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Effect of electropolymerisation conditions on the permeability of polyphenol films deposited on a vitreous carbon electrode

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ABSTRACT

Polymeric films were prepared from alkaline (NaOH) phenol aqueous solutions on a vitreous carbon (VC) electrode by potentiostatic or galvanostatic electro-oxidation. Permeation through such films was studied by rotating-disk electrode using the ferricyanide redox couple, and by cyclic voltammetry using phenate ions. The influence of the electropolymerisation controllable parameters such as NaOH and phenol concentrations, potential or current applied, electrosynthesis time, temperature and hydrodynamic conditions (electrode rotation + solution magnetic stirring) on the permeability of these polymeric films was examined. Conditions for the removal of phenol by electropolymerisation are discussed on the basis of the permeability of polyphenol films obtained by electrosynthesis. Permeable films were formed for a concentration of free hydroxyl anion larger of 0.1 M. An increase of the temperature to 85 °C favours the formation of highly permeable films, thus avoiding electrode fouling.

1. Introduction

In recent years there has been an increasing interest in the development of electrochemical polymerisation for the removal of phenols from aqueous solutions. The main advantage in proceeding by electropolymerisation is the low consumption of the electric charge compared with electrochemical mineralisation [1]. In this way, the removal of phenols from aqueous solutions by electrochemical polymerisation was conducted on granular activated carbon [2], carbon fibre [3], Ta/β–PbO$_2$ [1,4] and polyaniline/glassy carbon electrodes [5]. Nevertheless, electropolymerisation of phenolic compounds leads to the deposition of a non-conductive film that blocks the electrode activity and prevents further removal of phenol [6–11]. Many works have shown that diffusion of electroactive species through polymeric films depends on the electropolymerisation conditions such as the monomer concentration [12], the nature of the solvent used [13], the pH and background electrolyte [14], the degree of cross-linking of the polymer chains [15], the nature of the electrode [16], the electrodeposition modes (cyclic voltammetry and potentiostatic or galvanostatic electrolysis) [12,17], the applied potential [14,18] or current [19] and the electropolymerisation time (film thickness) [12].

The aim of our previous works [1,4,20,21] was to find the operating conditions that allow electropolymerisation to proceed as long as a current is supplied to the electrode; thus, the polymeric film inevitably deposited on the electrode surface must have the highest permeability for phenol molecules. The main operating conditions were described in Ref. [1]. The electrochemical response of phenate ion on bare VC and polyphenol film-coated VC was studied in 1 M NaOH aqueous solutions [20]. However using such high concentration of NaOH in the precursor phenol solution penalizes any eventual treatment based on the removal of phenols by electropolymerisation. The aim of this work was to measure by using a rotating-disk electrode the permeability for ferricyanide anion of polyphenol films deposited in alkaline medium on VC under various electropolymerisation conditions. In particular we are looking for the minimal concentration of NaOH which allows the continuous forming of a film of sufficient permeability not to block the electropolymerisation. The relative permeability for phenate anion was also evaluated by monitoring changes in cyclic voltammograms of phenol solution recorded on polyphenol film-coated VC as compared to bare VC. In order to optimise the concentration of NaOH in the precursor phenol solution particular attention was paid to its effect on the permeability of the polyphenol film.

2. Experimental

2.1. General

Cyclic and rotating-disk voltammetry and chronoamperometry measurements were performed using a computer controlled Eco Chemie Autolab Model 30 (Utrecht, The Netherlands). The conventional three-electrode cell system consisted of bare VC or

polyphenol film-covered VC (disk of 3 mm diameter, Metrohm) working electrode, a platinum spiral counter electrode and an Hg/Hg$_2$Cl$_2$/Cl$^-$ (saturated) reference electrode connected to the electrolytic solution by a long Luggin capillary placed near the working electrode and filled with 0.1 M Na$_2$SO$_4$. All the potentials are reported versus the above specified reference electrode. Before each experiment, the working electrode was polished to a mirror with 1 μm alumina slurries on polishing sheet (3 M 262X IMPERIAL Lapping Film) and subsequently washed with distilled water.

2.2. Preparation of polyphenol film-coated vitreous carbon electrode

Polyphenol films were prepared by oxidative electropolymerisation performed either galvanostatically or potentiostatically onto the disk of VC electrode surface from phenol aqueous solutions containing 0.1 M Na$_2$SO$_4$ and NaOH at various concentrations. Electropolymerisation was performed on a fixed electrode and without magnetic stirring unless otherwise instructed. The polyphenol film-coated electrodes were copiously rinsed with distilled water and used immediately in permeation experiments.

2.3. Polyphenol film permeability measurement

The permeability $P_{ferr.}^{film}$ of the polyphenol film for ferricyanide anion was measured with a rotating-disk electrode (RDE) in pH 7 phosphate (0.1 M) buffer solution containing 0.01 M potassium ferricyanide at 25 °C. The limiting current I_L of the electrochemical reduction of ferricyanide anion on the polyphenol film-covered RDE can be described by the following equation [22]:

$$I_L^{-1} = (nFAC_sP_{ferr.}^{film})^{-1} + (0.62nFAC_sD_s^{2/3}\nu^{-1/6})^{-1}\omega^{-1/2} \tag{1}$$

where A is the electrode area (cm^2), C_s is the concentration of ferricyanide anion in the solution (mol cm^{-3}), D_s is the ferricyanide diffusion coefficient in the solution (cm^2 s^{-1}), ν is the kinematic viscosity of the solution (cm^2 s^{-1}), ω is the angular rotation rate of the electrode rotation (rad s^{-1}) and n (=1) and F have their usual meanings.

The permeability of the polyphenol film for ferricyanide anion $P_{ferr.}^{film}$ was obtained from the intercepts of I_L^{-1} plots versus $\omega^{-1/2}$ at $\omega^{-1/2} = 0$. The solution permeability for ferricyanide $P_{ferr.}^{sol.}$ was obtained from the slopes of plots I_d versus $\omega^{1/2}$ where I_d is the limiting current at the bare VC electrode as described by Levich [22]:

$$I_d = 0.62nFAC_sD_s^{2/3}\nu^{-1/6}\omega^{1/2} = nFAC_sP_{ferr.}^{sol.} \tag{2}$$

The relative permeability of the polyphenol film for phenate anion $P_{Ph.}^{film}$ was assessed by subjecting the polyphenol film-coated electrode to cycling in the same solution used for the film preparation. The relative permeability for phenate anion $P_{Ph.}^{film}$, expressed as a percentage, is defined as the ratio of the oxidation peak current intensity during the 1st scan at the polyphenol film-coated electrode I_{film} over that at the bare electrode I_{bare} [23,24]:

$$P_{Ph.}^{film} = \frac{I_{film}}{I_{bare}} \times 100 \tag{3}$$

In practice, the permeability of the film of polyphenol for ferricyanide anions was calculated from voltammograms recorded at 25 °C on bare glassy carbon disk (freshly polished) and on this disk covered with the film even when the film was prepared at 85 °C. However, the permeability of the film of polyphenol for phenate anions was calculated from voltammograms recorded on bare VC and on polyphenol film-coated VC in the same solution and at the same temperature used for the preparation of the film.
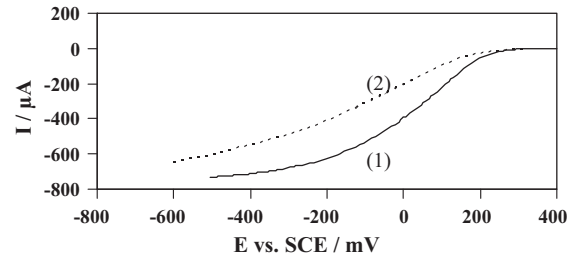

Fig. 1. Voltammograms on a VC rotated disk of 0.01 M potassium ferricyanide in pH 7 sodium phosphate (0.1 M) buffer solution at 25 °C. Scan rate: 10 mV s^{-1} and ω = 5000 rpm. (1) Bare VC; (2) polyphenol film electrosynthesized on VC rotating-disk electrode (ω = 1000 rpm) by anodic polarisation at 1800 mV during 60 min in a magnetically stirred 0.01 M phenol solution containing 0.1 M NaOH and 0.1 M Na$_2$SO$_4$ at 85 °C.

3. Results and discussion

3.1. General behaviour of the bare vitreous carbon and the polyphenol film

Fig. 1 shows typical rotating-disk voltammograms for the reduction of 0.01 M potassium ferricyanide solution at bare and polyphenol film-coated VC electrodes. The film did not affect the starting ferricyanide reduction potential but the current was strongly attenuated.

3.2. Polyphenol films prepared by potentiostatic oxidation

Polyphenol films were prepared by potentiostatic oxidation in order to highlight the influence on their permeability of oxygen evolution when it occurs simultaneously with electropolymerisation.

3.2.1. Influence of temperature

Values of film permeability were determined by plotting I_L^{-1} vs. $\omega^{-0.5}$ and extrapolating to very high rotation rate at $\omega^{-0.5} = 0$, where mass transport is totally film limited. Fig. 2 represents plots of I_L^{-1} vs. $\omega^{-0.5}$ for bare and polymer modified VC electrodes. Table 1 shows
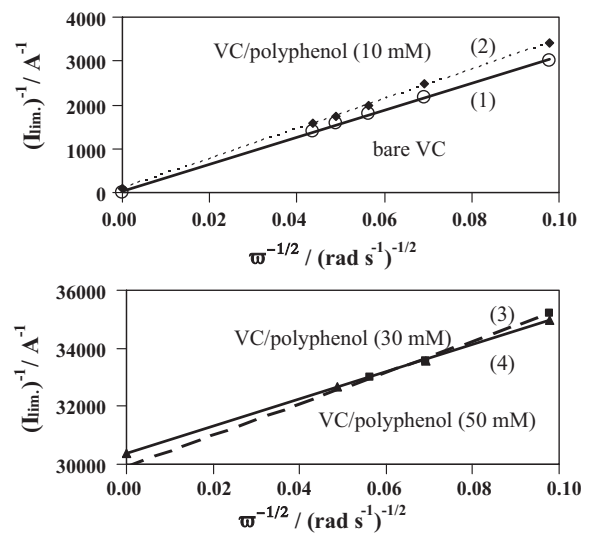

Fig. 2. Reciprocal Levich plots of limiting reduction currents for permeation of ferricyanide anion through films of polyphenol on a VC rotated disk. Scan rate: 10 mV s^{-1}. Polyphenol films were prepared at 85 °C on a rotating-disk electrode (ω = 1000 rpm) by anodic polarisation at 1800 mV during 30 min in a magnetically stirred 0.1 M NaOH and 0.1 M Na$_2$SO$_4$ aqueous solution with phenol concentrations: 0 M curve (1) (bare VC); 0.01 M curve (2); 0.03 M curve (3) and 0.05 M curve (4).

Table 1
Relationships between temperature and the permeability for ferricyanide anion of the polyphenol film $P_{ferr.}^{film}$ electrosynthesized on vitreous carbon electrode during 30 min at various applied potentials E from 0.01 M phenol aqueous solution containing 1 M NaOH and 0.1 M Na_2SO_4.

$T/^\circ C$	25			85		
E vs. SCE/mV	500	900	1200	500	600	700
$P_{ferr.}^{film} \times 10^4$/cm s^{-1}	0	5	221	0	1961	3349

the relationships between the temperature and the permeability of the polyphenol films electrosynthesized on VC during 30 min at various applied potentials from 0.01 M phenol aqueous solution containing 1 M NaOH and 0.1 M Na_2SO_4. Polyphenol films prepared at potentials less than 500 mV were not at all permeable at both 25 and 85 °C. Above 500 mV, the permeability increased substantially at 85 °C while polyphenol films remained almost impermeable until 900 mV at 25 °C.

The raising of permeability with temperature and applied potential (Table 1) may result from an increase in the polyphenol film growth rate; the diameter and density of the pores in the film are expected to strongly increase with the film growth rate. On the contrary, a film grown slowly is more compact and dense with less and narrower pores [15]. In summary, the larger permeability values were obtained at high temperature, which allows the use of lower potentials.

3.2.2. Influence of NaOH concentration

Fig. 3 shows cyclic voltammograms recorded on bare VC electrode at 85 °C in 0.01 M phenol aqueous solution containing 0.1 M Na_2SO_4 and NaOH at different concentrations. Decreasing the concentration of NaOH from 1 to 0.01 M had no effect on the peak potential but noticeably diminished the peak current of phenol oxidation indicating that the electrode passivation was more and more pronounced. Note that for 0.01 M NaOH the response of phenol (practically present as phenate) is expressed as a wave (curve 3).

Table 2 shows the relationships between the permeability for ferricyanide anion and the concentration of NaOH used during the polyphenol film preparation at various applied potentials. For NaOH concentration of 1 M, polyphenol films prepared at potentials below 500 mV are not at all permeable while the ones prepared at potential higher than 600 mV were highly permeable. In these conditions, comparison between values of $P_{ferr.}^{film}$ (Table 2) and $P_{ferr.}^{sol.}$ (Fig. 4) shows that phenol oxidation rate was limited by the low membrane permeability of polyphenol films prepared at potentials lower than 500 mV. On the contrary, the oxidation rate was limited by the solution for films prepared at potentials higher than 600 mV. Table 2 shows that polyphenol films with high permeability to ferricyanide anion were prepared at increasing potentials as the NaOH concentration decreased from 1 to 0.01 M. On the other hand, very low permeability values were observed even at high applied potentials for NaOH concentrations less than 0.1 M. These results are in
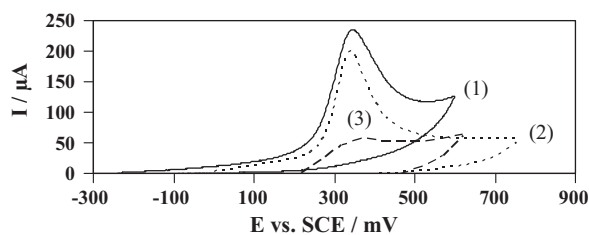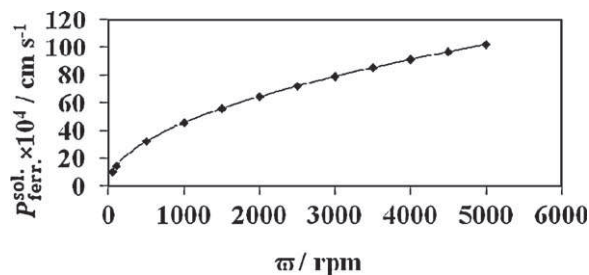

Fig. 4. Variation of the solution permeability for ferricyanide anion as a function of the electrode rotation rate.

agreement with cyclic voltammograms presented in Fig. 3 if we consider that the peak current of phenol oxidation decreased as the permeability of the polyphenol film diminished.

Cyclic voltammograms presented in Fig. 5 show that no phenol oxidation peak was observed for NaOH concentrations less than 0.1 M (curves 1 and 2) indicating that under these conditions the polyphenol films were impermeable to phenate anion. The relative permeability $P_{Ph.}^{film}$ for phenate anion of the polymer film prepared in 0.1 M NaOH was evaluated, according to Eq. (3), from curve 2 in Fig. 3 and curve 3 in Fig. 5. $P_{Ph.}^{film}$ is equal to 184%; this value, higher than 100%, suggests that the film permeability for phenate anion is governed by the preferential partitioning of the probe into the polyphenol film due to stronger interactions (electrostatic, hydrophobic, etc.) in the film than in the solution [24].

Phenol is a weak acid ($pK_a = 9.9$) and at an initial concentration of 0.01 M its reaction with NaOH initially at 1 M, 0.1 M, 0.05 M or 0.01 M leads to equilibrium concentrations of free OH$^-$ respectively equal to 0.99 M, 0.09 M, 0.04 M and 0.00 M. Consequently, at relatively high NaOH initial concentration (1 M and 0.1 M) there is enough free OH$^-$ to instantaneously neutralize the acidity arising at the electrode surface from water discharge occurring in parallel with polyphenol electrosynthesis. On the other hand, with low NaOH concentrations (0.05 and 0.01 M) the free OH$^-$ concentration is too weak to neutralize the totality of protons produced at the surface of the anode when the applied potential increases. Furthermore, the low values of permeability observed with the lower NaOH concentrations (0.05 and 0.01 M), even for experiments performed under magnetic stirring and with the rotating electrode ($\omega = 1000$ rpm), indicate that high acidity remained at the electrode surface (Table 2).

From Table 2, one can conclude that at 0.01 M phenol concentration and relatively high NaOH concentration (0.1 and 1 M), the permeability for ferricyanide anion increases as the potential applied increases. However, at low NaOH concentration (0.01 and 0.05 M), the permeability remains almost nil even at very high applied potential. Therefore, we think that the key factor influencing the permeability of the polyphenol films is the concentration of free OH$^-$ in the solution: $[OH^-]_{sol.} = [NaOH] - [PhOH]$;

Fig. 3. Effect of sodium hydroxide concentration on cyclic voltammograms (1st cycles). recorded on bare VC electrode in 0.01 M phenol aqueous solution containing 0.1 M Na_2SO_4 and NaOH at a concentration of 1 M (curve 1), 0.1 M (curve 2) and 0.01 M (curve 3). Scan rate: 100 mV s^{-1} and $T = 85\,^\circ C$.
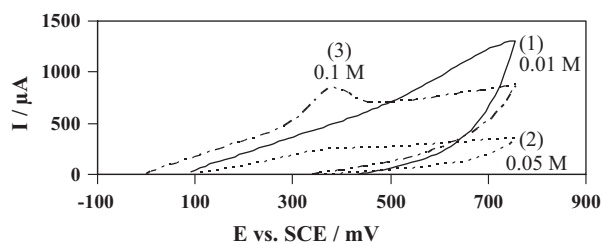

Fig. 5. Measurements of polyphenol film permeability for phenate ion. Scan rate: 100 mV s^{-1}. The polyphenol films were prepared by anodic polarisation at 1800 mV for 30 min at 85 °C in 0.01 M phenol aqueous solutions containing 0.1 M Na_2SO_4 and NaOH at 0.01 M (curve 1), 0.05 M (curve 2) and 0.1 M (curve 3).

Table 2
Relationships between the NaOH concentration in 0.01 M phenol aqueous solution containing 0.1 M Na$_2$SO$_4$ at 85 °C and the permeability for ferricyanide anion $P_{ferr.}^{film}$ of the polyphenol film electrosynthesized during 30 min on a vitreous carbon electrode at different applied potentials.

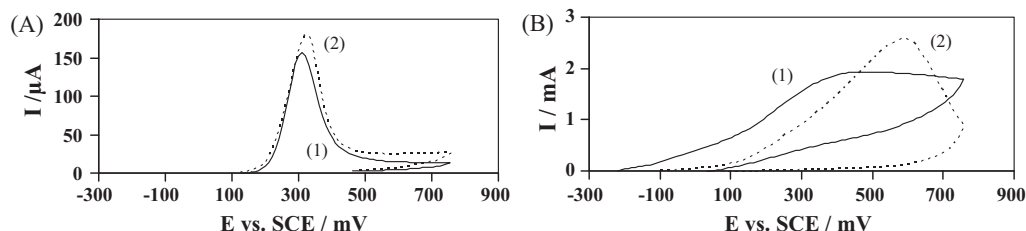| Hydrodynamic conditions	Fixed electrode and without magnetic stirring								Electrode rotation rate of 1000 rpm and under magnetic stirring			
[NaOH]/M	1				0.1				0.05		0.01	
E vs. SCE/mV	400	500	600	700	700	1300	1500	1800	1800	2500	1800	2500
$P_{ferr.}^{film} \times 10^4$/cm s^{-1}	0	0	1961	3349	0	0	9	925	5	5	3	3

Fig. 6. Cyclic voltammograms (first cycles) of 0.05 M phenol solution containing 0.1 M Na$_2$SO$_4$ and NaOH at 0.1 M (curve 1) and 0.15 M (curve 2) at 85 °C on (A) bare VC (B) VC electrodes covered by polyphenol films. Scan rate: 100 mV s^{-1}. Polyphenol films were electrosynthesized at 85 °C on a rotated disk (1000 rpm) VC electrode at an applied potential of 1800 mV in a magnetically stirred 0.05 M phenol solution containing 0.1 M Na$_2$SO$_4$ and NaOH at 0.1 M (curve 1) and 0.15 M (curve 2).

the present results show that the concentration of free OH$^-$ should be preferably higher than 0.1 M to prepare polyphenol films with noteworthy permeability values to ferricyanide anion. Indeed, polyphenol film prepared by anodic polarisation at 1800 mV for 30 min in 0.05 M phenol solution containing 0.1 M NaOH ([OH$^-$]$_{sol.}$ = 0.05 M) and 0.1 M Na$_2$SO$_4$ at 85 °C was not at all permeable for ferricyanide anion whereas the one prepared in the same conditions except that NaOH concentration was 0.15 M ([OH$^-$]$_{sol.}$ = 0.1 M) had a permeability equal to 149 × 10^{-4} cm s^{-1}. Fig. 6(A and B) shows cyclic voltammograms (first cycles) recorded at 85 °C respectively on bare and polyphenol film-coated VC electrodes in 0.05 M phenol solution containing 0.1 M Na$_2$SO$_4$ and 0.1 M NaOH (curve 1) or 0.15 M NaOH (curve 2). Curve 1 in Fig. 6(B) exhibits a weakly defined peak for phenol oxidation indicating a very low permeability of the corresponding polyphenol film to phenate anion. A large, but better defined peak was observed for 0.15 M NaOH (curve 2 in Fig. 6(B)) indicating that under these conditions the oxidation process occurred without inhibition and that the polyphenol film was highly permeable to phenate anion. It should be emphasized that the phenol oxidation peak on polyphenol film-coated electrodes (Fig. 6(B)) is moved toward higher potential values as compared to that on bare VC electrode (Fig. 6(A)).

These results have shown that the removal of phenol by electropolymerisation is possible by applying a higher potential as the NaOH concentration decreases.

3.2.3. Influence of phenol concentration

The effect of phenol concentration on the permeability of polyphenol films prepared at 85 °C on a VC rotating disk (ω = 1000 rpm) was studied by potentiostatic polarisation at 1800 mV during 30 min in magnetically stirred 0.01, 0.03 and 0.05 M phenol aqueous solutions containing 0.1 M NaOH and 0.1 M Na$_2$SO$_4$. Potentiostatic I–t curves (not shown) reveals that the limiting current at the stationary state fell dramatically when phenol concentration increased from 0.01 to 0.03 M. Cyclic voltammograms (not shown) recorded on polyphenol film-coated VC electrodes in the same solutions show that no phenol oxidation peak was observed for 0.03 M and 0.05 M phenol concentrations; the electrochemical response of phenol is expressed as a wave what prevents to calculate the relative permeability for phenate anion (almost impermeable); for 0.01 M phenol concentration, the relative permeability is equal to 143%. These results as well as those

presented in Section 3.2.2 for films respectively prepared in NaOH 0.1 M and 0.15 M may be explained in term of a decrease in the concentration of free OH$^-$ as the concentration of phenol in the solution rises. In particular, the decrease of the ability of the solution to oppose changes in pH when protons are formed on the electrode surface during water discharge can explain the origin of the permeability fall [21] (see Section 3.3.1).

3.2.4. Influence of electrolysis time

Polyphenol films were synthesized on a rotating (ω = 1000 rpm) VC electrode by anodic polarisation at 1800 mV for various electropolymerisation times (30–120 min) in a magnetically stirred 0.01 M phenol solution containing 0.1 M NaOH and 0.1 M Na$_2$SO$_4$ at 85 °C. Results presented in Table 3 reveal that the permeability decreased substantially with increasing the electropolymerisation time; similar results were obtained by Wang et al. [12]. This behaviour is interpreted in term of an increase in polyphenol film thickness with increasing electropolymerisation time; the polyphenol film thickness varies between 10 and 100 nm depending on the electropolymerisation conditions [25]. Fig. 7(A) shows that cyclic voltammograms of the ferricyanide anion are characterized by irreversible waves for 60 and 120 min electrosynthesis times while much more reversible peaks were observed for only 30 min. Values of the relative permeability for phenate anion, calculated from curves (2) and (3) in Fig. 7(B), were equal to 155% and 142% respectively for 60 and 120 min indicating that the polyphenol film permeability for phenate anion is independent of electrosynthesis times. Electropolymerisation can thus occur on pre-existing polymer layer obtained by electrolysis of phenol 0.01 M in alkaline (0.1 M NaOH) solution. This technique could be used as a way to remove phenol since under these conditions electropolymerisation proceeds as long as a current is applied to the electrode.

Table 3
Relationships between the electropolymerisation time in magnetically stirred 0.01 M phenol aqueous solution containing 0.1 M NaOH and 0.1 M Na$_2$SO$_4$ at 85 °C and the permeability $P_{ferr.}^{film}$ of the resulting polyphenol film for ferricyanide anion.

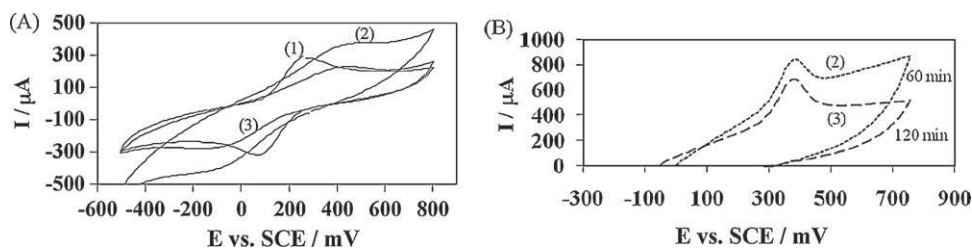| Electrosynthesis time/min	30	60	120
$P_{ferr.}^{film} \times 10^4$/cm s^{-1}	1720	1274	538

Fig. 7. Measurements of polyphenol film permeability for (A) ferricyanide and (B) phenate ions. Scan rate: (A) $500\,mV\,s^{-1}$ and (B) $100\,mV\,s^{-1}$. The polyphenol films were prepared by anodic polarisation on a rotating ($\omega = 1000$ rpm) VC electrode at 1800 mV for various electrolysis times in 0.01 M phenol aqueous solution containing 0.1 M NaOH and 0.1 M Na$_2$SO$_4$ at 85 °C. Electrolysis time: 30 min (curve 1); 60 min (curve 2) and 120 min (curve 3).

3.3. Polyphenol films prepared by galvanostatic oxidation

In practice, a treatment of phenolic compounds based on electropolymerisation should be conducted galvanostatically; as a consequence an increase of the potential is expected during the electropolymerisation. Therefore, the applied current must be determined by taking into account the transport properties of the polymeric film.

3.3.1. Influence of applied current

Fig. 8(A) exhibits galvanostatic E–t curves recorded during polyphenol films electrosynthesis on a rotating ($\omega = 1000$ rpm) VC electrode at various applied currents in a magnetically stirred 0.05 M phenol aqueous solution containing 0.15 M NaOH and 0.1 M Na$_2$SO$_4$ at 85 °C; different electrosynthesis times were chosen in such a way that the same electric charge ($Q = 3600$ mC) was passed in order to prepare polyphenol films having more or less the same thickness. Galvanostatic E–t curves presented in Fig. 8(A) show that the electrode potential remained constant at around 1300 mV during the first stage of the polyphenol film electrosynthesis. The length of this step decreased when applied current increased; then the potential rose rapidly until it reached a plateau at around 2000 mV. Table 4 shows that the permeability of the film for ferricyanide anion drops from $107 \times 10^{-4}\,cm\,s^{-1}$ to $2 \times 10^{-4}\,cm\,s^{-1}$ by increasing from 1 to 3 mA the current applied during the film electrosynthesis. This current dependency of the permeability is in agreement with cyclic voltammograms of ferricyanide anion recorded on polyphenol film-coated VC electrodes depicted in Fig. 8(B) in that the reduction peak current decreased as the current applied increased in the range 1–3 mA. Fig. 8(C and D) shows cyclic voltammograms of 0.05 M phenol aqueous solution containing 0.15 M NaOH and 0.1 M Na$_2$SO$_4$ recorded at 85 °C on polyphenol film-coated VC electrodes. Cyclic voltammograms in Fig. 8(D) show that the phenol oxidation peak recorded on polyphenol film-coated electrodes is larger to that on bare electrode and displaced to more positive potentials (curve 2 in Fig. 6(A)).

Table 4 shows that when the applied current increases one observes a decrease of the permeability of the film toward the ferricyanide anion while the relative permeability of the same film with regard to the phenol increases. The current intensity effect on the polyphenol film permeability can be explained by the discharge of

water which is source of protons. The current I applied during films electrosynthesis can be expressed as follows:

$$I = I_{\text{Ph.}} + I_{\text{H}_2\text{O}} \tag{4}$$

where $I_{\text{Ph.}}$ and $I_{\text{H}_2\text{O}}$ are the partial currents for respectively phenol and water electro-oxidation. $I_{\text{Ph.}}$ can be evaluated by the following equation: $I_{\text{Ph.}} = nFAk_{\text{Ph}}[\text{Ph}]_{\text{sol.}}$ considering that the concentration of phenol at the electrode surface was equal to zero because the applied current I was much higher than the limiting current of phenol oxidation. Indeed, for the example of Fig. 8, the limiting current of phenol oxidation (during electrosynthesis of the films) was equal to around 0.35 mA for $n = 1$, $A = 0.0707\,cm^2$, $k_{\text{Ph}} = 10^{-5}\,m\,s^{-1}$ and $[\text{Ph.}]_{\text{sol.}} = 0.05$ M. Thus, as I increased (from 1 to 3 mA), the partial current of water discharge $I_{\text{H}_2\text{O}}$ rose, producing an increase in oxygen evolution and the output of protons. The concentration of protons $[\text{H}^+]_{\text{ele.}}$ at the electrode surface can be correlated to $I_{\text{H}_2\text{O}}$ by: $I_{\text{H}_2\text{O}} = nFAk_{\text{H}^+}[\text{H}^-]_{\text{ele.}}$ considering that the bulk concentration of protons $[\text{H}^+]_{\text{sol.}}$ was equal to zero due to hydrodynamic conditions (electrode rotation, $\omega = 1000$ rpm plus magnetic stirring) and the relatively high concentration of free hydroxide ion in the solution ($[\text{OH}^-]_{\text{sol.}} = 0.1$ M). Thus, concentrations $[\text{H}^+]_{\text{ele.}}$, calculated for $n = 1$ and $k_{\text{H}^+} = 10^{-5}\,m\,s^{-1}$, were equal to around 0.1 M and 0.4 M respectively for I equal to 1 or 3 mA. These results show that for $I = 3$ mA, the concentration of protons at the electrode surface ($[\text{H}^+]_{\text{ele.}} = 0.4$ M) was four times higher than that of free hydroxide ion in the solution ($[\text{OH} - \text{H}^+]_{\text{sol.}} = 0.1$ M). As a result, the electrode/solution interface remained acid though electrosynthesis of the polyphenol film was performed with an electrode rotation rate of 1000 rpm and under magnetic stirring. If we assume that polyphenol films prepared here had the same thickness, the drop of permeability for ferricyanide anion (Table 4) can be explained by a stronger acidity at the electrode surface during polyphenol film electrosynthesis as I increased.

The contradictory between the increase in the apparent permeability for phenol (%) $P_{\text{Ph.}}^{\text{film}}$ and the dramatic decrease of the permeability for ferricyanide anion $P_{\text{ferr.}}^{\text{film}}$ when the applied current increases (Table 4) can be interpreted in term of a change in the microstructure of the polyphenol film. We think that increasing the applied current and therefore the concomitant oxygen evolution increases the density of small pores (permeable for phenate and not for ferricyanide anion) to the detriment of that of large ones (permeable for both phenate and ferricyanide anions). According to Rothwell et al.'s suggestion [18] we intend to study these films by scanning electron microscopy to understand these effects.

For the removal of phenol by electropolymerisation the operating conditions should favour a high permeability of the film for phenate anion. Comparison between values of $P_{\text{ferr.}}^{\text{film}}$ (Table 4) and $P_{\text{ferr.}}^{\text{sol.}}$ ($P_{\text{ferr.}}^{\text{sol.}} = 45 \times 10^{-4}\,cm\,s^{-1}$ for $\omega = 1000$ rpm; Fig. 4) shows that the rate of ferricyanide reduction was limited by the membrane permeability for polyphenol films prepared at currents higher than 2 mA whereas it was under solution transport control for currents lower than 1.5 mA. The above results show that electrolysis

Table 4
Relationships between the current I applied during the electrosynthesis of a polyphenol film deposited on a rotating ($\omega = 1000$ rpm) vitreous carbon electrode in a magnetically stirred 0.05 M phenol aqueous solution containing 0.15 M NaOH and 0.1 M Na$_2$SO$_4$ at 85 °C and the permeability $P_{\text{ferr.}}^{\text{film}}$ for ferricyanide anion and $P_{\text{ph.}}^{\text{film}}$ for phenol.

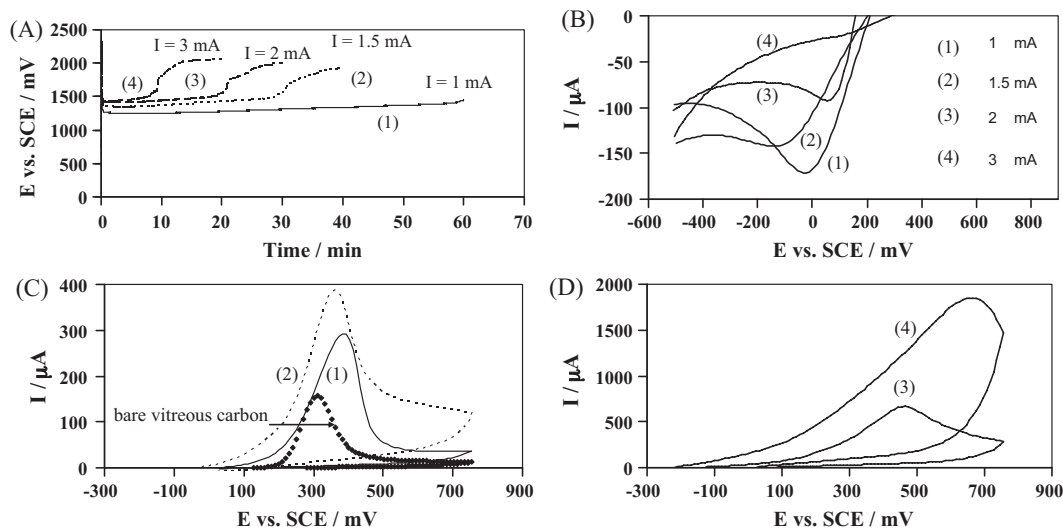| I/mA	1	1.5	2	3
Electrosynthesis time/min	60	40	30	20
$P_{\text{ferr.}}^{\text{film}} \times 10^4$/cm s^{-1}	107	45	29	2
$P_{\text{ph.}}^{\text{film}}$ (%)	176	233	399	1115

Fig. 8. (A) Galvanostatic E–t curves recorded during polyphenol films electrosynthesis on a rotating (ω = 1000 rpm) VC electrode at various applied currents in a magnetically stirred 0.05 M phenol aqueous solution containing 0.15 M NaOH and 0.1 M Na$_2$SO$_4$ at 85 °C. Applied current: (1) 1 mA for 60 min, (2) 1.5 mA for 40 min, (3) 2 mA for 30 min and (4) 3 mA for 20 min. (B–D) Measurements of polyphenol film permeability for (B) ferricyanide and (C and D) phenate ions. Scan rate: (B) 500 mV s^{-1} and (C and D) 100 mV s^{-1}.

performed at an applied current slightly higher than the limiting current of phenol oxidation should allow the removal of phenol.

3.3.2. Influence of electrode rotation and magnetic stirring

Galvanostatic E–t curves were recorded at 85 °C on a VC electrode at an applied current of 2 mA in 0.05 M phenol aqueous solution containing 0.15 M NaOH and 0.1 M Na$_2$SO$_4$; curves were registered either in a quiescent solution or for an electrode rotation rate of 1000 rpm and a magnetic stirring. The E–t curves have the same shape except that the potential plateau at 2000 mV was reached right from the beginning in the case of polyphenol film electrosynthesized in a quiet solution. The permeability for ferricyanide anion dropped from 29×10^{-4} cm s^{-1} (Table 4) for polyphenol film electrosynthesized on a rotating electrode and under magnetic stirring to zero in the case of a fixed electrode and unstirred phenol solution. As in Section 3.2.1, these results may be interpreted assuming an accumulation of high concentration of protons H$^+$ at the electrode surface which blocks the permeability of the polyphenol film electrosynthesized on a fixed electrode in unstirred solution [21].

4. Conclusions

This work demonstrates that the permeability of polyphenol films deposited by electrochemical polymerisation on a vitreous carbon electrode depends strongly on the composition of the starting phenol solution, temperature, applied potential or current, electrosynthesis time and hydrodynamic conditions. We have shown that the concentration of free OH$^-$ in the starting phenol solution ([OH$^-$]$_{sol.}$ = [NaOH] − [PhOH]) must be higher than around 0.1 M to prepare polyphenol films permeable to both ferricyanide and phenate anions; this was verified by varying NaOH concentration for the same concentration of phenol and vice versa; the relatively high free OH$^-$ concentration was necessary to instantaneously neutralize the acidity, at the electrode surface, arising from the concomitant oxygen evolution occurring during the polyphenol film electrosynthesis. Electrochemical polymerisation conducted at high temperature (85 °C) yields high permeable polyphenol films at low applied potentials. Nevertheless, polyphenol films that have suitable permeability were synthesized at low temperature but

at high applied potential. For the removal of phenol from wastewater by electropolymerisation, it would be better to use high temperature and low potential in order to minimize the parasitic reaction of oxygen evolution which affects the current yield. We have also shown that polyphenol films prepared at 1800 mV from 0.01 M phenol and 0.1 M NaOH have low permeability, especially when electrolysis time increases; this was interpreted in term of an increase in the polyphenol film thickness. The apparent permeability of polyphenol films prepared galvanostatically from 0.05 M phenol and 0.15 M NaOH at 85 °C increased for phenate anion as the applied current increased. These results could be interpreted in terms of (1) the increase in the local acidity at the electrode surface and (2) an increase in the density of small pores (permeable for phenate and not for ferricyanide anion) to the detriment of large pores (permeable for both phenate and ferricyanide anions) with increasing the concomitant oxygen evolution. It was shown that polyphenol films prepared on a rotating electrode and a stirred solution were more permeable than those synthesized on a fixed electrode and an unstirred solution.

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