Electrochemical Properties of Carbon-Paste Electrodes Spiked with Some 1,4-Naphthoquinone Derivatives

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The preparation and aqueous electrochemistry of a carbon-paste electrode, modified by 1,4-naphthoquinone and some of its derivatives are described. From a calculation of the half-wave potential as a function of the pH, potential-pH diagrams were constructed for each compound. The values of the formal potentials and the $\mathrm{p}K_\mathrm{a}'$ of some different redox and acid-base couples involved at various solution pHs were obtained. The influence of such substituents as methyl-, hydroxy-, chloro-, and amino- concerning the electrochemical behavior of surface 1,4-naphthoquinone is described. The electrochemical behavior of such electrodes was examined in buffered borate solutions and the formation of a complex between borate anion and *o*-naphthalenediols was characterized. Finally, the range of the pH at which the electrode function is consistent was determined.

The importance of quinones as a mediator for both electro-reduction and electro-oxidation processes has been known for several years; this has attracted many researchers to work in this area.[1,2] Klaus Lanz et al.[3] have been used naphthoquinone as a mediator for reducing nitroaromatic compounds in homogeneous aqueous solution. Considering the growing importance of mediators immobilized at the surface of various electrodes, and the high efficiency of such electrodes in facilitating electron transfer at slow electrochemical reactions, many studies have been considered for the preparation of electrodes coated with polymeric films having quinonic functions.[4—11] Schmidt and Schuhmann have prepared an electrode coated with poly(5-hydroxy-1,4-naphthoquinone) film by electropolymerization, and have applied this modified electrode for the electrocatalytic oxidation of reduced nicotinamide adenine dinucleotide (NADH).[12] Various similar studies have been made using polymer-modified electrodes containing other quinones.[13—16]

Anson and a co-worker have prepared a modified electrode by the adsorption of alizarin complexone on a graphite electrode to produce a electrocatalyst for the reduction of O_2 and H_2O_2.[17] A number of other research groups have provided modified electrodes by the adsorption of various compounds, including quinone functionalities.[18—23]

Carbon-paste electrodes (CPE's) containing various electroactive compounds have been extensively characterized in the literature.[1,24] Their use in evaluating electrochemical processes,[25,26] and, more specifically, concerning the electrocatalytic mechanism,[1,27—30] has been frequently reported. Furthermore, these electrodes are good replacements for other electrodes with modified surfaces (in many cases), owing to easy preparation, low cost and reproducibility of results.

We have prepared carbon-paste electrodes spiked by some of 1,4-naphthoquinone derivatives, such as 1,4-naphthoquinone, 5-hydroxy-1,4-naphthoquinone (juglone), 5-hydroxy-2-methyl-1,4-naphthoquinone (plumbagin), 2-amino-3-chloro-1,4-naphthoquinone, and 2,3-dichloro-1,4-naphthoquinone. The electrochemical behavior of 1,4-naphthoquinone derivatives spiked carbon-paste electrodes in solution depends on the nature of the naphthoquinone used in preparing the electrode; it also varies with the solution conditions. However, the common feature of all naphthoquinones arises from the presence of a quinone ring in their structure, providing a nearly reversible electron-transfer character for these compounds, and making them suitable as mediators. Moreover, the application of naphthoquinone spiked CPE's in the catalysis of slow electrode reactions requires a quite profound understanding of the electrochemical properties of such electrodes under various solution conditions. For this reason, this paper has been confined to describing the electrochemical behavior of carbon-paste electrodes spiked with some naphthoquinones in various buffered aqueous solutions by cyclic voltammetry. The potential-pH diagrams of these naphthoquinone derivatives were constructed; by using of these diagrams the apparent standard potentials of various naphthoquinone redox couples, together with the dissociation constant of intervening acid-base couples, were estimated. The effects of substituents at the naphthoquinone function were also studied. Finally, the electrochemical behavior of these electrodes was studied in a borate buffer solution; the complex formation between the borate anion and *o*-naphthalenediols resulting from the reduction of some naphthoquinones was characterized.

Experimental

i) Materials. 1,4-Naphthoquinone and its derivatives from Aldrich were used without further purification. Spectrographically pure graphite road (Grade II, from Johnson Matthey Chemicals Limited), ground to a fine powder, was used as a working electrode substrate. Solutions were prepared with redistilled water. The buffers used at different pH were, H_2SO_4 0.05 M+NaOH (for pH=0.5—1.5), H_3PO_4 0.1 M+NaOH (for pH=2—3), acetate buffer (for pH=3.5—6) and sodium dihydrogen phosphate 0.1 M+NaOH (for pH=6.5—13.5). All of the chemicals were of reagent-grade from Aldrich or Merck, and were used as received. N_2 gas with a purity of 99.999% was used for removing oxygen from solutions during the experiments (1 M=1 mol dm^{-3}).

ii) Working Electrode. The working electrode was constructed in a way similar to that described in the literature.$^{30)}$ A 1% (w/w) naphthoquinone-spiked carbon powder was made by dissolving a given quantity of naphthoquinone in acetone and mixing with 99-times its weight of graphite powder. In the case of 2-amino-3-chloro-1,4-naphthoquinone, diethyl ether was used as a solvent, because of its interaction with acetone.$^{31)}$ The solvent was evaporated by stirring. A 1 : 1 (w/w) mixture of 1% naphthoquinone-spiked carbon powder and mineral oil (high viscosity, from Fluka) was blended. The resulting naphthoquinone-spiked carbon paste (NQCP) was then inserted into the bottom of a polypropylene tube having an internal diameter of ca. 2.5 mm. The electrical connection was implemented by a copper wire lead fitted into a polypropylene tube. Such an electrode was satisfactorily used in cyclic voltammetry.

iii) Apparatus. Cyclic voltammetry was carried out at a thermostated temperature of 25±0.1 °C by using a potentiostat (polarecord E626 from Metrohm) in conjunction with a function generator (VA scanner E612 from Metrohm) and a Hewlett–Packard 7015A X–Y recorder. The potentials were measured with respect to a saturated calomel electrode (EA 404 from Metrohm); a platinum wire (EA 202 Metrohm) was used as an auxiliary electrode.

Results and Discussion

1) 1,4-Naphthoquinone-Spiked Carbon-Paste Electrode (1,4-NQCPE). The electrochemical properties of 1,4-NQCPE were studied by cyclic voltammetry in aqueous buffered solutions at pH between 0.5—13 in the absence of dioxygen. Over a potential range corresponding to the electroactivity domain of the solvent, cyclic voltammograms show a single reduction peak and a corresponding oxidation peak (Fig. 1a). At this range of the potential, the free carbon-paste electrode shows no peaks (Fig. 1b); however, in the presence of oxygen, the limitation of negative potentials corresponds to the reduction of dioxygen (Fig. 1c).

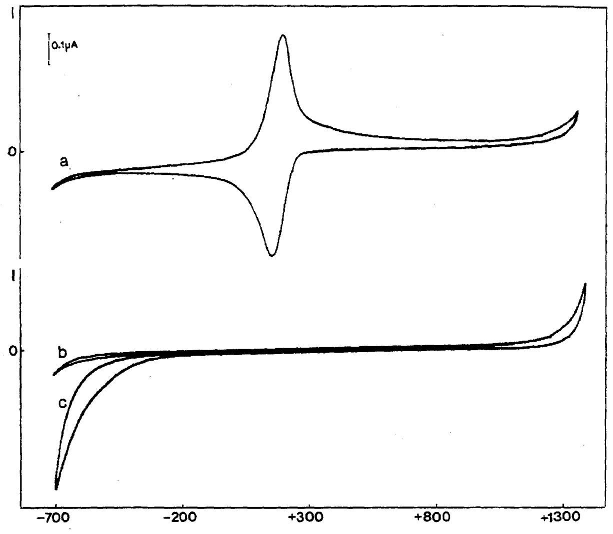


Fig. 1. Cyclic voltammograms of a) 1,4-NQCPE, b) free carbon paste electrode, in deoxygenated aqueous 0.5 M H_2SO_4, c) as b in O_2 saturated solution. scan rate: 5 mV s^{-1}.

As shown in Fig. 1a, the peak current ratio (I_{pa}/I_{pc}) is greater than unity. However, this ratio decreases and approaches unity with increasing pH, and becomes less than unity when it exceeds 6.5. Such a situation can indicate of kinetic or other complications in the electrode process.$^{32)}$ The half-wave potentials ($E_{1/2}$) were calculated as the average of the anodic and cathodic peak potentials of the cyclic voltammograms ((E_a+E_c)/2) recorded at a potential scan rate of 5 mV s^{-1},$^{18)}$ they are plotted in Fig. 2 as a function of the solution pH. This diagram comprises three linear segments with different slopes: −54 mV (pH<9.67), −28.3 mV (9.67<pH<11.74), and −13.5 mV (pH>11.74) per unit of pH. This means that parallel to the variation of the solution pH and electrode potential, four different forms of 1,4-naphthoquinone can be produced at the electrode surface. One of these is an oxidized form (Q); the other three are reduced forms of 1,4-naphthoquinone. The electrode surface reaction occurring at a pH below 9.67 is a two-proton, two-electron process involving the reduction of 1,4-naphthoquinone to 1,4-naphthalenediol in a forward scan, and the back oxidation of the later prod-

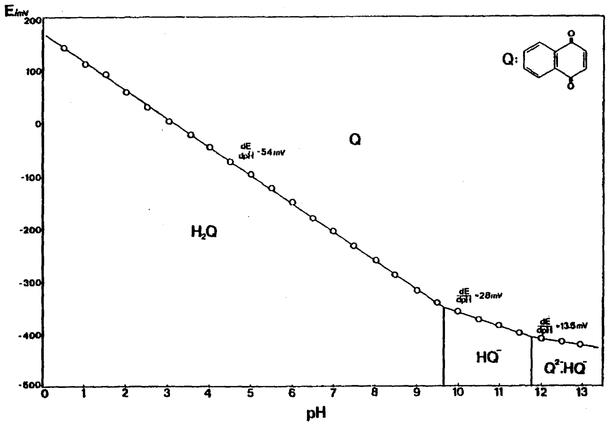
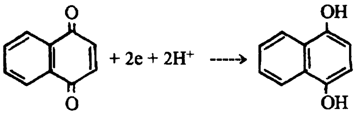


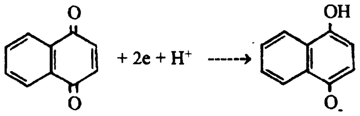
Fig. 2. pH–potential diagram for NQCPE. The symbol Q stands for the molecule of 1,4-naphthoquinone shown in the figure.

uct to 1,4-naphthoquinone in reverse scan (Scheme 1). However, for the pH ranging from 9.67 to 11.74, Q undergoes a one-proton, two-electron reduction producing HQ^-, and vice versa (Scheme 2).

Finally, the electrode surface reaction at a pH higher than 11.74 is related to a four-electron, one-proton reduction (Scheme 3).



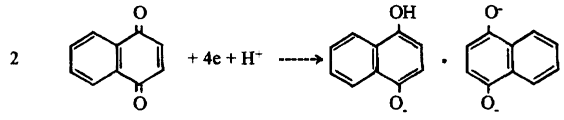
Scheme 1.



Scheme 2.

We assume the existence of such a dimerized species by analogy with the case of 5-hydroxy and 5-hydroxy-2-methyl-1,4-naphthoquinone, indicated in the literature.[33)]

The values of $E^{O'}$ and $\mathrm{p}K_\mathrm{a}'$ for all possible equilibria between the conjugated forms of 1,4-naphthoquinone are quoted in Tables 1 and 2. The uncertinities involved in the estimation of each $E^{O'}$ and $\mathrm{p}K_\mathrm{a}'$ value were calculated from different linear segments of potential-pH diagrams by a common method described in literatures.[34)] A comparison of the data obtained in this study with



Scheme 3.

Table 1. Redox Equilibria in the NQCPE's Systems

Electrode	Reaction	$E^{O'}$(V/SHE)$^{a)}$	$E^{O'}$(V/SHE)	$E^{O'}(V/SHE)^{b)}$	Reference
1,4-NQCPE:	$Q+2e+2H^+=H_2Q$	0.169±0.002	0.409±0.002	0.485	35),38)
	$Q+2e+H^+=HQ^-$	−0.075±0.006	0.166±0.006		
	$2Q+4e+H^+=Q^2\cdot HQ^-$	−0.248±0.008	−0.007±0.008		
PCPE:	$HQ+2e+2H^+=H_3Q$	0.072±0.004	0.313±0.004	0.343	33)
	$HQ+2e+H^+=H_2Q^-$	−0.106±0.005	0.135±0.005	0.142	33)
	$Q^-\cdot HQ+4e+3H^+=2H_2Q^-$	0.071±0.008	0.312±0.008	0.274	33)
	$Q^-\cdot HQ+4e+2H^+=H_2Q^-\cdot HQ^{2-}$	−0.178±0.008	0.063±0.008	0.097	33)
JCPE:	$HQ+2e+2H^+=H_3Q$	0.146±0.002	0.387±0.002	0.417	33)
				0.428	37)
	$HQ+2e+H^+=H_2Q^-$	−0.011±0.003	0.230±0.003	0.213	33)
	$Q^-\cdot HQ+4e+3H^+=2H_2Q^-$	0.121±0.009	0.362±0.009	0.339	33)
DCNQCPE:	$CQ+2e+2H^+=H_2CQ$	0.179±0.002	0.420±0.002		
	$CQ+2e+H^+=HCQ^-$	−0.028±0.006	0.213±0.006		
	$2CQ+4e+H^+=CQ^{2-}\cdot HCQ^-$	−0.209±0.008	0.032±0.008		
ACNQCPE:	$QNH_2+2e+3H^+=H_2QNH_3{}^+$	0.061±0.009	0.302±0.009		
	$QNH_2+2e+2H^+=H_2QNH_2$	−0.020±0.007	0.221±0.007		
	$2QNH_2+4e+3H^+=H_2QNH_2\cdot HQNH_2{}^-$	−0.122±0.005	0.119±0.005		
	$QNH_2+2e+H^+=H_2QNH_2{}^-$	−0.210±0.003	0.031±0.003		

a) $E^{o'}$, formal potential at 95% confidence limits, obtained from the intercept of each linear segment with Y axis in Figs. 2, 5, 6, 7, and 8 respectively. b) Literature data.

Table 2. Acid-Base Equilibria in the NQCPE's Systems

Electrode	Reaction	$\mathrm{p}K_\mathrm{a}'^{b)}$	$\mathrm{p}K_\mathrm{a}'^{c)}$	Reference
1,4-NQCPE:	$H_2Q=HQ^-+H^+$	9.67±0.08	9.3,9.4	35),43)
	$2HQ^-=Q^{2-}\cdot HQ^-+H^+$	11.74±0.09	10.9,11.2	43),35)
PCPE:	$2HQ=Q^-\cdot HQ+H^+$	10.31±0.05	9.01	33)
	$H_3Q=H_2Q^-+H^+$	6.62±0.10	6.83	33)
	$2H_2Q^-=H_2Q^-\cdot HQ^{2-}+H^+$	12.33±0.13	12.10	33)
JCPE:	$2HQ=Q^-\cdot HQ+H^+$	9.60±0.07	8.60,8.0,8.70	33),37),44)
	$H_3Q=H_2Q^-+H^+$	6.40±0.07	6.96,6.60,7.00	33),37),44)
DCNQCPE:	$H_2CQ=HCQ^-+H^+$	8.30±0.06		
	$2HCQ^-=CQ^{2-}\cdot HCQ^-+H^+$	10.75±0.05		
ACNQCPE:	$H_2QNH_3{}^+=H_2QNH_2+H^+$	2.55±0.14		
	$2H_2QNH_2=H_2QNH_2\cdot HQNH_2{}^-+H^+$	6.70±0.09		
	$H_2QNH_2\cdot HQNH_2{}^-=2HQNH_2{}^-+H^+$	8.76±0.02		

b) The values indicate the apparent acidity constant at 95% confidence limits. c) Literature data.

those determined by other research groups[35—38] shows some discrepancies. This can be mainly due to the fact that all studies accomplished by others correspond to solvated forms of 1,4-naphthoquinone in aqueous, non-aqueous or mixed solvents media.[37,39—42] In our case, however, the compound is fixed on the surface of the electrode. Therefore, as is expected, the literature data for a comparison will be somewhat incoherent.

The shift of the anodic and cathodic peaks towards negative potentials by increasing the solution pH arise from the pH dependency of the electrode process. However, it is expected that the peak-to-peak separation (ΔE_p) remains constant during the displacement of peaks; however, the dependence of ΔE_p on the pH is irregular. Indeed, it has been shown that the electrochemical reversibility of the immobilized quinones is affected by the solution pH; this is manifested in the dependence of ΔE_p on the pH value.[18] Moreover, an effect of the pH on the rate constant of the electrochemical process is known for quinones, though this dependence is usually more complicated and non-monotonic.[44] In the case of 1,4-NQCPE, it seems that the irregular variation of ΔE_p with the solution pH has an origin similar to that of the immobilized quinone electrodes.[18] It has also been shown that in the case of quinone- immobilized electrodes the reversibility of the electrochemical process increases with increasing solution pH.[18] Such an effect is clearly observed for 1,4-NQCPE when the solution pH become>6. Parallel to the shift in the peak potentials towards more negative potentials by increasing the solution pH, the peak currents also gradually decrease. This variation is rapid for pHs<4 and pH>10; in pHs between 4 and 10, however the peak currents vary slowly. This effect is valid with some approximation in the range of the working pH for all naphthoquinone-spiked carbon-paste electrodes. Figure 3 illustrates such a behavior for a plumbagin-spiked electrode.

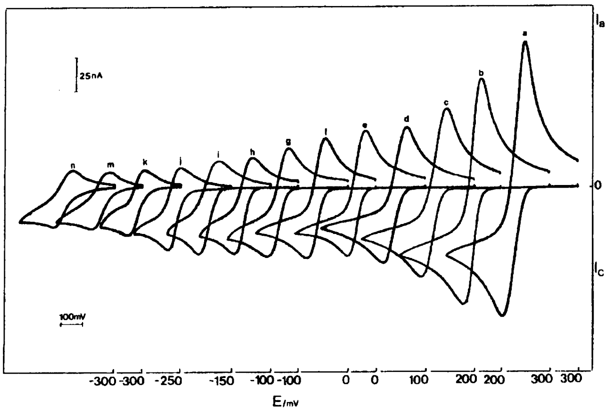


Fig. 3. Cyclic voltammograms of PCPE at scan rate of 5 mV s^{-1} in various solution pH, a) 1.01, b) 2.05, c) 3.02, d) 4.00, e) 5.01, f) 6.02, g) 7.00, h) 8.04, i) 9.02, j) 10.01, k) 11.00, m) 12.00, n) 13.01. Potentials refers to the starting potential of scan.

For 1,4-NQCPE, at a solution pH 0.51, the difference between the peak potential of the anodic and cathodic peaks (ΔE_p) was about 30 mV, and independent of v at low scan rates (e.g. $\Delta E_p=34$ mV for 1,4-naphthoquinone at $v<50$ mV s^{-1}) (Fig. 4). Therefore, at this limited range of the sweep rate, ΔE_p is in quite good agreement with a reversible electron- transfer process. At a higher scan rate (500 mV s^{-1} $>v>$ 50 mV s^{-1}) ΔE_p become proportional to $\log v$ (Fig. 4), while the formal potential remains constant at various potential scan rates. This allows the suggestion that the cathodic and anodic transfer coefficients (α_c and α_a) are about 0.5 under this condition.[18]

2) 5-Hydroxy-2-methyl-1,4-naphthoquinone (Plumbagin) Spiked Carbon-Paste Electrode (PCPE). The behavior of this electrode was studied in aqueous buffered solutions at pH ranging from 0.5 to 13.52 in the absence of dioxygen. An $E_{1/2}$–pH diagram of this electrode is shown in Fig. 5; five different forms of plumbagin can exist in various solution pH, three of which are reduced forms and two others are oxidized forms. The slopes of this diagram at various regions of pH are as follows: −58 mV (for pH<6.62), −31 mV (for 6.62<pH<10.3), −48 mV (for 10.3<pH<12.33), and −28 mV (for pH>12.33) per pH unit. The −48 mV/pH unit refers to the fact that at this range of pH values, the oxidized form exists as a dimer,[33] and the electrode reaction is a four-electron, three-proton reduction of this dimer to the dehydro-anionic form (H_2Q^-) and a subsequent re-oxidation of this product back to the dimer (Scheme 4).

However, at pH>12.33 both the oxidized and reduced forms exist as dimers, and the −28 mV/pH unit refers

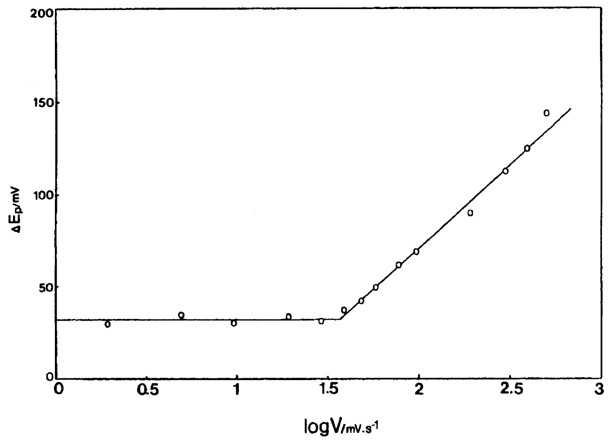
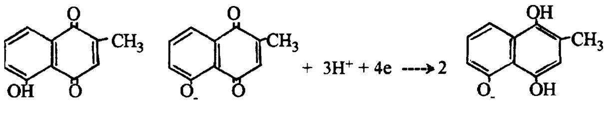


Fig. 4. Dependence of the peak-to-peak separation, ΔE_p, on the potential scan rate for 1,4-NQCPE in H_2SO_4 0.5 M.



Scheme 4.

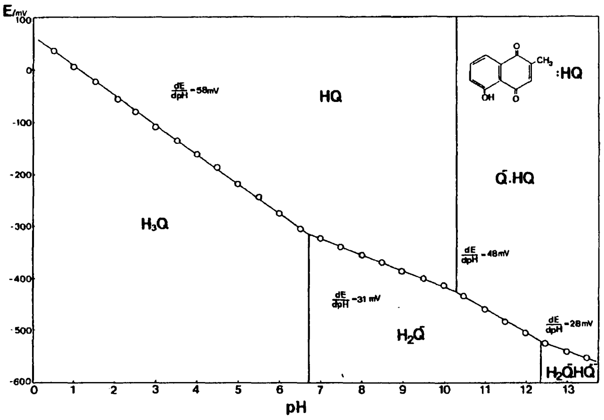


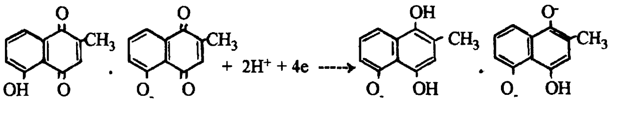
Fig. 5. pH–potential diagram for PCPE. The symbol HQ stands for the molecule of plumbagin shown in the figure.

to a four-electron, two proton redox process (Scheme 5).

The data given in Tables 1 and 2 are the apparent standard redox potentials ($E^{O'}$) and the pK'_a values of different forms, which exist in various pH at the surface of an electrode. These values are also compared with other literature data.

3) 5-Hydroxy-1,4-naphthoquinone (Juglone)-Spiked Carbon-Paste Electrode (JCPE). The electrochemical behavior of JCPE has been studied in buffered solutions at pH between 0.5—13 by cyclic voltammetry. The half-wave potentials ($E_{1/2}$) are plotted as a function of the solution pH in Fig. 6. As shown in this figure, three linear regions can be distinguished on the potential-pH diagram of a juglone-spiked electrode with the shapes of −56.5 mV (pH<6.40), −31.5 mV (6.40<pH<9.60), and −45 mV (pH>9.60) per unit of pH, respectively. Accordingly, four different forms of juglone can be obtained at the surface of an electrode following a change in the solution pH, two of which are the oxidized forms; the other two are the reduced forms. In the pH range below 6.40, both the oxidized and reduced forms of juglone on the electrode surface remain unchanged. A slope of −45 mV per pH unit, in pH over 9.60, refer to a redox process with a proton/electron ratio of 3 : 4. This can be explained by the formation of quinone-quinol dimers, similar to the case of plumbagin.[33] The apparent standard redox potentials. $E^{O'}$ and pK'_a values of different forms of juglone at the surface of electrode are listed in Tables 1 and 2.

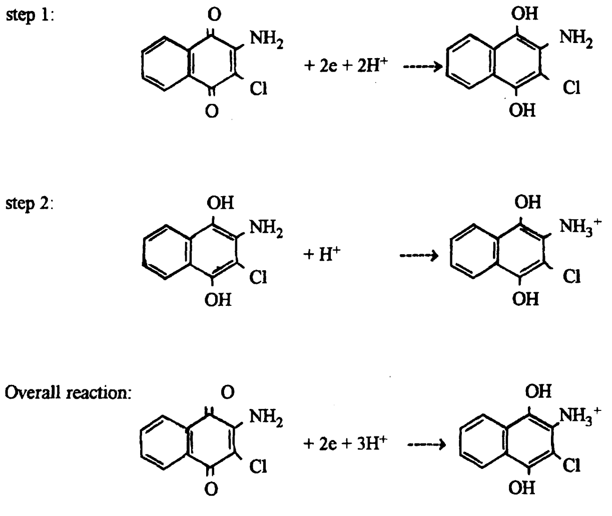
4) 2,3-Dichloro-1,4-naphthoquinone-Spiked Carbon-Paste Electrode (DCNQCPE). The electrochemical behavior of DCNQCPE has been studied in various buffered aqueous solutions (pH=0.5 to 13.5) by cyclic voltammetry. The potential-pH diagram of this electrode is illustrated in Fig. 7. This diagram presents three linear segments with slopes of: −55 mV (at pH<8.30), −30 mV (at 8.30<pH<10.75), and −13.1 mV (at pH>10.75) per pH unit. A slope of −13.1 mV/pH unit corresponds to a four-electron, one-proton redox process which is similar to the case of 1,4-NQCPE. According to the potential–pH diagram, four different forms can be found during the variation of the pH; one of these forms is oxidized and three others are reduced forms. The data resulting from this diagram, $E^{O'}$ and pK'_a values, are summarized in Tables 1 and 2.



Scheme 5.

5) 2-Amino-3-chloro-1,4-naphthoquinone-Spiked Carbon-Paste Electrode (ACNQCPE). A cyclic voltammetric study of ACNQCPE has been accomplished in aqueous solution with various buffered pH (pH=0.25 to 12). The corresponding potential–pH diagram is presented in Fig. 8. Four linear segments were obtained from this diagram, having slopes of: −88.97 mV (at pH<2.50), −57.11 mV (2.50<pH<6.71), −41.81 mV (6.71<pH<8.76), and −31.84 mV (at pH>8.76) per pH unit, respectively. The slope of −88.97 mV/pH unit refers to a two-electron, three-proton redox process (Scheme 6).

The conversion of the quinonic group to a phenolic group during the electrochemical reduction of 2-amino-3-chloro-1,4-naphthoquinone (step 1) causes an increase in the basicity of this compound, because of the involvement of a nonbonding electron pair on the nitrogen atom in the amine group by tautomerization, mesomeric interaction and an inductive effect of carbonyl group on the quinonic ring.[47] Such a situation provokes the reduction of 2-amino-3-chloro-1,4-naphthoquinone within a two-electron, three-proton process, as presented by the overall reaction in Scheme 6. The slopes of −57.11, −41.81, and −31.84 mV per pH unit indicate the transfer of two-proton, two-electron; four-electron, three-proton; and two-electron, one-proton in redox processes, respectively. Accordingly, five forms result from a variation of solution pH; one of them is



Scheme 6.

an oxidized form, while four others are reduced forms at the electrode surface.

The apparent standard redox potentials and the pK'_a values of different forms obtained from this potential–pH diagram are given in Tables 1 and 2.

6) Effect of a Borate Buffer. The use of a borate buffer ($12 > \text{pH} > 8$) instead of a phosphate buffer has no influence on the shape and position of cyclic voltammograms obtained for a 1,4-naphthoquinone-spiked electrode. When the paste electrode is spiked by plumbagin, the use of a borate buffer affects the cyclic voltammograms compared with that observed in solutions buffered with phosphate. This variation includes a disappearance of the oxidation peak corresponding to the reduction peak of plumbagin and the appearance of a new broad oxidation peak at more positive potentials. The height of this later peak increases with increasing the concentration of the borate anion at a fixed solution pH (Fig. 9B). This can be associated with the formation of a complex between borate anion and the *ortho*-quinol resulting from a reduction of plumbagin at the surface of the electrode and a subsequent oxidation of the formed complex at more positive potentials. The complexation between *o*-quinols and the borate anion in an aqueous–MeOH solution was previously reported by M.O.F.Goulart et al.[44] On the other hand, the height of this new oxidation peak decreases with increasing solution pH, and disappears when the pH becomes>11 (Fig. 9A). This is parallel to the reappearance of the quinol oxidation peak, which is the sign of a destruction of the borate-*o*-quinol complex at the electrode surface (see Fig. 3). Moreover, this effect may be related to the formation of a quinone–quinol dimer at a pH over 10.3. The electrochemical behavior of JCPE in the presence of the borate anion is similar to that observed for PCPE.

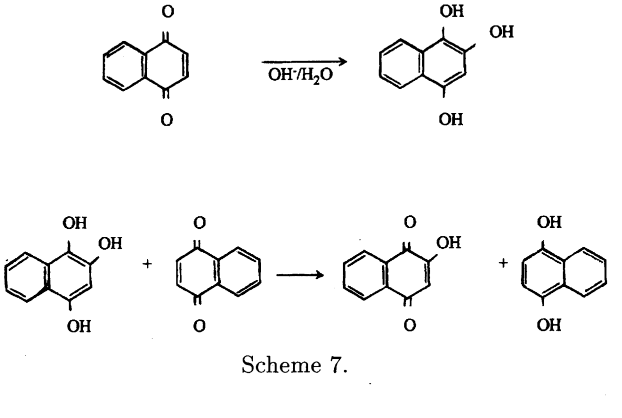
7) Decomposition of NQCPE's in Alkaline Solution. Of the five 1,4-naphthoquinones spiked carbon-paste electrodes, four of them exhibited significant decomposition in an alkaline solution; only PCPE is very stable in an alkaline medium in the region of the studied solution pH's (pH<13.52). This may arise from the effect of either a methyl substituent on one quinonoide double bond or a hydroxy substituent on a fused benzene ring protecting both quinonoid double bonds.[35] Contrarily to a modified electrode with poly (plumbagin),[13] this electrode is very stable in all solution pHs.

1,4-NQCPE begins to decompose in a solution having a pH above 10.1. Decomposition appears as a prepeak in the cyclic voltammograms (Fig. 10B). This prepeak is obviously observed at a slow scan rate of the potential (5 mV s^{-1}). The result is in quite satisfactory agreement with those reported by other research groups.[33,35,47]

In a solution with pH>9.5, the DCNQCPE begins to decompose much slower than do other electrodes, because at a 2 mV s^{-1} scan rate a prepeak is observed when the pH exceeds 9.5; at a scan rate of 10 mV s^{-1}, however, the prepeak appears in a pH of more than 13.5 (Fig. 10A). The decomposition of JCPE and ACNQCPE begins at pH>11 and pH>9.51, respectively. The decomposition of ACNQCPE at a lower alkaline pH can be attributed to the alkaline hydrolysis of the amino group, as reported in the literature for similar quinones.[48] The decomposition of these NQCPE's become rapid when the solution pH is increased. The decomposition of quinones at the surface of electrodes immersed in an alkaline solution is caused by the addition of OH$^-$ ions at the quinone moiety, leading, among other products, to the formation of the corresponding hydroquinone.[35,47,49] The reactions involved are likely to be due to a nucleophilic attack of the hydroxide ion on a quinonoid double bond, giving the hydroxy-substituted hydroquinone, which may then be oxidized by an unreacted quinone, similar to the case of 1,4-naphthoquinone.[35] This is illustrated below in Scheme 7 for 1,4-naphthoquinone; analogous reactions are possible for the other quinones.

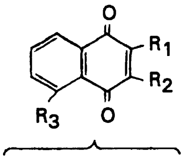
8) The Effects of Substituents. Several effects may be induced by the arrival of substituents on the quinone function. The electron-donating or -withdrawing properties of the substituent may influence the electron transfer by the quinone moiety and then may be caused a shift in the half-wave potential to more negative or more positive potentials respectively. A change in the redox mechanism may occur at each pH value of the solution; for example, and additional acid-base reaction can result. Steric effects resulting due to substituents may also play a role in the reduction process. Finally, the formation of electroactive degradation products, hydrogen bonds formed between the carbonyl function (acceptor) and the substituent of interest (donor), can sometimes influence the electrochemical properties.

Therefore, as a measure of the effects of some substituents on the electrochemical properties of 1,4-naphthoquinone, the half-wave potentials of all surface compounds studied at one particular pH are given in Table 3. For this purpose, pH 5 was selected as a common point, because all surface compounds are reduced in a two-proton, two-electron process at this pH (see



Scheme 7.

Table 3. The Values of Half-Wave Potentials, $E_{1/2}$, of NQCPE's in pH=5

Structure			Compound	$E_{1/2}$ (V/SCE) (±0.001)
				
R_1:	R_2:	R_3:		
H	H	H	1,4-Naphthoquinone	−0.096
CH_3	H	OH	Plumbagin	−0.304
H	H	OH	Juglone	−0.140
Cl	Cl	H	2,3-Dichloro-1,4-naphthoquinone	−0.098
NH_2	Cl	H	2-Amino-3-chloro-1,4-naphthoquinone	−0.304

Figs. 2, 5, 6, 7, and 8).

i) Hydroxy Substituent: The substitution of a hydroxy group at position 5 of the quinone moiety in 1,4-naphthoquinone (JCPE) causes a change in the reduction mechanism, as can be observed in the $E_{1/2}$–pH plots for the compound (see Figs. 2 and 6). Similar effects have been reported for some hydroxy-1,4-naphthoquinone by other workers.[33,47] In addition, such a substitution results in a shift of $E_{1/2}$ of about 44 mV to more negative values, which is due to the electron-donating character of the OH group (comparable to 215 mV for hydroxy substituent in 2-position).[47]

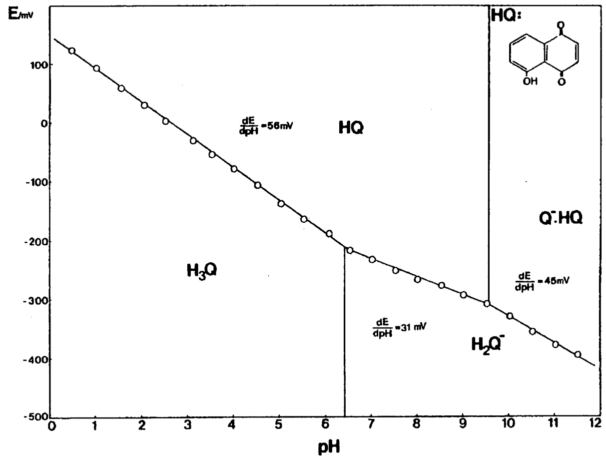


Fig. 6. pH–potential diagram for JCPE. The symbol HQ stands for the molecule of juglone shown in the figure.

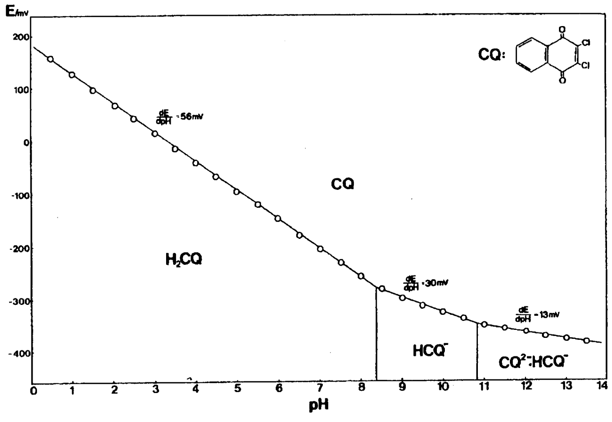


Fig. 7. pH–potential diagram for DCNQCPE. The symbol CQ stands for the molecule of 2,3-dichloro-1, 4-naphthoquinone shown in the figure.

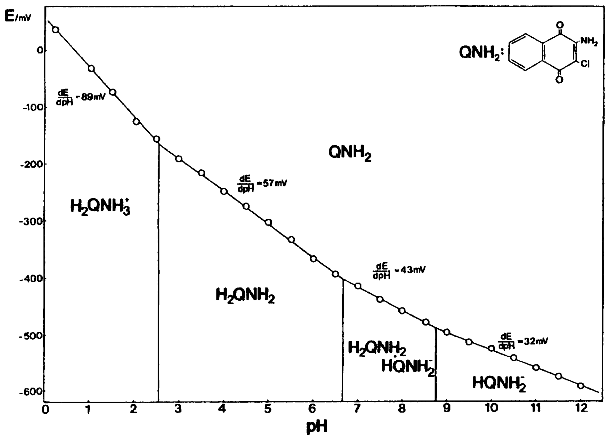


Fig. 8. pH–potential diagram for ACNQCPE. The symbol QNH_2 stands for the molecule of this compound shown in the figure.

The substitution of one methyl group at the 2-position of juglone (plumbagin) results in a shift of $E_{1/2}$ of about 124 mV to more negative values against 1,4-naphthoquinone, which is due to the simultaneous electron-donating properties of the methyl and hydroxy groups. Moreover, a change in the reduction mechanism can be observed following these substitutions (see Figs. 2, 5, and 6).

ii) Amino Substituents: A comparison between the 1,4-naphthoquinone and amino- and chloro-substituted one shows a shift of 208 mV in $E_{1/2}$ to more negative values. This result is related to the electron-donating character of the amino group, because a mesomeric interaction between the lone pair on nitrogen and the quinone moiety can occur, which explains this shift in $E_{1/2}$.[47,50] Also, hydrogen bonds between the

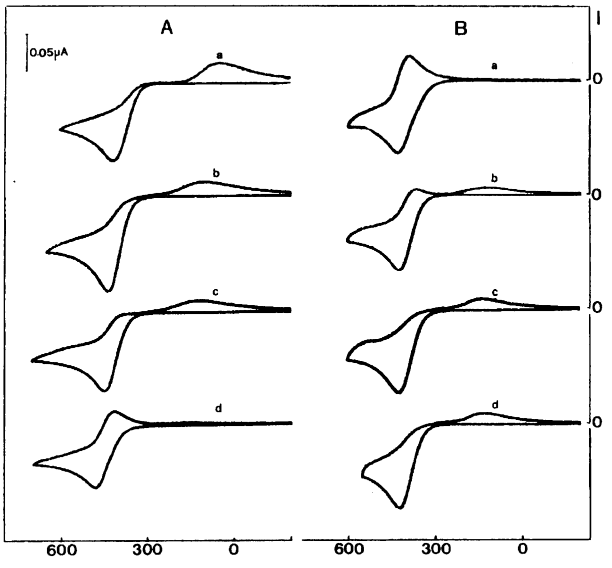


Fig. 9. Cyclic voltammograms of plumbagin in borate buffer at: A) various solution pH: a) 8.23 b) 9.17, c) 10.01 and d) 11.00, (BO_2^-)=0.1 M). B) various concentration of borate anion: a) 1 mM, b) 5 mM, c) 50 mM, d) 100 mM, (NaCl)=0.1 M, pH=9.3), scan rate 5 mV s^{-1}.

amino and carbonyl groups of the quinone moiety may stabilize the quinonoid form, and may thus be partly responsible for the negative shift of $E_{1/2}$.[51]

Finally, $E_{1/2}$ of 1,4-naphthoquinone with two substituents of chloro groups against unsubstituted 1,4-naphthoquinone is shifted a few mV towards negative potentials.

Conclusions

An investigation of the electrochemical behavior of carbon-paste electrodes spiked with some 1,4-naphthoquinone derivatives show nearly reversible properties of such modifying compounds; the formation of different forms with a variation of the solution pH is detected. The values of the formal potential and pK_a' of some different redox and acid-base couples involved in this study were calculated using $E_{1/2}$–pH diagrams. From this study, we would like to point out the possibility of preparing other redox-compound spiked carbon-paste electrodes. This method should allow electrochemical studies of insoluble redox compounds in aqueous media, and, thus, more accurate predictions of the conditions under which specific reactions could be effected. Also, a better understanding of the redox processes can be obtained. This method can also be applied for preparing modified electrodes with redox functions, such as organometallic or organic mediators for slow electrochemical reactions of some biological systems and other function for analytical purposes, such as electrocatalysis and sensors. The advantages of these electrodes are low cost, easy preparation and application, high stability and reproducibility against other modified electrodes.

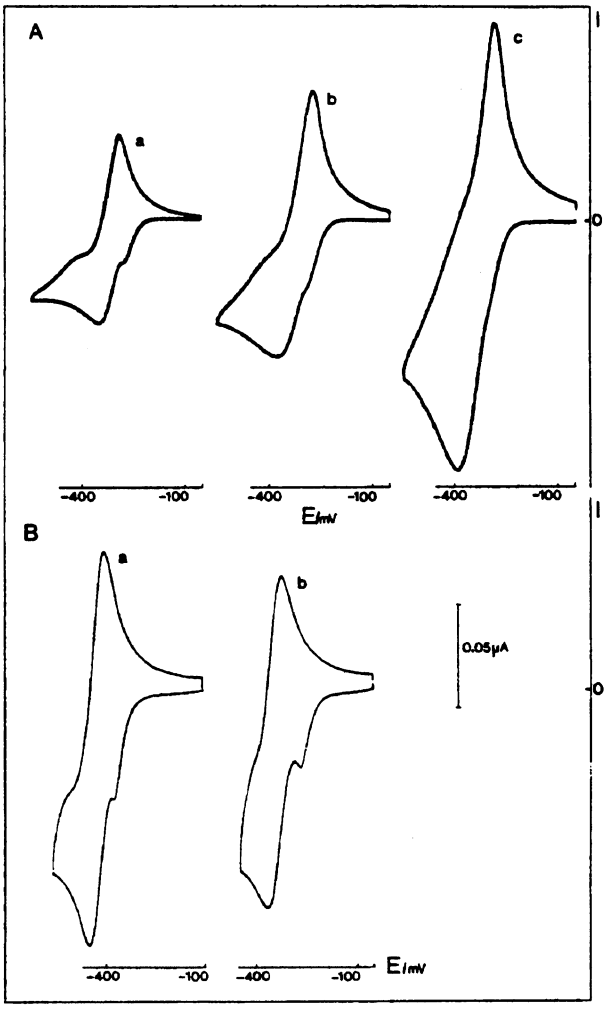


Fig. 10. Cyclic voltammograms of: A) CDNQCPE in solution pH=10 at scan rates: a) 2 mV s^{-1}, b) 5 mV s^{-1}, c) 10 mV s^{-1}. B) 1,4-NQCPE in 0.1 M phosphate buffer: a) pH=10.51 and b) pH=11.51), scan rate 5 mV s^{-1}.

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