4]. Therefore, we believe that the results presented in this paper can be used for other electrode substrates.

Finally, it appears that, answering the question that motivated this work and contrary to previous reports [13, 14], the possibilities for incorporating enzymes during electropolymerization of aniline at compatible pH values and in appropriate buffers are limited.

4. Conclusions

The identity of the counterion plays an important role in the electrochemical behaviour and morphology of PANI films formed in acetate buffer solution on tin dioxide electrodes. Of the nitrate, perchlorate and halide counterions tested, nitrate led to the highest electrochemical response. The lower conductivities of the films with respect to films formed in sulphuric acid solution are reflected in the cyclic voltammetric and impedance results, and also in the colours of the films and their hydrophobic character. Films formed in acetate buffer are flat and porous, whereas electropolymerization in sulphuric acid solution leads to films with a fibrous structure. PANI films formed in acetate buffer and then placed in acid solution, rapidly exhibit the features of PANI resulting from electropolymerization in acid solution, demonstrating the rapidity of protonation/deprotonation.

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