The mediatory activity of meso-tetraphenylporphyrin iron(III) complex immobilized in Nafion film on a Pt electrode in the oxidation of 1,2- and 1,4-hydroquinones

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Abstract: This paper presents the results of an investigation of the properties of a modified platinum electrode with *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film and its catalytic activity in the electrochemical oxidation of selected hydroquinone and catechol derivatives. The redox activity of iron complexes of porphyrins was characterized in aqueous solutions of perchloric acid by means of cyclic voltammetry and differential pulse voltammetry. Both the increase in the anodic peak currents of the investigated compounds during oxidation on the platinum electrode modified with *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film (FeTPhP/Nafion/Pt) and the considerable decrease in the cathodic peak currents related to the porphyrine complexes reduction point to mediatory activity. The increase in the oxidation currents observed during the preparative electrolyses indicates that the modified platinum electrode, FeTPhP/Nafion/Pt, exhibits catalytic properties. The preparative electrooxidation of the investigated 1,2- and 1,4-hydroquinone derivatives showed that over 90% conversion of the substrate occurs in the shortest time on platinum modified with iron complex of porphyrin immobilized in Nafion film.

Key words: *meso*-Tetraphenylporphyrin iron(III) complex, nafion, hydroquinones, chemically modified electrode, redox mediator

1. Introduction

Hydroquinones are used in a variety of applications. They can be used as reagents for photography, dyeing fur, plastic production, and in the pharmaceutical industry.[1] What is more, catechol derivatives play an important role in mammalian metabolism and many compounds of this type are known to be secondary metabolites of higher plants. Additionally, some antibiotics of microbial origin contain catechol substructures. Both catechol itself and its monosubstituted derivatives (–OH, –CH$_3$, –OCH$_3$, –CHO, and –COOH) are active against *Pseudomonas* and *Bacillus*, but not *Penicillium* species. Hydroxychavicol inhibits a greater number of microorganisms, including *Pseudomonas*, *Cladosporium*, and *Pythium* species. Some flavonoids and catechols play the role of antimicrobial agents[2] and due to this they should attract attention for further investigation.[3] Thus, it seems that there is an urgent need to develop innovative sensors based on chemically modified electrodes to detect 1,2- and 1,4-hydroquinones, a class of neurotransmitters. This would constitute an innovative and promising new approach to the electrochemical detection of this class of compounds. To the best of our knowledge, this approach remains currently unexplored.

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A glassy carbon or platinum electrode, when subjected to an appropriate pretreatment procedure, exhibits a minimal propensity for surface fouling with products of electrode processes. The electrochemical irreversibility means that some organic compounds, such as catechol and hydroquinone derivatives, can undergo oxidation only at potentials considerably shifted from their standard redox potentials. Therefore, some chemically modified electrodes with various active mediators immobilized at the electrode surface can be used for the mediated electrooxidation of catechol and 1,4-hydroquinone derivatives in acidic solutions. [4−10] The electrode materials were mainly glassy carbon, platinum, gold, and graphite. However, in some cases the adsorbed or immobilized mediators on the electrodes were instable. [7] Regarding this immobilization of the electrocatalysts into the electrode, an ion-exchange polymer matrix could solve this problem. One of the best solutions to this case might be a platinum electrode coated with Nafion film that contains the immobilized catalyst. [11−26] Nafion itself is not electroactive, but may become electroactivated after its protons of $-SO_3H$ groups are replaced with electroactive cations or complexes (X^{n+}):

$$n(-SO_3H)_{polym.} + X^{n+}_{soln.} \rightarrow [X^{n+}(-SO_3^-)_n]_{polym.} + nH^+_{soln.}$$
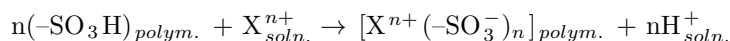
The immobilization of metalloporphyrins or their complexes into polymer-coated electrodes has been developed intensively over the past years due to the fact that these materials are efficient electrocatalysts for chemical applications. [1−8] It has been shown that such chemically modified electrodes can be used as tools in fundamental electrochemical investigations as chemical sensors and in energy-producing or electrochromic devices, and that they can be applied for the investigation of electrocatalytical properties. [4−6] Certain metalloporphyrins after their immobilization in a polymer film on an electrode surface can act as redox mediators for the oxidation of organic compounds. Iron complexes of porphyrins can be effective mediators for the oxidation of some phenol and hydroquinone derivatives. [6−8] So far, the electrochemical oxidation of hydroquinones and catechols at a platinum electrode modified with porphyrin iron complex immobilized in Nafion film has not been studied.

The aim of this work was to investigate the mediatory activity of platinum modified with *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film in the electrochemical oxidation processes of 1,4-hydroquinone (**1**), 2,3,5,6-tetrabromo-1,4-hydroquinone (**2**), 2-chloro-1,4-hydroquinone (**3**), 2,5-di-*tert*-butyl-1,4-hydroquinone (**4**), 2,6-dimethyl-1,4-hydroquinone (**5**), catechol (**6**), tetrabromocatechol (**7**), and 3,5-di-tert-butylcatechol (**8**).

2. Results and discussion

2.1. Characteristics of platinum modified with *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film

It has been observed [27,28] that in the redox catalysis of organic compounds the normal potential of the mediator's redox system should be higher than the normal potentials of substrates, but in general it should be lower than the half-wave potential of the substrate's reduced form. It means that for the oxidation process the catalysis can occur when the half-wave potential of the substrate's reduced form is higher than the normal potential of the mediator's redox couple, and that it is in turn higher than the substrate's normal potential. Thus, in the given conditions the mediator (its reduced form) should undergo oxidation at a lower potential than that of the organic compound, the substrate. However, this is not a necessary condition in chemical catalysis. In such case, the organic compound can be more electroactive than the mediator, as it has been observed in cyclic voltammetry measurements for the following compounds: 2,3,5,6-tetrabromo-1,4-hydroquinone (**2**) and 2,5-di-

tert-butyl-1,4-hydroquinone (**4**) (Table 1). The investigated compounds **2** and **4** exhibit lower overpotentials for the oxidation process than the mediator, *meso*-tetraphenylporphyrin iron(III) complex. For that to take place, the rate constant of the mediator's electrooxidation process (Table 2) (its anodic regeneration) is expected to be higher than the rate constant of electrooxidation of the organic substrate. In consequence, the catalytic (stoichiometric) amounts of the mediator can repeatedly oxidize large amounts of the organic substrate and yield higher amounts of product.

Table 1. The oxidation potentials (E_{substr}) for the investigated substrates: 1,2 and 1,4-hydroquinones **1**–**8** determined from the cyclic voltammetry measurements at a Pt electrode in a aqueous 0.1 M $NaClO_4$ solution. (The oxidation potential (E_{med}) of the applied mediator: *meso*-tetraphenylporphyrin iron(III) complex is 0.494 V.)

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
E_{substr} [V]	0.582	0.370	0.577	0.367	0.545	0.775	0.633	0.584

Cyclic voltammetry, differential pulse voltammetry, preparative electrooxidation, and UV/Vis measurements were performed for the purpose of studying the properties of platinum modified with *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film.

Figure 1 shows typical voltammetry plots of *meso*-tetraphenylporphyrin iron(III) complex in an aqueous 0.1 M $NaClO_4$ solution on uncoated Pt (Figure 1a) and on Pt modified with *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film, FeTPhP/Nafion/Pt (Figure 1b).
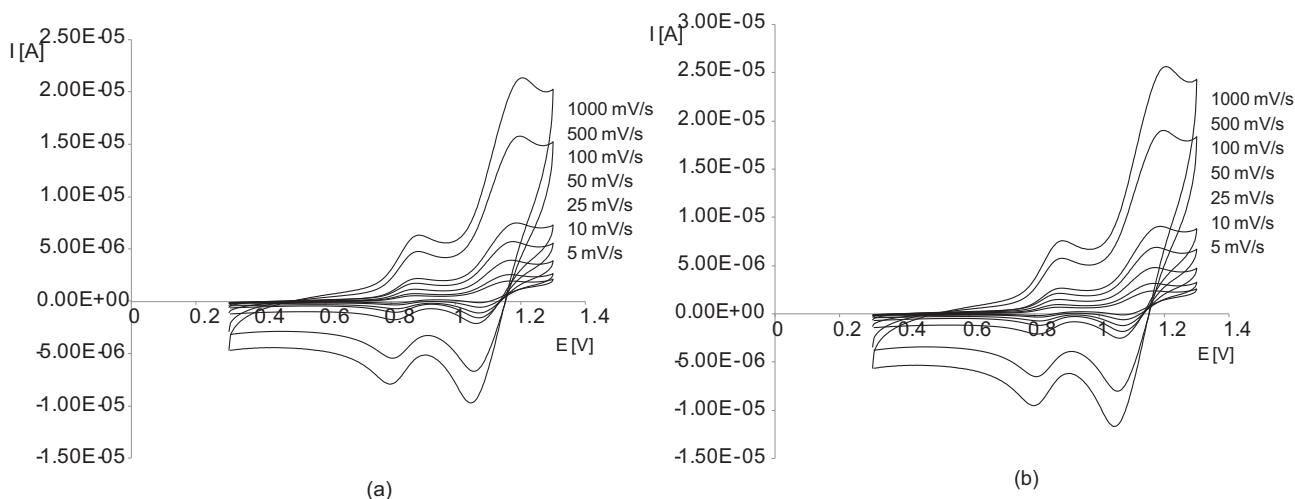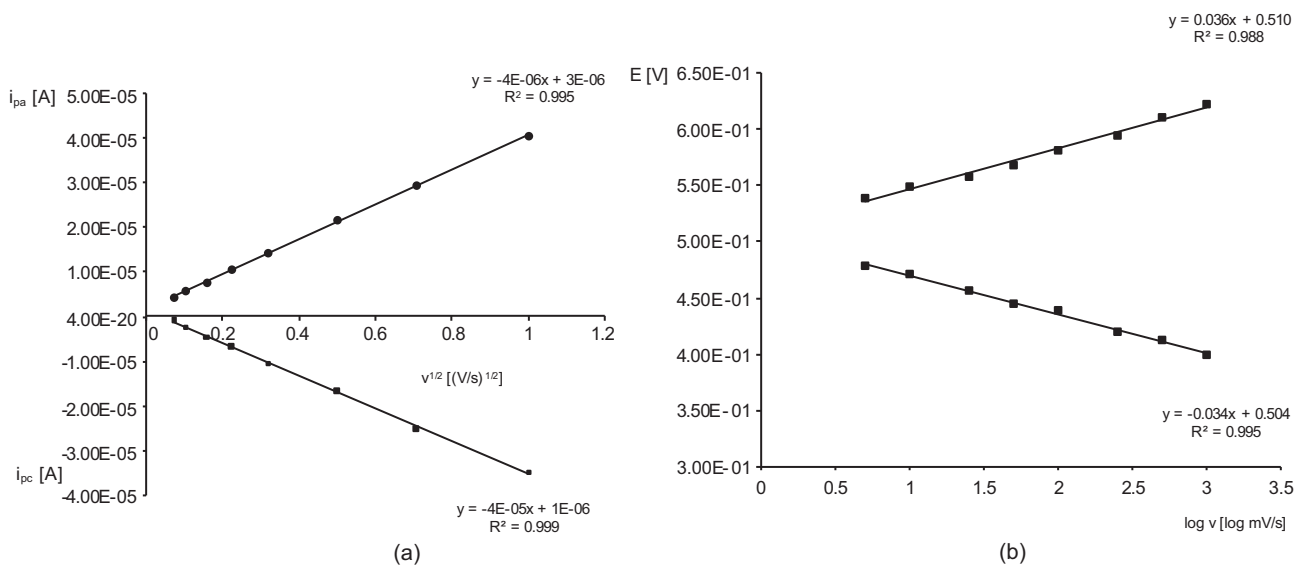

Figure 1. The voltammograms of a) 10^{-3} M *meso*-tetraphenylporphyrin iron(III) complex in a 0.1 M $NaClO_4$ solution on Pt, v = 5–100 mV/s; b) *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion coated on Pt (FeTPhP/Nafion/Pt), v = 5–1000 mV/s; all potentials vs. SCE.

The anodic and cathodic peaks of *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film coated on Pt (Figure 1b) are higher and better shaped as compared to the peaks for uncoated Pt in a solution containing *meso*-tetraphenylporphyrin iron(III) complex (Figure 1a), which suggests that the reversibility of *meso*-tetraphenylporphyrin iron(III) complex is higher in Nafion film than in the solution. The values of the

anodic and cathodic currents and the character of voltammograms remained steady even after repeated potential scanning (20 scans), which proves that *meso*-tetraphenylporphyrin iron(III) complex is effectively immobilized in Nafion film coated on platinum.

The character of the recorded current was also studied. Taking into account the dependence i_{pa} and i_{pc} = f($v^{1/2}$) (Figure 2a), we determined the range within which transport of the substance to the platinum surface occurred under the linear diffusion process. In relation to this, the CV voltammograms for different scan rates were recorded. The linear dependence was observed within scan rates 5–100 mV/s. The dependences of E_{pa} and E_{pc} on *log*v (Figure 2b) for *meso*-tetraphenylporphyrin iron(III) complex on FeTPhP/Nafion/Pt within the scan range v = 5–100 mV/s are also linear. This could imply a linear diffusion of electroactive species towards the electrode surface. Therefore, the apparent diffusion coefficients (D_{app}) for these forms, in the solution, were also calculated from the Randles–Ševčik equation: $i_p = (2.69 \times 10^5)n^{3/2} A C_0 v^{1/2} D^{1/2}$ (where n is the number of electrons, A - electrode area [cm^2], C_0 - concentration in the bulk [mol/cm^3], v - sweep rate [mV/s], D_{app} - apparent diffusion coefficient). The dependence of I_p = f($v^{1/2}$) in the diffusion controlled region obeys the Randles–Ševčik equation. Since the slope of this plot is linear, it can be combined with the amount of electroactive species immobilized (obtained by coulometric integration of the voltammetric peaks under thin-layer conditions) and the known film thickness in order to calculate the values of the apparent diffusion coefficients (D_{app}) of *meso*-tetraphenylporphyrin iron(III) complex within the coating film.[29,30] The D_{app} values were calculated by using the following equation: $D_{app} = S \times L/2.69 \times 10^5 \times m$, [cm^2 s^{-1}], where S is the slope of I_p = f($v^{1/2}$) plot, L is the film thickness, and m is the number of moles of *meso*-tetraphenylporphyrin iron(III) complex incorporated in the film (Table 2).

Figure 2. a) The dependence of i_{pa} and i_{pc} on $v^{1/2}$ for *meso*-tetraphenylporphyrin iron(III) complex using FeTPhP/Nafion/Pt, v = 5–1000 mV/s. b) The dependence of E_{pa} and E_{pc} on *log*v for *meso*-tetraphenylporphyrin iron(III) complex on FeTPhP/Nafion/Pt, v = 5–1000 mV/s.

Table 2. The diffusion coefficients D_{app} and the standard rate constants k_s of the electrode processes for *meso*-tetraphenylporphyrin iron(III) complex (FeTPhP) dissolved in NaClO$_4$ solution and after immobilization in Nafion on a platinum electrode.

Compound		$D_{anod.1}$ [cm^2 s^{-1}]	$D_{anod.2}$ [cm^2 s^{-1}]	$D_{cat.1}$ [cm^2 s^{-1}]	$D_{cat.2}$ [cm^2 s^{-1}]	$k_{s\,anod1}$ [cm s^{-1}]	$k_{s\,anod2}$ [cm s^{-1}]	$k_{s\,cat.1}$ [cm s^{-1}]	$k_{s\,cat.2}$ [cm s^{-1}]
H$_2$TPhP	Solution 0.1 M NaClO$_4$	7.10×10^{-5}	1.08×10^{-5}	4.07×10^{-6}	1.45×10^{-5}	2.34×10^{-3}	3.57×10^{-1}	1.21×10^{-1}	2.69×10^{-2}
H$_2$TPhP	Nafion film	5.03×10^{-8}	2.11×10^{-8}	2.34×10^{-9}	3.41×10^{-9}	3.45×10^{-4}	5.19×10^{-2}	4.01×10^{-2}	4.12×10^{-3}
FeTPhP	Solution 0.1 M NaClO$_4$	3.59×10^{-5}	6.55×10^{-6}	2.75×10^{-6}	1.02×10^{-5}	1.45×10^{-3}	1.78×10^{-1}	8.34×10^{-2}	1.06×10^{-2}
FeTPhP	Nafion film	3.40×10^{-8}	1.26×10^{-8}	1.67×10^{-9}	2.31×10^{-9}	1.96×10^{-4}	3.78×10^{-2}	3.04×10^{-2}	2.79×10^{-3}

According to the atomic force microscopy (AFM) measurements performed in tapping mode the thickness of Nafion film with immobilized *meso*-tetraphenylporphyrin iron(III) or nonocomplexed *meso*-tetraphenylporphyrin in the covered area was 36 nm. Since the electrode area was kept constant during the low and high scan rate measurements, the exact size of the electrode area had no influence on the D_{app} estimation. The diffusion coefficients D_{app} and the standard rate constants k_s of the electrode processes for *meso*-tetraphenylporphyrin iron(III) complex (FeTPhP) dissolved in NaClO$_4$ solution and after immobilization in Nafion on the platinum electrode surface are summarized in Table 2. For the purpose of comparison of electrode behavior with the complexed form the noncomplexed *meso*-tetraphenylporphyrin (H$_2$TPhP) was also used in measurements.

As can be seen from Table 2 the diffusion coefficients D_{app} and the standard rate constants k_s of the electrode processes for noncomplexed *meso*-tetraphenylporphyrin (H$_2$TPhP) are lower by about three ($D_{anod.}$, $D_{cat.}$) and about one ($k_{s\,anod}$, $k_{s\,cat.}$) orders of magnitude after immobilization in Nafion film on the platinum electrode surface as compared to these values if dissolved in aqueous NaClO$_4$ solution. A similar situation is observed for the *meso*-tetraphenylporphyrin iron(III) complex (FeTPhP) after immobilization in Nafion on the platinum electrode surface and if dissolved in aqueous NaClO$_4$ solution. Such behavior can be attributed to the higher viscosity of the Nafion film and the electrostatic interactions occurring within the film as compared to aqueous solutions. Moreover, lower $D_{anod.}$, $D_{cat.}$, $k_{s\,anod}$, and $k_{s\,cat.}$ values in Nafion film can suggest that the concentration of H$_2$TPhP and FeTPhP might be lower as a result of the morphological and structural changes in Nafion.

2.2. Electrochemical impedance spectroscopy (EIS)

To characterize the difference in resistance of the uncoated platinum electrode and platinum electrode coated with Nafion film containing *meso*-tetraphenylporphyrin iron(III) complex immobilized in it the electrochemical impedance spectroscopy (EIS) was performed before and after electrooxidation. Figure 3 shows the EIS results in the form of Nyquist plots. Upon the analysis of EIS measurements it can be observed that at OCP (the open circuit potential 0.360 V) the behavior is close to that of a nonideal capacitor, but the oxidation process of Fe(II) ions in the *meso*-tetraphenylporphyrin complex is clearly occurring. The spectrum shows a significant difference in the shape: the Pt electrode gives an almost straight line and the Nafion film coated Pt electrode shows a little rounded line with less slope, which could be evidence of charge separation at the Nafion film/Pt substrate interface. The values of impedance increase for the Pt electrode coated with Nafion film, which might be due to the limitations imposed on charge transfer by the polymer coating. However, for the platinum electrode coated

with Nafion film with *meso*-tetraphenylporphyrin iron(III) complex immobilized in it the values of impedance decrease. Thus the results of impedance measurements show that the electrode process is much easier for the Pt electrode with *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film as compared to uncoated Pt and coated Pt with Nafion film only.

2.3. Stability of platinum modified with *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film

The possible decrease in electrochemical activity for the FeTPhP/Nafion/Pt electrode during electrochemical measurement was investigated before it was used for the electrocatalytic oxidation of 1,2- and 1,4-hydroquinones. The anodic and cathodic charges, q_a and q_c, in consecutive potential scan cycles were calculated for this purpose. It turned out that the anodic and cathodic peak currents of the *meso*-tetraphenylporphyrin iron(III) complex did not decrease. Consequently, the electrochemical activity of FeTPhP/Nafion/Pt was not reduced during successive scans, without any change in the half-wave potential, $E_{1/2}$. The next objective was to determine the electroactive surface coverage (Γ) with the *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion on platinum.

Twenty voltammetric cycles were performed for this purpose on FeTPhP/Nafion/Pt within the scan rate range 0.01–0.10 V/s in a 0.1 M aqueous solution of $NaClO_4$. The value of Γ can be calculated from Faraday's law, $\Gamma = Q/nFA$, where Q is the charge [C] calculated by integration of the anodic peak (with rejection of the background current), n is the number of electrons, F is Faraday's constant, and A is the surface area of the conducting electrode phase in cm^2. The value of surface coverage Γ within the scan rate range 0.01–0.10 V/s was linear, which confirms that the *meso*-tetraphenylporphyrin iron(III) complex was not removed from the electrode and did not migrate into an aqueous solution after repeated scanning (Figure 4).

2.4. Mediatory activity of *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film coated on platinum

### 2.4.1. Cyclic voltammetry and differential pulse voltammetry measurements

The following measurements were taken in order to investigate the mediatory properties of the *meso*-tetraphenylporphyrin iron(III) complex: cyclic voltammetry (Figures 5a, 5b, and 6) and differential pulse voltammetry (Figures 7 and 8) of the investigated compounds **1**–**8** on uncoated Pt (Figures 6 and 8, curve a), on uncoated Pt with *meso*-tetraphenylporphyrin iron(III) complex dissolved in a 0.1 M aqueous solution of $NaClO_4$ (Pt + TPhP) (Figures 6 and 8, curve b), and on Pt coated with *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film (FeTPhP/Nafion/Pt) (Figures 6 and 8, curve c).

On the cyclic voltammograms the peak related to the oxidation of tetrabromocatechol appeared at E_a = 0.611 V (Figures 6 and 8). The best results were obtained for the modified electrode, i.e. with *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film coated on Pt (Figures 6 and 8, curve c). In this case, the currents of anodic oxidation were higher compared to the unmodified Pt electrode. The considerable increase in the values of the anodic and cathodic currents, as well as the decrease in ΔE_p within the range 5–11 mV (Table 3) observed on the voltammograms of the investigated compounds **1**–**8** performed on FeTPhP/Nafion/Pt points to increased activity of the mediator. On the other hand, the diminution of the cathodic current related to reduction of *meso*-tetraphenylporphyrin iron(III) on FeTPhP/Nafion/Pt in the case when the organic compound is present in the solution confirms the mediatory activity of the *meso*-

tetraphenylporphyrin iron(III) complex in the electrooxidation of the investigated hydroquinones and catechols **1**–**8**.
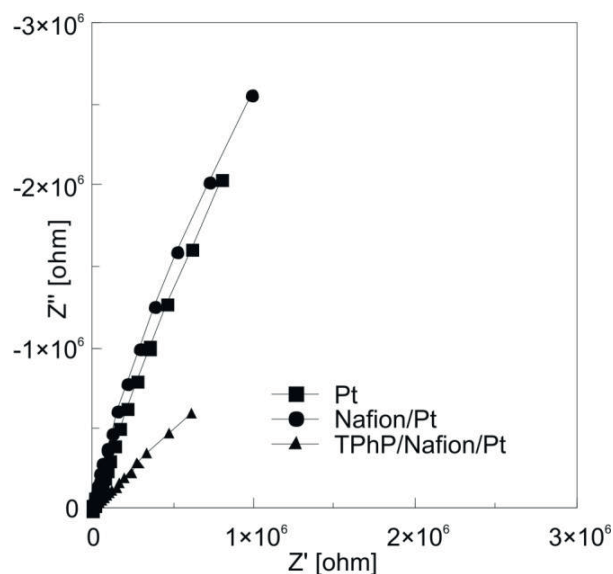
Figure 3. Electrochemical impedance spectra – Nyquist' plots of: Pt electrode, Nafion film on Pt electrode (Nafion/Pt) and Nafion film with *meso*-tetraphenylporphyrin iron(III) complex immobilized in it coated on Pt (FeTPhP/Nafion/Pt), all recorded in 0.1 M aqueous solution of NaClO$_4$.
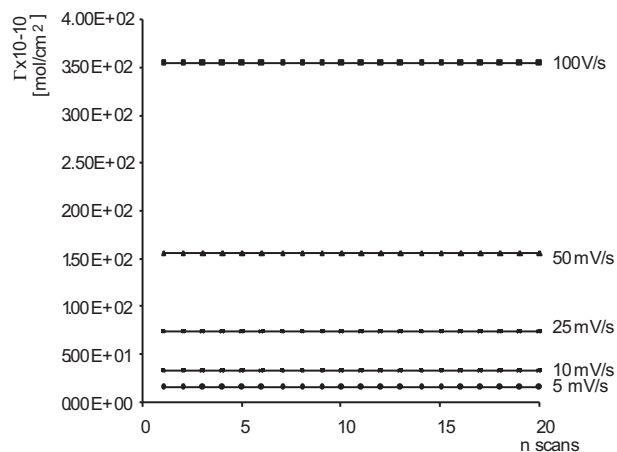
Figure 4. The electroactive surface coverage (Γ) on modified Pt with *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film (FeTPhP/Nafion/Pt) after immersion in a 0.1 M NaClO$_4$ solution, the scan rate range: 5–100 mV/s.
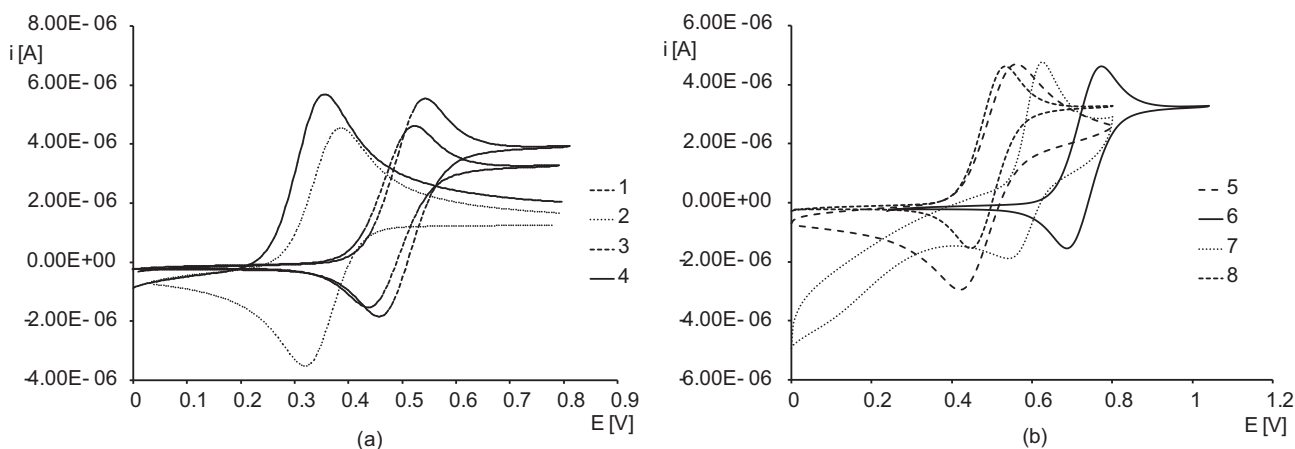
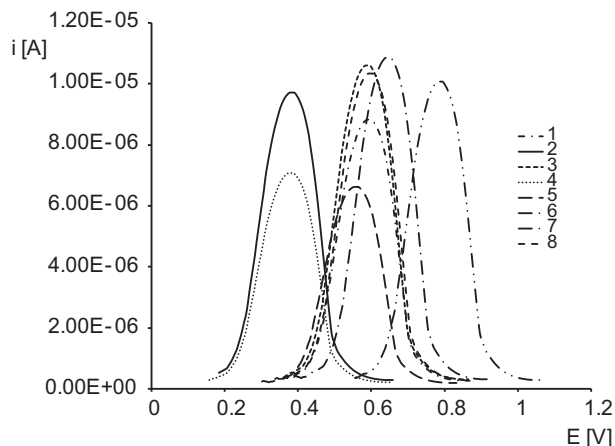**Figure 5.** The cyclic voltammograms: a) of **1**–**4** (4.0 × 10^{-3} M) and b) **5** and **6** (4.0 × 10^{-3} M) in 0.1 M NaClO$_4$ on uncoated Pt, v = 50 mV/s, I cycle, v = 50 mV/s, I cycle; all potentials vs. SCE, T = 298 K.

Furthermore, the simultaneous electrochemical behavior of 1,4- and 1,2-hydroquinones **1**–**8** at the Pt electrode modified with the *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film was studied by means of cyclic voltammetry and differential pulse voltammetry. At the beginning of the study the concentration of investigated 1,2- and 1,4-hydroquinones **1**–**8** in the voltammetric cell was equal to 5.0 × 10^{-3} M and
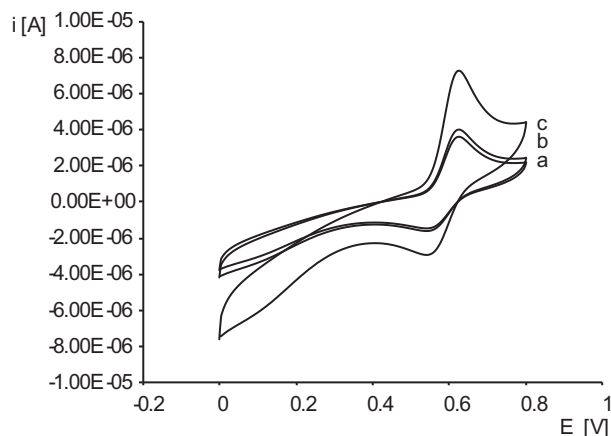
Figure 6. The cyclic voltammograms of a) tetrabromo-catechol (4.0×10^{-3} M) in a 0.1 M NaClO$_4$ on un-coated Pt, v = 50 mV/s, I cycle, b) tetrabromocate-chol (4.0×10^{-3} M) in a 0.1 M NaClO$_4$ on uncoated Pt with *meso*-tetraphenylporphyrin iron(III) complex (4.0×10^{-3} M) in the solution (Pt), v = 50 mV/s, I cy-cle, c) tetrabromocatechol (4.0×10^{-3} M) in 0.1 M NaClO$_4$ on modified Pt coated with Nafion film contain-ing *meso*-tetraphenylporphyrin iron(III) complex immobi-lized in (FeTPhP/Nafion/Pt), v = 50 mV/s, I cycle; all potentials *vs.* SCE, T = 298 K.

Figure 7. Differential pulse voltammograms of **1**–**8** (4.0×10^{-3} M) in a 0.1 M NaClO$_4$ on uncoated Pt, v = 50 mV/s, I cycle, v = 50 mV/s, I cycle; all potentials vs. SCE, T = 298 K.

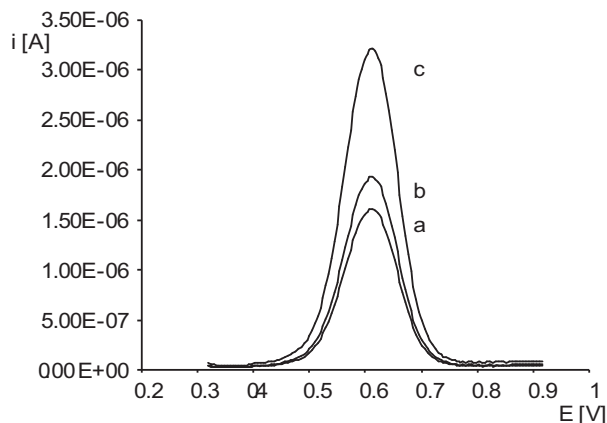**Figure 8.** Differential pulse voltammograms of a) tetrabromocatechol (4.0×10^{-3} M) in a 0.1 M NaClO$_4$ on uncoated Pt, v = 50 mV/s, I cycle, b) tetrabromocatechol (4.0×10^{-3} M) in a 0.1 M NaClO$_4$ on uncoated Pt with *meso*-tetraphenylporphyrin iron(III) complex (4.0×10^{-3} M) in the solution (Pt), v = 50 mV/s, I cycle, c) tetrabromocatechol (4.0×10^{-3} M) in 0.1 M NaClO$_4$ on modified Pt coated with Nafion film containing *meso*-tetraphenylporphyrin iron(III) complex immobilized in (FeTPhP/Nafion/Pt), v = 50 mV/s, I cycle; all potentials vs. SCE, T = 298 K.

then it had been changed according to the ratios 0.01, 0.10, 0.50, 1.00, 5.00, and 10.00 during the determination. It was observed that when the concentration of 1,4- and 1,2-hydroquinones was equal and the separation of oxidation potentials of these compounds was less than 0.070 V then the identification of the compounds was

difficult or unlikely. In the case of the equimolar mixture of 1, 3, 5, 8 or mixture of 2 and 4, or mixture of 7 and 8 overlapping of the oxidation peaks at the voltammograms occurred. When the separation of oxidation potentials of these compounds in the equimolar mixture was higher than 0.070 V overlapping of the peaks did not occur and the simultaneous electrochemical determination of 1,4- and 1,2-hydroquinones at the modified Pt electrode was possible. Furthermore, in the case as the concentration ratios of all investigated hydroquinones **1**–**8** were of 0.01 or 0.10 the presence of the compound in a smaller amount had no effect on the recorded oxidation peak current of the other compound.

Table 3. The results for the electrooxidation of the investigated 1,2- and 1,4-hydroquinones **1**–**8**. The concentration of **1**–**8** was 5×10^{-3} M in an aqueous 0.1 M $NaClO_4$ solution, on uncoated Pt at $E_{substr.}$ (**1** 0.582 V, **2** 0.370 V, **3** 0.577 V, **4** 0.367 V, **5** 0.545 V, **6** 0.775 V, **7** 0.633 V, **8** 0.584 V) on uncoated Pt with *meso*-tetraphenylporphyrin iron(III) complex (10^{-3} M) dissolved in a solution of aqueous 0.1 M $NaClO_4$ (Pt + TPhP in the solution) at E_{med} (0.494 V), and on Pt coated with Nafion film with immobilized *meso*-tetraphenylporphyrin iron(III) complex (FeTPhP/Nafion/Pt) at E_{med}, all potentials are given vs. SCE.

Compound	Electrode	Electro-oxidation time [min]	Di_a [μA] vs on Pt at $E_{substr.}$	DE_p [mV]	Final products and yields (for 100% of conversion)	
1	Pt at $E_{substr.}$	55	-	-	1,4-benzoquinone	54%
	Pt + FeTPhP in a solution at E_{med}	43	2.18 (*1.8×*)	0	1,4-benzoquinone	72%
	Pt/Nafion/FeTPhP at E_{med}	30	2.53 (*2×*)	5	1,4-benzoquinone	87%
2	Pt at E_{substr}	60	-	-	2,3,5,6-tetrabromo-1,4-benzoquinone	55%
	Pt + FeTPhP in a solution at E_{med}	48	1.93 (*1.5×*)	0	2,3,5,6-tetrabromo-1,4-benzoquinone	73%
	Pt/Nafion/FeTPhP at E_{med}	32	2.32 (*1.9×*)	6	2,3,5,6-tetrabromo-1,4-benzoquinone	91%
3	Pt at E_{substr}	78	-	-	2-chloro-1,4-benzoquinone	48%
	Pt + FeTPhP in a solution at E_{med}	55	2.39 (*1.9×*)	0	2-chloro-1,4-benzoquinone	72%
	Pt/Nafion/FeTPhP at E_{med}	41	2.43 (*2.1×*)	9	2-chloro-1,4-benzoquinone	92%
4	Pt at E_{substr}	56	-	-	2,5-di-*tert*-butyl-1,4-benzoquinone	51%
	Pt + FeTPhP in a solution at E_{med}	43	2.18 (*1.7×*)	0	2,5-di-*tert*-butyl-1,4-benzoquinone	73%
	Pt/Nafion/FeTPhP at E_{med}	30	2.53 (*1.8×*)	5	2,5-di-*tert*-butyl-1,4-benzoquinone	91%
5	Pt at E_{substr}	46	-	-	2,6-dimethyl-1,4-benzoquinone	47%
	Pt + FeTPhP in a solution at E_{med}	44	2.45 (*1.9×*)	0	2,6-dimethyl-1,4-benzoquinone	72%
	Pt/Nafion/FeTPhP at E_{med}	33	2.78 (*2.3×*)	6	2,6-dimethyl-1,4-benzoquinone	94%
6	Pt at E_{substr}	52	-	-	1,2-benzoquinone	64%
	Pt + FeTPhP in a solution at E_{med}	40	2.18 (*1.9×*)	0	1,2-benzoquinone	72%
	Pt/Nafion/FeTPhP at E_{med}	31	2.53 (*2.1×*)	8	1,2-benzoquinone	93%
7	Pt at E_{substr}	62	-	-	3,4,5,6-tetrabromo-1,2-benzoquinone	55%
	Pt + FeTPhP in a solution at E_{med}	45	2.63 (*1.9×*)	0	3,4,5,6-tetrabromo-1,2-benzoquinone	73%
	Pt/Nafion/FeTPhP at E_{med}	31	3.19 (*2.1×*)	9	3,4,5,6-tetrabromo-1,2-benzoquinone	90%
8	Pt at E_{substr}	58	-	-	3,5-di-tert-butyl-1,2-benzoquinone	48%
	Pt + FeTPhP in a solution at E_{med}	53	2.12 (*1.5×*)	0	3,5-di-tert-butyl-1,2-benzoquinone	72%
	Pt/Nafion/FeTPhP at E_{med}	39	2.64 (*1.9×*)	11	3,5-di-tert-butyl-1,2-benzoquinone	93%

2.4.2. Scanning electron microscopy (SEM) measurements

In order to determine the difference in surface morphology before and after immobilization of *meso*-tetraphenyl-porphyrin iron(III) complex in Nafion film on the platinum electrode SEM measurements were performed. The SEM images of the investigated electrodes are shown in Figure 9. Figure 9a shows the surface of the uncoated Pt electrode. The Pt electrode after coating with Nafion film is shown in Figure 9b and the Pt electrode coated with Nafion film containing *meso*-tetraphenylporphyrin iron(III) complex immobilized in it is presented in Figure 9c. The Nafion film forms a smooth layer on the platinum surface. In contrast, Nafion film with *meso*-tetraphenylporphyrin iron(III) complex immobilized in it contains numerous crystalline structures of different sizes and shapes. The structures belongs to the crystal conglomerates of the *meso*-tetraphenylporphyrin iron(III) complex. These structures remain unchanged after mediatory electroreduction processes of the investigated compounds **1**–**8.**
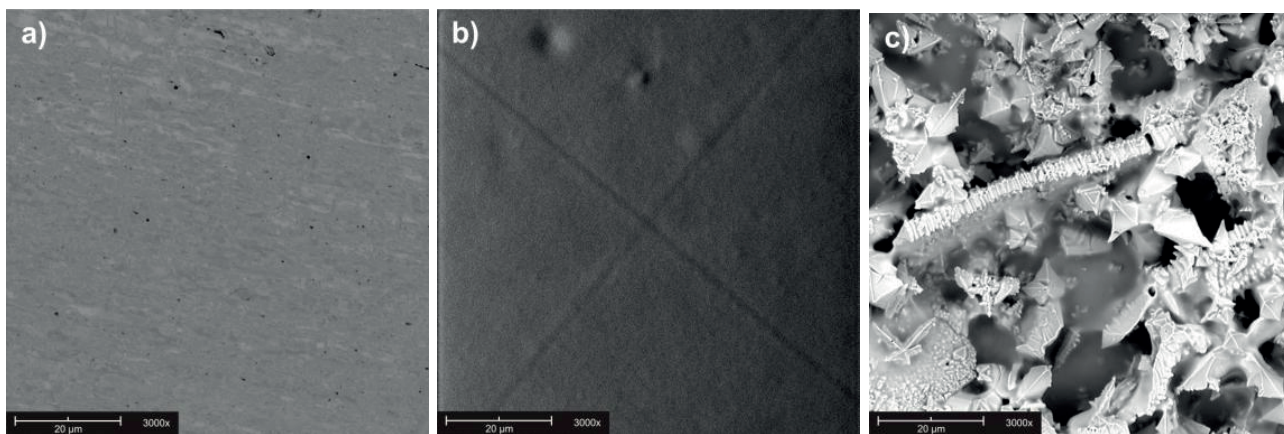

Figure 9. Scanning microscopy images of a) uncoated Pt electrode surface; b) Pt electrode surface after coating with Nafion film; c) Pt electrode surface coated with Nafion film containing *meso*-tetraphenylporphyrin iron(III) complex immobilized in it.

## 2.4.3. Electrooxidation of 1,2- and 1,4-hydroquinones 1–8 with controlled potential

Electrooxidation with controlled potential of the investigated compounds **1**–**8** was carried out in order to investigate the mediatory properties of *meso*-tetraphenylporphyrin iron(III) complex. The electrooxidation of **1**–**8** on uncoated Pt was done at potential of oxidation of a given substrate $E_{substr.}$. The electrooxidation of **1**–**8** on uncoated Pt with *meso*-tetraphenylporphyrin iron(III) complex dissolved in solution (Pt + TPhP) was done at potential of oxidation of the mediator (i.e. *meso*-tetraphenylporphyrin iron(III) complex), $E_{med.}$. The electrooxidation of **1**–**8** on Pt coated with Nafion film with *meso*-tetraphenylporphyrin iron(III) complex immobilized in (FeTPhP/Nafion/Pt) was also done at potential of oxidation of the mediator, $E_{med.}$. As a result, 1,2- and 1,4-benzoquinones were respectively obtained as the final products of the relevant electrooxidation processes (Table 3). The best results were observed for Pt coated with Nafion film containing *meso*-tetraphenylporphyrin iron(III) complex immobilized in (FeTPhP/Nafion/Pt). As compared to uncoated Pt, the shortest electrooxidation times and the highest yields were observed using the FeTPhP/Nafion/Pt modified electrode (Table 3). The longest electrolysis time was observed when the oxidation was carried out at the uncoated Pt and without *meso*-tetraphenylporphyrin iron(III) complex in the solution.

The above observations were confirmed by the UV-VIS spectra of the electrooxidized 1,2- and 1,4-hydroquinone solutions (10^{-2} M). An increase in absorbance values was observed for solutions of hydroquinones electrooxidized on Pt coated with Nafion film containing immobilized *meso*-tetraphenylporphyrin iron(III) complex (FeTPhP/Nafion/Pt) as compared to uncoated Pt and with *meso*-tetraphenylporphyrin iron(III) complex present in the solution (Figure 10). Cyclic voltammetry measurements were also performed in order to check the possibility of an electroanalytical determination of 1,2- and 1,4-hydroquinone derivatives **1**–**8** with use of the anodic current peak at the E_{substr} potentials.

It was discovered that in the mediated electrooxidation the peak current of the investigated compounds at the surface of the Pt electrode modified with *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film (FeTPhP/Nafion/Pt) was linearly dependent and proportional to the concentration of the substrate within the range 2.0×10^{-5}–8.0×10^{-3} M. In all cases the detection limit was 2.0×10^{-5} M (Figure 11).
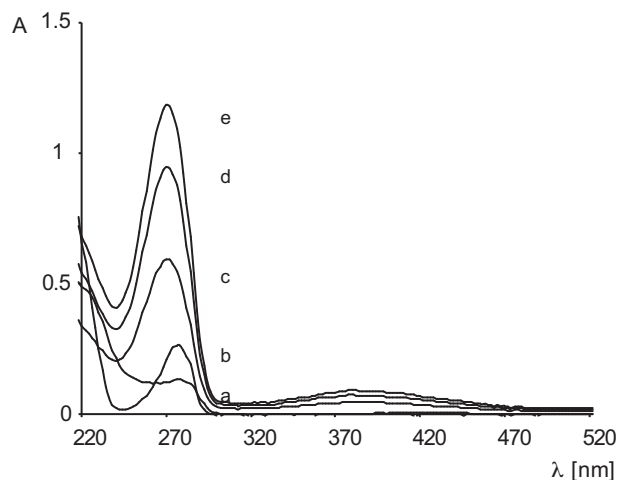
Figure 10. The UV-VIS spectra: a) of tetrabromocatechol (5.0×10^{-5} M) in 0.1 M $NaClO_4$ before electrooxidation, b) tetrabromocatechol (5.0×10^{-5} M) in 0.1 M $NaClO_4$ after electrooxidation on uncoated Pt at $E_{med.}$, c) tetrabromocatechol (5.0×10^{-5} M) in 0.1 M $NaClO_4$ after electrooxidation on uncoated Pt at $E_{substr.}$, d) tetrabromocatechol (5.0×10^{-5} M) in 0.1 M $NaClO_4$ after electrooxidation on uncoated Pt with *meso*-tetraphenylporphyrin iron(III) complex (10^{-3} M) in the solution (Pt), at E_{med}, e) tetrabromocatechol (5.0×10^{-5} M) in 0.1 M $NaClO_4$ after electrooxidation on Pt coated with Nafion film containing *meso*-tetraphenylporphyrin iron(III) complex immobilized in (FeTPhP/Nafion/Pt) at E_{med}.
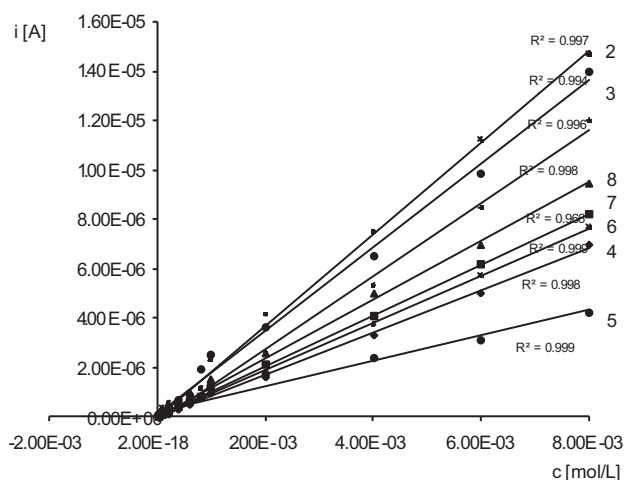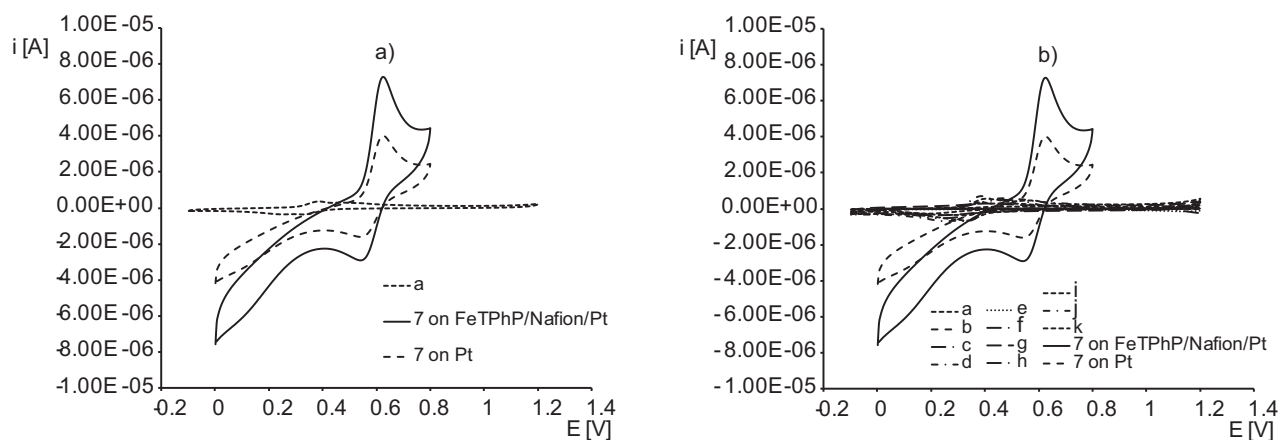
Figure 11. The plot of the electrocatalytic peak currents from the cyclic voltammetry measurements on modified Pt coated with Nafion film containing *meso*-tetraphenylporphyrin iron(III) complex immobilized in FeTPhP/Nafion/Pt. (1,4-hydroquinone (**1**), 2,3,5,6-tetrabromo-1,4-hydroquinone (**2**), 2-chloro-1,4-hydroquinone (**3**), 2,5-di-*tert*-butyl-1,4-hydroquinone (**4**), 2,6-dimethyl-1,4-hydroquinone (**5**), catechol (**6**), tetrabromocatechol (**7**) and 3,5-di-tert-butylcatechol (**8**); Concentration range: 2.0×10^{-5}–8.0×10^{-3} M).

2.4.4. Effect of interferences

It was studied whether the phenols and amines commonly found in waste waters from plastic production and the pharmaceutical industry, such as 2,6-difluorophenol (a), 2,6-dichlorophenol (b), 2,3,5,6-tetrafluorophenol (c),

4−aminophenol (d), N,N-dimethylaniline (e), N,N-diethylaniline (f), N-methylaniline (g), 2,6-dimethylaniline (h), 2,6-diethylaniline (i), 2,6-difluoroaniline (j), and 2,3,5,6-tetrafluoroaniline (k), would interfere with the determination of 1,4- and 1,2-hydroquinones using the described method and modified electrode under the experimental conditions (Figure 12). The investigated 1,2- and 1,4-hydroquinones concentration in the voltammetric cell was equal to 2.0×10^{-5} M and was fixed during the study, whereas the other phenols and amines were present at levels ranging from 5.0×10^{-6} M to 5.0×10^{-2} M. The concentration ratios of the studied phenols and amines to the investigated 1,2- and 1,4-hydroquinones were 0.01, 0.10, 0.50, 1.00, 5.00, and 10.00. The presence of 2,6-dichlorophenol and 2,3,5,6-tetrafluorophenol had a major effect on the recorded peak current (only the concentration ratio of 0.01 did not decrease the signal). 2,6-Difluorophenol caused a minor decrease in the 1,2- and 1,4-hydroquinones signal only at 5- and 10-fold higher concentrations of the phenols and amines mentioned above. 2,6-Dimethylaniline, 2,6-diethylaniline, 2,6-difluoroaniline, 2,3,5,6-tetrafluoroaniline, N,N-dimethylaniline, N,N-diethylaniline, and N-methylaniline generally had no effect on 1,2- and 1,4-hydroquinones peak current.

Figure 12. The cyclic voltammograms of: a) tetrabromocatechol (4.0×10^{-3} M) and 2,6-difluorophenol (a) (4.0×10^{-3} M), b) tetrabromocatechol (4.0×10^{-3} M) and interfering compounds **a**–**k** (4.0×10^{-3} M) in a 0.1 M NaClO$_4$ on uncoated Pt and on modified Pt coated with Nafion film containing *meso*-tetraphenylporphyrin iron(III) complex immobilized in (FeTPhP/Nafion/Pt), v = 50 mV/s, I cycle; all potentials vs. SCE, T = 298 K.

The mediatory activity of *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film coated on Pt was determined. The results were compared with those obtained for uncoated Pt without *meso*-tetraphenylporphyrin iron(III) complex. The character and height of the anodic and cathodic peaks were maintained even after several cycles, which proves that the immobilization of *meso*-tetraphenylporphyrin iron(III) complex in Nafion film coated on platinum is effective and durable. The equilibrium indicating the constant amount of *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film coated on platinum during voltammetry measurements in a 0.1 M aqueous solution of NaClO$_4$ was achieved after the second cycle. The corresponding 1,2- and 1,4-benzenoquinones are the main final products of the electrochemical oxidation of the investigated 1,4-hydroquinones and catechols **1**–**8** on Pt modified with *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film. The immobilization of *meso*-tetraphenylporphyrin iron(III) complex in Nafion film coated on Pt results in an increase in the oxidation peak currents of the investigated compounds and a considerable decrease or even absence of the cathodic reduction peak of porphyrin complex, as the process is performed at the potential of the mediator oxidation, in comparison to the same process on uncoated Pt

without porphyrin complex. The results point to the enhancement of the process yield in the presence of *meso*-tetraphenylporphyrin iron(III) complex. The preparative electrooxidation for the investigated compounds **1**–**8** shows a substantial decrease in the duration of the process when *meso*-tetraphenylporphyrin iron(III) complex is immobilized in Nafion film coated on Pt or is dissolved in a solution containing 1,4-hydroquinones and catechols **1**–**8**. This is accompanied by an increase in the absorption band heights in the UV-Vis spectra (Figure 10) as the oxidation process is performed on platinum modified with *meso*-tetraphenylporphyrin iron(III) complex immobilized in Nafion film. Finally, the process of 1,2- and 1,4-hydroquinones mediated electrooxidation on FeTPhP/Nafion/Pt was used for testing their possible qualitative determination in aqueous solutions, and a linear dependence of anodic current vs. concentration was obtained within the range of 2.0×10^{-5}–8.0×10^{-3} M with a correlation coefficient of 0.9996 and a detection limit of 2.0×10^{-5} M.

3. Experimental

The cyclic voltammetry and differential pulse voltammetry measurements were performed under an argon atmosphere using an AUTOLAB PGSTAT 10 (Eco Chemie BV) in a three-electrode system, where the working and modified electrode was a Pt disc ($\phi = 2$ mm, area 0.0314 cm^2), the reference electrode was saturated calomel electrode (SCE), and the counter electrode was a cylindrical platinum gauze (5.0 cm^2). The preparative electrooxidation was performed in potentiostatic conditions also in the three-electrode system, but this time the Pt plate was used as the working and modified electrode (area: 1.0 cm^2). A drop (4.0 μL, and 100 μL in case of the Pt plate for preparative electrooxidation) of stock solution of Nafion 117 with dissolved *meso*-tetraphenylporphyrin iron(III) complex was applied on the Pt surface using a micropipette and the solvent was allowed to evaporate in open air. The stock solution was prepared by dissolving *meso*-tetraphenylporphyrin iron(III) complex (Fluka) in 100 mL of ethanol and then 1 μL of this solution was mixed with 1 mL of Nafion 117 (Aldrich, wt. 5%) prior to use. The resulting chemically modified electrode (FeTPhP/Nafion/Pt) was thoroughly rinsed with triple distilled water. The electrooxidation of the investigated compounds **1**–**8** (0.5 mmol of each compound in a 0.1 M aqueous solution of NaClO$_4$) was carried out under potentiostatic conditions in a glass cell (50 mL) at 25 °C on uncoated Pt at the potentials of the substrate electrooxidation E$_{substr.}$ and at the mediator electrooxidation E$_{med.}$, on uncoated Pt with *meso*-tetraphenylporphyrin iron(III) complex (10^{-3} M) ions in a 0.1 M aqueous solution of NaClO$_4$ (Pt + TPhP in solution) at E$_{med}$, and on Pt coated with Nafion film containing *meso*-tetraphenylporphyrin iron(III) complex immobilized in FeTPhP/Nafion/Pt at E$_{med}$ (Table 1).

The final products were extracted with CH$_2$Cl$_2$ and CHCl$_3$ from the electrolyte solution and then identified by means of comparing their UV-Vis, IR, ^{1}H NMR spectra, and melting points with literature data. The UV-Vis spectra were performed on a SPECORD M 42, the IR spectra on a SPECORD M 80, the ^{1}H NMR on a VARIAN 200 MHz, and the melting points were recorded on a Mel Temp II apparatus. The topography of the Pt electrode modified with *meso*-tetraphenylporphyrin iron(III) immobilized in Nafion film (FeTPhP/Nafion/Pt) was evaluated with an atomic force microscope (SOLVER P47, NT - MDT). The atomic force microscopy (AFM) measurements of area surface and film thickness were performed under ambient conditions in tapping mode using a MikroMasch cantilever with radius 20 nm, stiffness 40 N/m, and resonance frequency 170 kHz. Studies of EIS were performed by potentiostat/galvanostat Autolab PGSTAT 128N with an FRA2 module (Metrohm Autolab B.V, Utrecht, the Netherlands). The EIS spectra were registered at the

equilibrium potential within the frequency range of 0.01 Hz to 10 kHz with signal perturbation amplitude of 10 mV. Surface morphology of the electrodes was observed by scanning electron microscope (Phenom, FEI Company).

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