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Electrosynthesis and characterisation of poly(Nile blue) films

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ABSTRACT

The phenoxazine dye, Nile blue-A, has been electropolymerised on glassy carbon electrodes by potential cycling in phosphate buffer solution at pH 5.3, 6.0, and 7.0. The electrochemical behaviour was studied by cyclic voltammetry and electrochemical impedance spectroscopy in phosphate buffer solution, also adding KCl, NaCl, LiCl, K_2SO_4, or Na_2SO_4 in order to evaluate counterion effects. The redox process of the polymer film presented an equal number of electrons and protons and the studies with different electrolyte compositions showed influence of the cations and anions on the electrochemical behaviour. The best polymer electrochemical properties were obtained in pH 5.3 electrolyte for the polymer prepared at pH 6.0, important information for application in electrochemical sensors and biosensors.

1. Introduction

The electropolymerisation of redox dyes including phenothiazine, phenazine and phenoxazine derivatives to obtain surface-modified electrodes covered by the corresponding semi-conducting polymer films has become attractive and the subject of many reports in the literature during the last decade e.g. [1–3]. These modified electrodes can act as mediators for the electrocatalysis of important biomolecules such as the coenzyme NADH and haemoglobin [4,5]. They also have advantages such as simple one-step preparation, high stability, and reproducibility [2,6,7]. Phenazines have been widely used for the development of sensors and biosensors in recent years due to these properties [3,8].

Poly(neutral red) (PNR) has been synthesised by electrochemical polymerisation and extensively used as mediator on carbon film electrodes for the construction of various biosensor assemblies, for example for the detection of glucose, pyruvate, and alcohol [9–11]. Nile blue (NB), another well-known electroactive phenoxazine dye (Scheme 1), can be easily dissolved in aqueous solutions and be immobilised on the surface of solid electrodes by adsorption or electropolymerisation [12–16]. It has been used as a redox mediator to modify solid electrodes especially for the electrocatalytic oxidation of the nicotinamide coenzymes NADH and NADPH [17–19].

Electrochemical impedance spectroscopy (EIS) is one of the more useful methods to characterise these polymer films [20–22]. It gives valuable information concerning the phenomena involved in the overall redox processes as well as the bulk and interfacial characteristics of the polyphenazine films. Impedance studies have been performed because of their experimental simplicity, sensitivity to changes in structure of the interfacial region and to electrode modification.

The aim of this work is to investigate the formation of poly(Nile blue) (PNB) films on glassy carbon substrates by potential cycling electropolymerisation, with optimisation of the polymerisation conditions. Electrochemical characterisation of the polymer film and cation and anion effects was carried out by cyclic voltammetry (CV) and EIS in electrolyte buffer solutions with different pH values. The results are compared with those of other phenazine dyes, such as PNR [10,11,23,24].

2. Experimental

2.1. Materials

Nile blue A as a sulphate salt ($2C_{20}H_{20}N_3O{\cdot}SO_4$) was purchased from Fluka (Switzerland) and used without further purification. Phosphate buffer solutions of concentration 0.1 M with different pH values from 5.3 to 8.0 were prepared from sodium di-hydrogenphosphate and di-sodium hydrogenphosphate (Riedel-de-Haën, Germany), and then making final adjustments to the pH with 5 M NaOH (Riedel-de Haën, Germany) solution.

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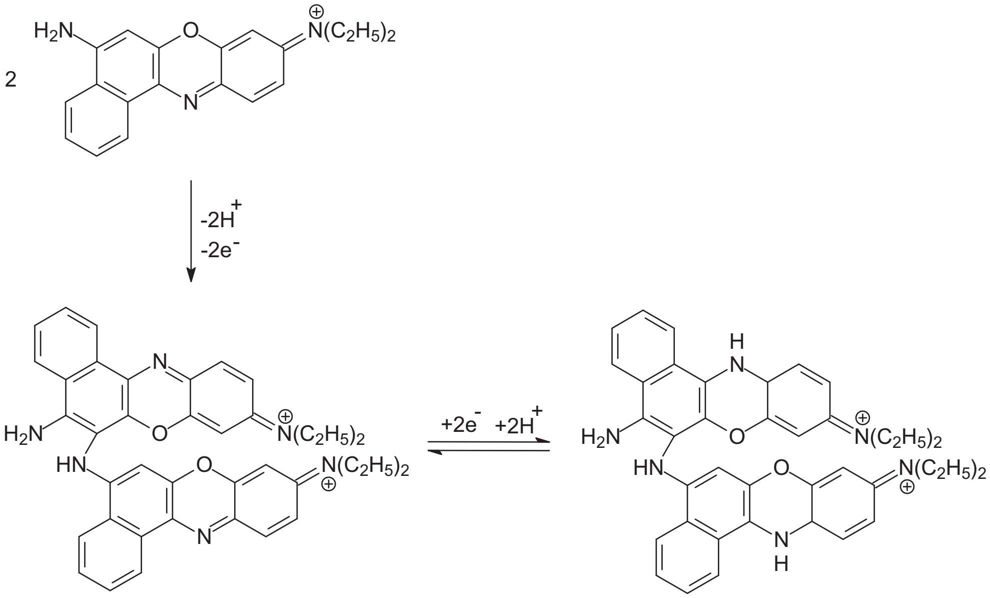


Scheme 1. Possible mechanism of NB dimer formation.

The electrolytes used for the characterisation of PNB modified electrodes were 0.1 M KCl (Aldrich, Germany), 0.1 M NaCl (Riedel-de Haën, Germany), 0.1 M LiCl (Panreac, Spain), 0.033 M Na_2SO_4 (Merck, Germany), 0.033 M K_2SO_4 (Riedel-de Haën, Germany), and 0.1 M KNO_3 (Riedel-de Haën, Germany).

Millipore Milli-Q nanopure water (resistivity $\geqslant 18$ MΩ cm), and analytical grade reagents were used for the preparation of all solutions. Experiments were performed at room temperature, 25 ± 1 °C.

2.2. Instrumentation

A three-electrode electrochemical cell was used for all experiments. It contained a glassy carbon working electrode, without or with modification by PNB, a platinum foil as counter electrode, and a saturated calomel electrode (SCE) as reference.

All CV measurements were performed using a computer-controlled µ-Autolab Type II potentiostat/galvanostat with GPES 4.9 software (Metrohm-Autolab, The Netherlands).

Electrochemical impedance measurements were carried out with a PC-controlled Solartron 1250 Frequency Response Analyser coupled to Solartron 1286 Electrochemical Interface using ZPlot 2.4 software (Solartron Analytical, UK). A sinusoidal voltage perturbation of root-mean-square amplitude 10 mV was applied in the frequency range between 65 kHz and 0.1 Hz with 10 frequency steps per decade, integration time 60 s. Fitting to electrical equivalent circuits was performed with ZView 3.2 software (Scribner, USA).

The pH measurements were carried out with a CRISON 2001 micro-pH meter at room temperature.

2.3. Preparation of poly(Nile blue) modified electrodes

The working electrode was a glassy carbon disc electrode with a diameter of 5.5 mm. The electrode was cleaned by polishing with diamond spray (Kemet International Ltd., UK) and then sonicated in Milli-Q nanopure water and then rinsed with nanopure water. Before use, electrochemical pre-treatment of the electrode was done by cycling the potential in the range -0.6 V to +1.2 V vs. SCE at a scan rate of 50 mV s^{-1} in 0.1 M potassium phosphate buffer solution at pH 5.3, in order to decrease the background currents and to increase the potential window.

NB was polymerised electrochemically by cycling in the potential range between -0.6 and +1.2 V vs. SCE at a scan rate of 50 mV s^{-1} for 17 cycles in 0.1 M sodium phosphate buffer at pH 5.3, 6.0 or 7.0, containing 0.1–1.0 mM NB monomer.

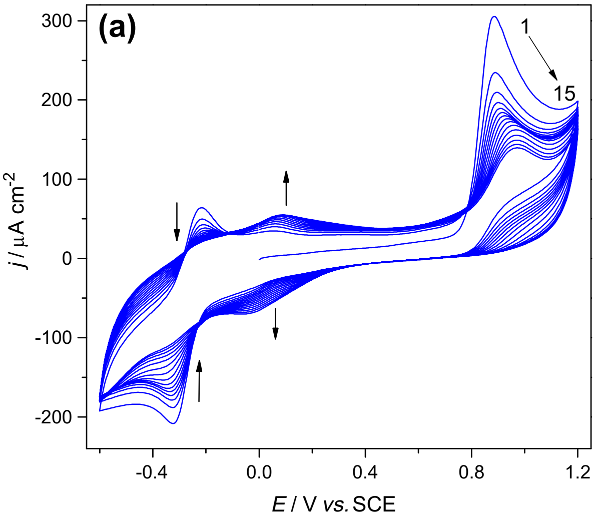
3. Results and discussion

3.1. Electrochemical polymerisation of Nile blue at the glassy carbon electrode

Poly(Nile blue) modified electrodes were prepared by potential cycling electropolymerisation on glassy carbon electrodes as described in Section 2. Different concentrations of NB monomer were used in 0.1 M phosphate buffer at different pHs (5.3, 6.0, and 7.0) to find the best polymerisation conditions.

Fig. 1 shows cyclic voltammograms recorded during the potential cycling. The irreversible oxidation peak at +0.87 V is due to monomer radical formation. The unpaired electron in the radical cation is delocalized. Thus, the attacking site of NB molecules is probably either the amine group or the neighbouring ortho carbon atom in the aromatic ring – in either case a C–N bond is formed. Radical dimerisation via the carbon–nitrogen coupling route leads to radical cations of the dimers which can react with the other monomers to eventually form PNB [25]. The possible electrodimerisation path of NB is shown in Scheme 1.

Two redox couples were observed in the cyclic voltammograms in the potential range between -0.6 V and +1.2 V, Fig. 1. The first redox couple at more negative potentials (centred at around -0.3 V) corresponds to oxidation/reduction of the monomer. With continuing cycling, the oxidation peak at -0.22 V decreased in height and the peak potential shifted in the positive direction; the related reduction peak at -0.34 V also decreased and moved to more negative potentials. The second redox couple at ~0.0 V, corresponding to the oxidation/reduction of NB polymer, increased in height with the number of cycles, reflecting the growth of the PNB film. Similar features for the electrochemical polymerisation of NB were also reported in [13]. With continuous cycling, PNB forms a film on the electrode surface and, due to the decrease in monomer concentration close to the electrode substrate surface, the NB peak at ~ -0.3 V diminishes, completely disappearing by the 17th cycle.



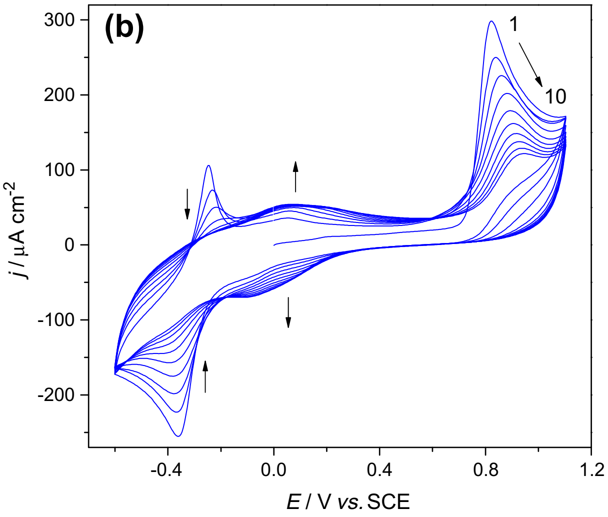


Fig. 1. Cyclic voltammograms of 0.5 mM NB in 0.1 M phosphate buffer at (a) pH 5.3 and (b) pH 6.0. Scan rate: 50 mV s^{-1}.

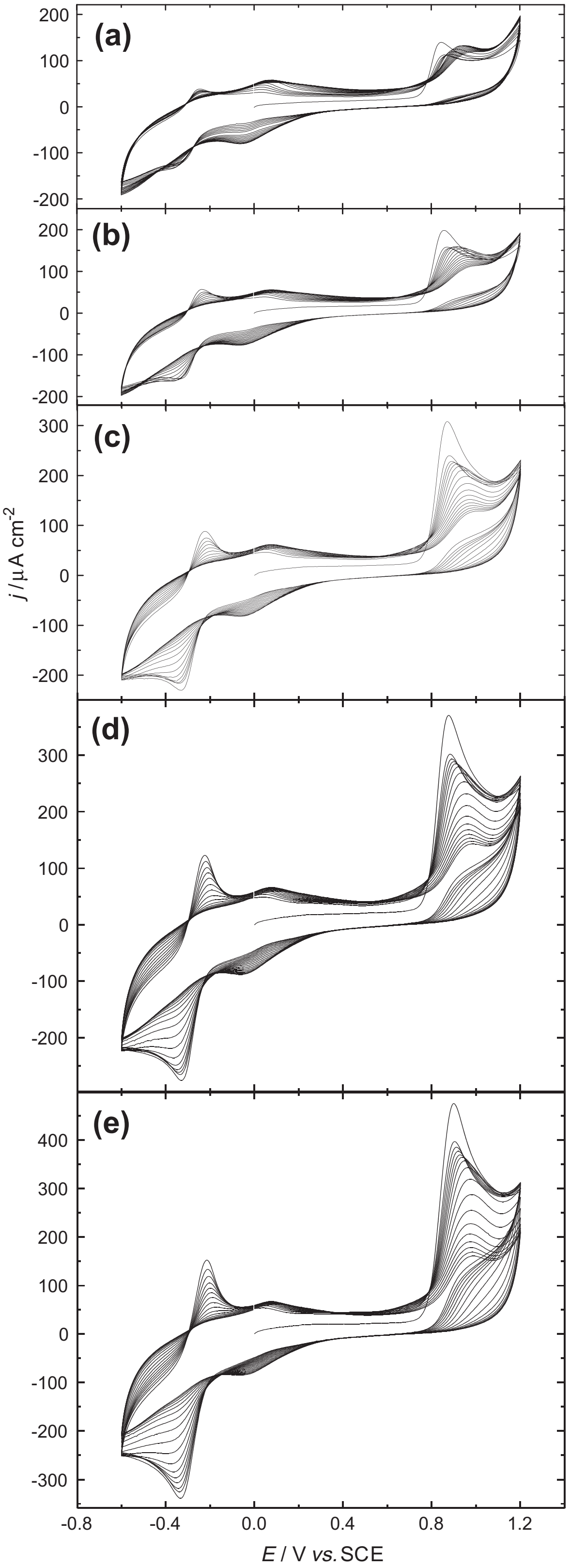


Fig. 2. Cyclic voltammograms of (a) 0.1 mM, (b) 0.2 mM, (c) 0.5 mM, (d) 0.7 mM, and (e) 1 mM NB in 0.1 M phosphate buffer at pH 5.3. Scan rate: 50 mV s^{-1}.

Taking into account the cyclic voltammograms recorded during NB electropolymerisation at different pH, the polymerisation conditions were optimised. An increase in NB concentration at pH 5.3 clearly shows an increase in the monomer oxidation and reduction peaks (∼−0.3 V) as well as in radical formation at +0.9 V, Fig. 2. While the monomer peaks decrease in size with the number of cycles, at the same time the polymer redox couple appears at 0.0 and 0.1 V and increases, indicating polymerisation of NB. The electropolymerisation rate depends slightly on monomer concentration.

The polymer oxidation peak ceases to increase after 10 cycles at pH 5.3 and after 6 cycles at pH 6.0 but the reduction peak continues increasing up to 15 and 12 cycles, respectively, Fig. 3. This reveals that polymer nucleation (first few cycles), i.e. formation of dimers and trimers, is followed by oligomerisation and then further polymer growth. Moreover, the fact that the polymer oxidation peak potential shifts towards more positive potentials, indicates changes in polymer structure (Fig. 2).

The increase in height of the PNB reduction peaks was greatest in 0.1 M phosphate buffer at pH 5.3 containing 0.5 mM NB monomer. For NB polymerisation in 0.1 M phosphate buffer at pH 6.0 with 0.5 mM NB, the peak currents of the redox couple of NB at ∼−0.3 V were larger but decreased faster with the number of cycles than those at pH 5.3 (Fig. 1b). At pH 7.0, polymerisation occurred in a different way: the polymer peaks at ∼0.0 V did not increase linearly with the number of cycles and disappeared after the third scan. The reason might be due to the low solubility of NB monomer in

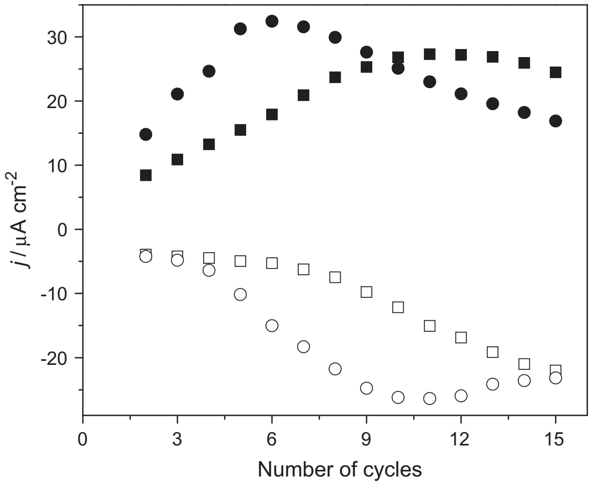


Fig. 3. Dependence of oxidation/reduction peak growth of NB polymer at ~0 V vs. on the number of cycles in 0.1 M phosphate buffer at (■ and □) pH 5.3 and (● and □) pH 6.0. Filled symbols refer to oxidation, empty symbols to reduction peaks. NB concentration 0.5 mM.

neutral solutions because of its amino group, which is not protonated at this pH, and benzene ring [12].

Electropolymerisation using various NB concentrations, between 0.1 mM and 1.0 mM, were also tested but with less good results. The fastest polymer formation was found with 0.5 mM and 0.7 mM of NB and therefore 0.5 mM of NB was chosen and used for further investigations. It may be that higher concentrations did not allow long-chain polymers to fall and the short-chain polymers are less adherent to the electrode.

In order to quantify the coverage of GC electrode with the PNB film, the charge corresponding to polymer oxidation (Q) and the surface concentration (Γ) of PNB on the GC electrode were calculated from CVs at a scan rate of 50 mV s^{-1}, assuming that two electrons per monomer are involved in the oxidation process, using the following equation [26]:

$$\Gamma = Q/(nFA) \tag{1}$$

where n is the number of electrons, A is the electrode area (cm^2), and F is the Faraday constant. The results are listed in Table 1, where it can be seen that the surface concentration and the PNB film charge values are higher when the pH of the phosphate buffer solution used during polymerisation is higher, meaning that the thickest PNB film was obtained at pH 7.0. For comparison, PNR film on GC electrodes polymerised in 0.025 M potassium phosphate buffer at pH 5.5 + 0.1 M KNO$_3$, give values of Q and surface concentration in the range of 1.3–2.0 µC cm^{-2}, and 2–3 nmol cm^{-2}, respectively [24]. Thus, it appears that the PNB film is thicker than the PNR film on the same electrode substrate.

Similar polymerisation conditions have also been used for other phenazine dyes, such as PNR in weakly acidic potassium phosphate buffer (at pH 5.5) containing KNO$_3$ with 1 mM NR monomer [10,11,23,24]. It is known that NO$_3^-$ catalyses the polymerisation of some phenazine dyes such as NR and methylene blue [1,3]. However, in this work addition of NO$_3^-$ led to a decrease in the solubility of NB monomer in the buffer solution which negatively affected the rate of polymer film growth.

Table 1
Charge corresponding to polymer oxidation, Q, and the surface concentration, Γ, of PNB in 0.1 M phosphate buffer (PB) at pH 5.3, from cyclic voltammograms at a scan rate of 50 mV s^{-1}.

Polymer[a]	Buffer used for polymerisation	Q/µC cm^{-2}	Γ/nmol cm^{-2}
PNB$_1$	0.1 M PB, pH 5.3	20	75
PNB$_2$	0.1 M PB, pH 6.0	29	110
PNB$_3$	0.1 M PB, pH 7.0	33	126

[a] The only difference between PNB$_1$, PNB$_2$, and PNB$_3$ is the pH of electrolyte used in the electropolymerisation.

3.2. Electrochemical characterisation of PNB films

Electrochemical characterisation first involved investigation of the influence of pH. This was done with polymer films PNB$_1$ (PNB film deposited from solution at pH 5.3) and PNB$_2$ (PNB film deposited from solution at pH 6.0). Cyclic voltammograms in 0.1 M phosphate buffer at different pHs from 5.3 to 8.0 at different scan rates, from 10 to 200 mV s^{-1}, were recorded. The best peak shapes and the slope of the peak current dependence of scan rate were obtained with PNB$_2$ at pH 5.3. Thus, the results obtained with PNB$_2$ are presented in this section.

Fig. 4 shows cyclic voltammograms recorded at a PNB$_2$-modified glassy carbon electrode at various potential scan rates. Two redox couples were observed in the CV of the PNB film in phosphate buffer solution. The redox couple (I) at more negative potentials is ascribed to the NB monomer-type conjugation structure in PNB and the other couple and (II) at positive potentials to the redox reaction of PNB [13]. All results discussed below were obtained from the redox couple at negative potentials, since redox couple (II) was not so well-defined.

Fig. 4 shows that both oxidation and reduction peak currents increase with increasing scan rate at the same time as the oxidation peak potentials shift to more positive and reduction peak to more negative values, increasing peak separation. The peak current densities (j) are linearly proportional to potential scan rate (v), indicative of an adsorbed species-controlled electrode process (inset in Fig. 4). The slope corresponding to the oxidation process is greater than that of the reduction process, suggesting that expulsion of the positive counter ion is faster than its diffusion into the polymer film [27,28], to be discussed further in Section 3.3. However, in the case of PNR modified electrodes in 0.1 M sodium phosphate buffer at pH 5.5, the peak current is proportional to the square root of potential scan rate, a diffusion-controlled process [10]. This reflects the fact that PNR and PNB have different types of polymer structure.

To evaluate the reversibility of the process, the peak-to-peak separation and the ratio of the oxidation to reduction peak currents were calculated. In Fig. 4, the peak-to-peak separation was found

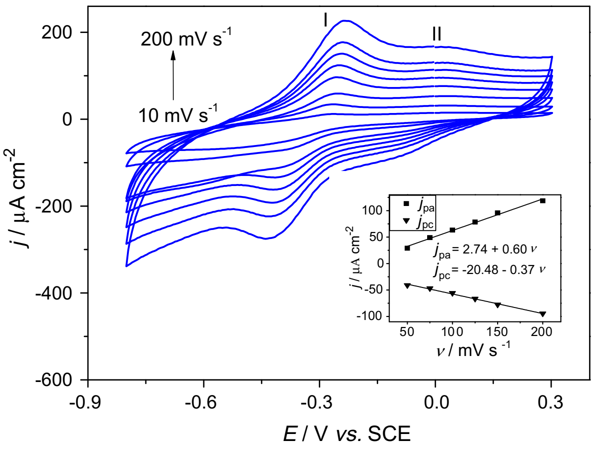


Fig. 4. Cyclic voltammograms of PNB$_2$ in 0.1 M phosphate buffer at pH 5.3. Scan rates: 10, 25, 50, 75, 100, 125, 150, 200 mV s^{-1}. Inset: plots of peak current density (j) vs. scan rates (v) for PNB$_2$, calculated from the cyclic voltammograms.

to be 131 mV at a scan rate of 50 mV s^{-1}. The value of I_{pa}/I_{pc} at 50 mV s^{-1} was calculated as 0.80, showing a quasi-reversible redox process.

A linear dependence of peak potential and peak current on pH was obtained for the PNB-modified electrode; see Fig. 5, where the data for PNB_2 are presented. The slopes of peak current densities vs. pH were −6.7 μA cm^{-2} pH^{-1} for oxidation and −16.1 μA cm^{-2} pH^{-1} for the reduction process. The plot of the peak potentials, E_p, vs. pH, was linear with a slope of −54 and −65 mV pH^{-1} for the oxidation and reduction processes, respectively, close to the theoretical value of −59 mV pH^{-1} for a process involving equal numbers of protons and electrons [27]. According to the structure of NB (Scheme 1), the number of electrons and protons transferred in the electropolymerisation is two, in agreement with the literature [12–14]. The values of the midpoint potentials, i.e. the average of the anodic and cathodic peak potentials ($E_m = (E_{pa} + E_{pc})/2$) [28], were −332 ± 9 mV for PNB_1, −323 ± 7 mV for PNB_2, and −352 ± 4 mV for PNB_3 vs. SCE at a scan rate of 50 mV s^{-1} in 0.1 M phosphate buffer at pH 5.3. These small variations can be attributed to differences in the polymer structure and morphology when prepared under different conditions.

3.3. The influence of the cations and anions of the supporting electrolyte on the electrochemical behaviour of PNB

Cyclic voltammetry experiments were undertaken to investigate whether there is an influence of different cations on the electrochemical properties of PNB-modified GC electrodes. The electrolyte used was 0.1 M phosphate buffer at pH 5.3 to which one of 0.1 M of NaCl, KCl, LiCl or 0.033 M of Na_2SO_4 or K_2SO_4 was added, in order to keep the same ionic strength of the electrolyte solution. In all cases, the electrochemical redox process was found to be surface-confined from linear plots of peak current density vs. scan rate obtained from the cyclic voltammograms in the range 10–150 mV s^{-1}. Above 150 mV s^{-1}, the peaks were misshaped and it was difficult to analyze them.

Although there is a mixture of cations and anions in these solutions, owing to the presence of the buffer, differences in behaviour can indicate the influence of changing the species inserted or expelled from the polymer film. Analysis of the results in the different buffer electrolyte solutions tested is given in Table 2. Reduction peak currents are generally higher than oxidation currents, as always found for these types of polymer. Comparison should be made within the oxidation or reduction current values and shows clearly that those in the presence of lithium cation are smaller. Hydrated electrolyte cations can migrate from the solution into the polymer network to compensate the more negative charge in the polymer on its reduction (the positive charge can be already compensated for by inclusion of anions in the matrix), thus behaving as counter ions, and the unhydrated cations are expected to be expelled on re-oxidation. For the electrolyte with LiCl, diffusion through the polymer matrix led to a smaller current and thence charge passed during the redox process because of the larger hydrated cation radius of Li^+, as observed for PNR [28].

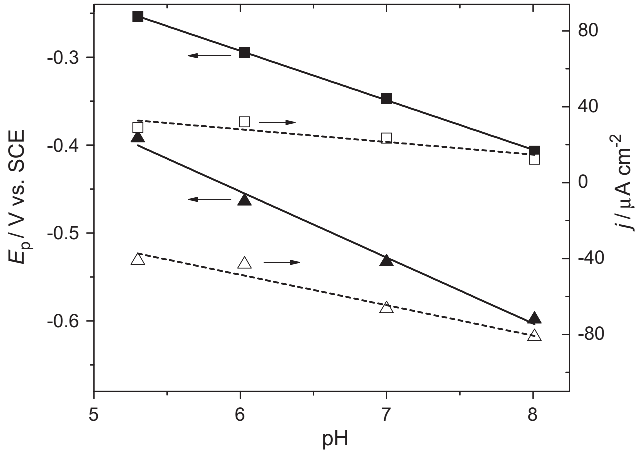


Fig. 5. Plot of peak potential, E_p, and peak current density, j, of PNB_2 vs. pH values of 0.1 M phosphate buffer. Squares indicate oxidation and triangles reduction; filled symbols refer to j and unfilled ones to E_p.

Table 2

Peak potentials and currents for PNB_2-modified electrode taken from CV in 0.1 M PB at pH 5.3 including different anions and cations. Scan rate: 25 mV s^{-1}.

Electrolyte	$E_{p,ox}$/V vs. SCE	j_{ox}/μA cm^{-2}	$E_{p,red}$/V vs. SCE	j_{red}/μA cm^{-2}
0.1 M KCl	−0.266	24.1	−0.390	−41.6
0.1 M NaCl	−0.264	23.3	−0.382	−34.7
0.1 M LiCl	−0.264	17.1	−0.387	−33.1
0.033 M K_2SO_4	−0.264	27.9	−0.386	−42.2
0.033 M Na_2SO_4	−0.261	26.1	−0.388	−40.3

Regarding the anions, sulphate and chloride anions compete with phosphate anions from buffer solution. Moreover, NB salt by itself already has SO_4^{2-} as a counter ion. Although phosphate ion was present in all cases the influence of other electrolyte anions was observed from CVs. The peak currents and the dependence of the peak current on the scan rate were higher in electrolyte solution containing SO_4^{2-} than that with Cl^- (Table 2), suggesting better accommodation of SO_4^{2-} as a counter anion within the polymer film, although its size is greater than that of Cl^-.

3.4. Characterisation of PNB by EIS

GC electrodes modified with PNB were characterised by EIS in 0.1 M phosphate buffer at pH 5.3 and 6.0 at four different applied potentials. Two values were chosen close to the oxidation and reduction peaks found from cyclic voltammetry, at −0.26 and −0.39 V respectively. At the third potential used of 0.0 V there was a small oxidation wave, attributed to a redox process of PNB; the fourth value of +0.24 V was more positive than all redox peaks. The spectra for PNB_1, PNB_2, and PNB_3-modified electrodes were recorded in 0.1 M phosphate buffer at pH 5.3 and 6.0 and it was found that the spectra for all modified electrodes were very similar. Therefore, the complex plane spectra shown in Fig. 6 are for PNB_2-modified electrodes at pH 5.3, since this electrode gave the best results in cyclic voltammetric profiles (see Section 3.2).

In Fig. 6, it can be seen that the impedance values at more positive potentials (+0.24 and 0.00 V) were almost two times greater than those at negative potentials, highest at +0.24 V; at −0.26 and −0.39 V, the values are very similar, as are the spectral profiles.

The spectra in Fig. 6 were analysed by fitting to an electrical equivalent circuit model, Fig. 7. The model includes a cell resistance (R_Ω) in series with a parallel combination of a constant phase element (CPE) and charge transfer resistance (R_{ct}). The CPE is modelled as a non-ideal capacitor and is given by $CPE = -1/(i\omega C)^\alpha$, where C is the capacitance, ω is the frequency in rad s^{-1}, and the exponent α reflects the surface non-uniformity and porosity of the polymer film, where $\alpha = 1$ corresponds to a perfectly uniform and smooth surface [27]. The cell resistance is ∼24 Ω cm^2 at pH 5.3 and ∼20 Ω cm^2 at pH 6.0. The calculated values of the other parameters for PNB_2 in 0.1 M phosphate buffer at pH 5.3 and 6.0 are shown in Table 3. R_{ct} decreased with more negative potential, indicating easier charge transfer because of the electrochemical process of PNB occurring. The double layer capacitance (C_{dl}) increased, whereas

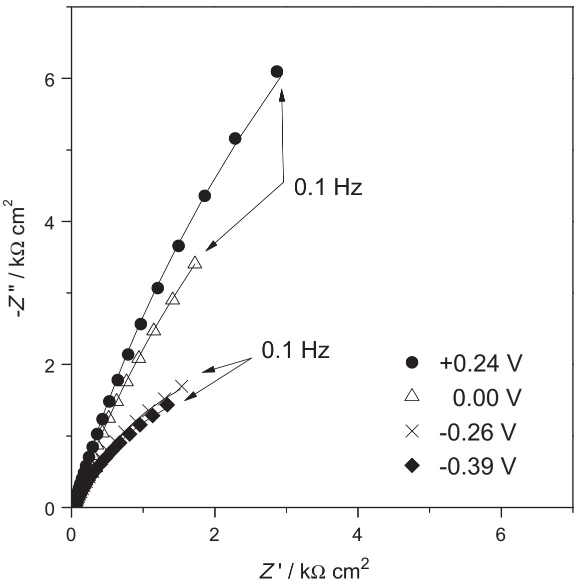


Fig. 6. Complex plane electrochemical impedance spectra for PNB$_2$-modified GC electrode in 0.1 M phosphate buffer at pH 5.3 at different applied potentials.

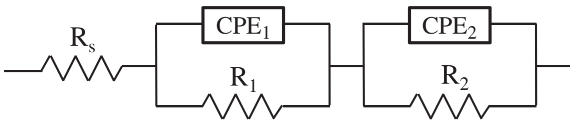


Fig. 7. Equivalent circuit used for fitting of electrochemical impedance spectra of Fig. 6. R_s solution resistance; CPE$_1$ double layer capacitance (C_{dl}); R_1 charge transfer resistance (R_{ct}); CPE$_2$ PNB film capacitance (C_f); R_2 PNB film resistance (R_f).

Table 3
Data obtained from analysis of the impedance spectra for PNB$_2$-modified electrode in 0.1 M potassium phosphate buffer at different pHs from equivalent circuit fitting.

E/V vs. SCE	C_{dl}/μF cm^{-2} s$^{\alpha-1}$	α_1	R_{ct}/kΩ cm^2
pH 5.3			
+0.24	199	0.823	37.9
0.00	350	0.789	27.2
−0.26	499	0.744	6.27
−0.39	568	0.731	5.35
pH 6.0			
+0.24	190	0.818	49.3
0.00	299	0.785	40.9
−0.30	491	0.743	5.91
−0.46	1038	0.733	0.51

the potential decreased showing a higher conductivity when the redox process of PNB occurred. The exponent α decreased from 0.82 to 0.73 with more negative potential, indicating a less smooth electrode surface as counter ions are incorporated.

4. Conclusions

Electropolymerisation of Nile blue A has been achieved on GC electrodes by potential cycling in 0.1 M phosphate buffer at different values of pH: 5.3, 6.0, and 7.0. The electrochemical properties of the resulting polymer have been investigated by cyclic voltammetry and electrochemical impedance spectroscopy. According to the cyclic voltammetry results, both oxidation and reduction peak currents show an adsorption-controlled process. Although polymerisation was the best in pH 5.3 solution, the better electrochemical properties such as peak shape and the dependence of peak currents on the applied potential scan rates were obtained for PNB film polymerised in pH 6.0 electrolyte solution.

The effect of different cations and anions on electrochemical properties of PNB modified electrode was probed in 0.1 M phosphate buffer electrolyte at pH 5.3 to which one of 0.1 M of NaCl, KCl, LiCl or 0.033 M of Na$_2$SO$_4$, or K$_2$SO$_4$ was added. The various cations and anions did not change the oxidation or reduction mechanism and the electrochemical process was found to be surface-controlled in all cases. Diffusion through to the polymer matrix was easiest with K$^+$ cation, which has the smallest hydrated cation radius.

EIS data show that R_{ct} decreased with more negative potential, indicating easier charge transfer because of the electrochemical process of PNB occurring. The exponent α decreased from going to more negative potential, indicating a less smooth electrode surface as counter ions are incorporated.

The results obtained in this work are important for the appropriate choice of media for application of poly(Nile blue) films as redox mediators and potential electrocatalysts in electrochemical sensors and biosensors, to be addressed in future work.

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