

Modified Carbon Paste Electrode: An Electroanalytical Tool for Estimation of Thermodynamic Parameters of Water Insoluble Quinones

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In this paper preparation and aqueous electrochemistry of carbon paste electrodes modified by 11 different water-insoluble o-quinones are described. Potential-pH diagrams were constructed based on estimation of the half-wave potential as a function of pH for each compound. The values of formal potential and pK'_a of some different redox and acid-base couples involved at various pHs were obtained. Furthermore, influence of some substituents on the electrochemical behavior of spiking compounds, their formal potentials and pK'_a values are discussed.

INTRODUCTION

Simple and substituted ortho- and para- quinones constitute a broad range of organic compounds with various interesting activities [1-5]. Many natural substances acquire their effects from the presence of at least one quinonic ring in their structures. The main activities of these compounds correspond to their reversible electron transfer behavior [6]. It is also found that in many cases, the electron transfer process occurs through two one-electron steps via a semiquinone free radical production mechanism [7]. The reduced form of quinonic compounds produces ortho or para diphenols which can appear as undissociated (acid) or dissociated (mono or dibasic) forms depending on pH. Therefore, determining the formal potential of quinonic compounds and pK'_a of their reduced forms, specially in water, is of importance. This is easily achieved in the case of simple and water soluble quinones, or those having hydrophilic substituents, using electrochemical or spectroscopic methods [8]. While, for water insoluble quinones, non-aqueous or mixed solvents are used [7,9]. Recently, Petrova et al.

have demonstrated the possibility of estimating formal potentials and acid-base constants of some weakly soluble or insoluble hydroxy-1, 4-naphthoquinone of plant origin in water using thin layer voltammetry on a pyrolytic graphite electrode [10]. In this method, the weakly soluble naphthoquinones were used as mM solutions in water, whereas the water insoluble one was deposited as a very thin film layer on the surface of a carbon working electrode from dimethylformamide solution. More recently, the authors have shown that the carbon paste electrodes modified by water-insoluble naphthoquinones are the suitable tools for distinguishing the different redox and acid-base forms of modifiers during the variation of electrode potential and pH. The plot of potential-pH diagrams easily makes possible the estimation of formal potentials and acid-base equilibrium constants, as well as the occurrence of any dimerization process following the hydrogen bond formation [11]. Moreover, the data obtained by this procedure are often in good agreement with those of other methods.

In this paper, the electrochemical properties of carbon paste electrodes spiked with 11 different water insoluble o-quinones in various buffered aqueous solutions studied by cyclic voltammetry are reported. The formal potentials of different redox couples, together with the dissociation constants of various acid-base couples involved in the electrode processes, are estimated and the effects of substituents on the o-quinone activity are also discussed.

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EXPERIMENTAL

Chemicals

9,10-phenanthrenequinone and 4-amino-o-naphthoquinone, purchased from Aldrich, were used without further purification. Other o-quinones, coumestans and benzofurane derivatives were synthesized electrochemically and utilized after purification [12-16]. The buffers used at different pH were $\text{H}_2\text{SO}_4 + \text{NaOH}$ (for pH = 0.5-1.5), $\text{H}_3\text{PO}_4 + \text{NaOH}$ (for pH = 2-3), acetate buffer (for pH = 3.5-6) and $\text{NaH}_2\text{PO}_4 + \text{NaOH}$ (for pH = 6.5-12). All buffers were prepared in bidistilled water by reagent grade chemicals from Aldrich or Merck with ionic strength adjusted at 0.3 M. Nitrogen gas with a purity of 99,999% was used to remove oxygen from solutions during the experiments.

Working Electrode

The working electrodes were constructed in a way similar to that described in [11]. In all cases, the paste was spiked by 1% (w/w) of the desired o-quinone.

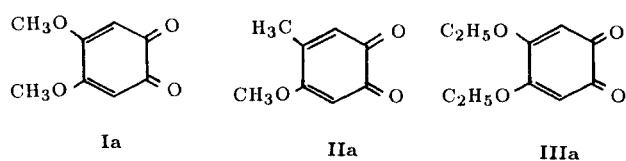
Instrumentation

Cyclic voltammetry was carried out at a thermostated temperature of $25 \pm 1^\circ\text{C}$ using a potentiostat (Polarcord 626 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

4,5-Disubstituted-O-Benzoquinone Spiked Carbon Paste Electrodes

Three disubstituted o-benzoquinone, namely 4,5-dimethoxy-, (Ia), 4-methoxy-5-methyl-, (IIa) and 4,5-diethoxy-, (IIIa), o-benzoquinone (Scheme 1) were used as paste spiking materials. The electrochemical behavior of constructed carbon paste electrodes were studied by cyclic voltammetry in aqueous buffered solutions at pH between 0.5-12 in the absence of dioxygen. Over a potential range corresponding to the electroactivity domain of the solvent, cyclic voltammograms of all o-quinones show a single reduction peak and a corresponding oxidation peak (Figure 1a). The peak current ratio, ($I_{p,a}/I_{p,c}$), is nearly equal to unity



Scheme 1

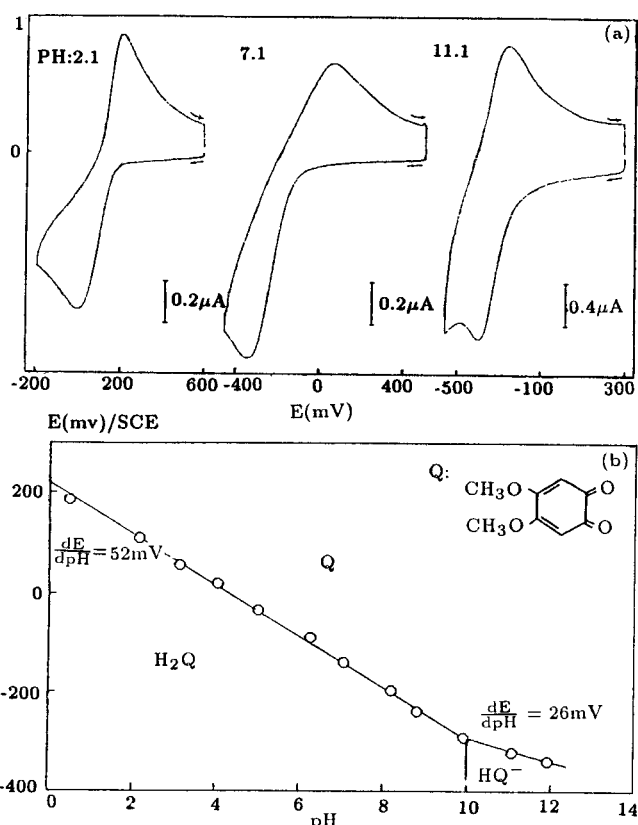


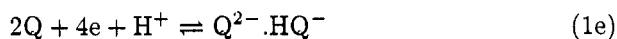
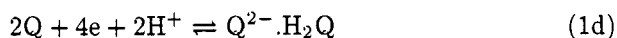
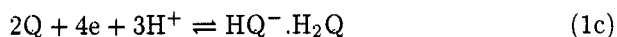
Figure 1. a) Cyclic voltammograms of 4,5-dimethoxy-o-benzoquinone spiked carbon paste electrode recorded at three different pH. Scan rate: 50 mVs^{-1} , b) $E_{1/2}$ -pH diagram of 4,5-dimethoxy-o-benzoquinone plotted as described in text.

and remains almost constant with respect to change in pH.

Whereas, the peak potentials are shifted towards more negative values with increase in pH, indicating the pH dependency of electrode processes. However, the variation of ΔE_p ($E_{p,a} - E_{p,c}$), with respect to pH, is irregular and it seems that this irregularity has an origin similar to that of the immobilized quinone electrodes [17,18]. It has also been shown that in the case of quinone modified carbon paste electrodes, the reversibility of the electrochemical processes varies with changes in pH [11]. Such an effect is clearly observed in the present case. However, considering the ΔE_p values, the processes approach full-reversibility for $9 > \text{pH} > 2$. Consequently, assuming that the electrode process has a nernstian behavior at low scan rates and that both anodic and cathodic peaks shift equally with increase in the potential sweep rate ($\alpha_c \sim \alpha_a \sim 0.5$) [11], the half-wave potentials ($E_{1/2}$) were calculated as the average of the anodic and cathodic peak potentials of the cyclic voltammograms, $[(E_{p,a} + E_{p,c})/2]$ [17], recorded at a potential scan rate of 50 mVs^{-1} . A potential-pH diagram is constructed for each compound by plotting the calculated $E_{1/2}$ values as a

function of pH. Figure 1b shows such a diagram for 4,5-dimethoxy-*o*-benzoquinone(I). In the case of (I) and (II), the $E_{1/2}$ -pH diagrams comprise two linear segments with different slopes of -52 mV(pH < 10) and -27 mV (pH > 10) for (I) and -52 mV (pH < 10.8) and -23 mV (pH > 10.8) for (II) per unit of pH. This means that parallel to the variation of pH and electrode potential, three different forms can be produced for each compound at the electrode surface, one in an oxidized form and the other two in reduced forms.

On the basis of the above mentioned slopes, it can be concluded that the electrode surface reactions occurring at the pH below 10 and 10.8 are the two-electron, two-proton processes involving the reduction of (Ia) and (IIa) to the corresponding *o*-hydroquinones, i.e., (Ib) and (IIb), respectively, in a forward scan and the back-oxidation of the latter products to (Ia) and (IIa) in a reverse scan (Equation 1a). Whereas, the electrode surface reactions at pH ranges higher than 10, for I, and 10.8, for II, correspond to the one-proton, two-electron processes (Equation 1b).



However, in the case of these quinones, the values obtained for both linear segments of $E_{1/2}$ -pH plot are lower than the expected values for two-electron, two-proton, (ca. ~ 59 mV) and two-electron, one-proton, (ca. ~ 29 mV), processes respectively. Such a situation is assumed for the production of a dimerized species by analogy with the case of some quinonic compounds indicated in the literature [10,11] (Equations 1c-1e). In other word, these quinones can be reduced by some parallel ways, mainly as Schemes 1a and 1b and partially via other ways. The more the dimerization processes are dominant, the less the slopes are than the expected Nernstian values.

The values of $E^{\circ'}$ and pK'_a for all possible equilibria between the conjugated forms of I and II are quoted in Tables 1 and 2. A comparison of the data obtained in this study with those determined by other means [12,13] shows some discrepancy. This can be mainly due to the fact that the other results correspond to the solvated forms of *o*-quinones in non-aqueous solvent; whereas, in the case presented here, the compound is fixed on the surface of the electrode. Therefore, it is logical that incoherence would be observed.

On the other hand, the pK'_a values obtained by this method for the reduced forms of I and II (i.e.,

Ib and IIb) agree sufficiently with those predicted theoretically by the Hammett equation, proposed for substituted phenols [19] (see Table 2). Moreover, it is observed that pK'_a values vary in the following order of Ib < IIb, which is probably due to an interaction between 5-methoxy- and 1-hydroxy- groups in Ib, enhancing the acidity of the latter product. Such behavior has already been reported for 4-methoxy- and 4-methylcatechol [20,21].

Now, a comparison between the formal potentials of 4-methoxy-, 4-methoxy-5-methyl- and 4,5-dimethoxy-*o*-benzoquinone appears very interesting. The electrochemical behavior of 4-methoxy-*o*-benzoquinone was investigated by cyclic voltammetry at gold electrode in aqueous solutions with a buffered pH up to 8, since for pH higher than this value *o*-quinone is decomposed [22]. The $E_{1/2}$ -pH diagram shows a single straight line for full pH range studied here and a formal potential of 0.422 V/SCE was also reported. As expected, substitution of a methyl group with an electron donating character in position 5 of 4-methoxy-*o*-benzoquinone increases the electron density of the benzene cycle and facilitates its oxidation, appearing as a 200 mV decrease in the formal potential of 5-methoxy- substituted compound compared to that of the unsubstituted one. Moreover, 5-methoxy-substituted compound is more stable and no decomposition is observed for it at pH > 8, which is resulted from the occupation of 4 and 5 positions on the benzene ring.

On the other hand, methoxy group is known to exhibit a more electron donating character than the methyl group and, hence, the substitution of methyl by methoxy in IIa produces Ia and practically increases the electron density of the benzene ring. This causes a minor shift of formal potential of Ia towards less positive values (see Table 1).

Cyclic voltammetry of 4,5-diethoxy-*o*-benzoquinone, (IIIa), spiked carbon paste electrode in aqueous solutions exhibits the voltammograms with higher ΔE_p than those obtained for I and II. The peak separation increases with an increase in pH and this restrains the plot of $E_{1/2}$ -pH diagram beyond pH ~ 7 (see Figure 2). From this diagram, four different forms, one oxidized and three reduced, can be distinguished for different pH and electrode potentials. The $E_{1/2}$ -pH plot shows also three linear regions with slopes of -46 , -29 and -14 mV per unit of pH, respectively. On the basis of these values and assumption of a nearly Nernstian behavior for electrode surface processes, one can deduce the number of protons involved in each process. At pH < $pK_{a1} = 3.22$ and for $dE/dpH = -46$ mV, a three-proton, four-electron process is considered (Equation 1c). At $3.22 < pH < 4.94$ and for $dE/dpH = -29$ mV, a two-proton, four-electron process occurs (Equation 1d).

Table 1. Redox equilibria at the surface of some o-quinone spiked carbon paste electrodes.

Spiking O-Quinone	Redox Couple	Electrode Reaction	E ^{o'} _a (V/SCE)	E ^{o'} (V/SHE)	E ^{o'} (V/SHE)	Ref.
I	Ia/Ib	${}^b\text{Q} + 2\text{e} + 2\text{H}^+ = \text{H}_2\text{Q}$	0.218	0.459	0.461 ^c	[12,13]
	Ia/Ic	$\text{Q} + 2\text{e} + \text{H}^+ = \text{HQ}^-$	-0.050	0.191		
II	IIa/IIb	$\text{Q} + 2\text{e} + 2\text{H}^+ = \text{H}_2\text{Q}$	0.227	0.468	0.401 ^c	[12,13]
	IIa/IIc	$\text{Q} + 2\text{e} + \text{H}^+ = \text{HQ}^-$	-0.109	0.132		
III	IIIa/IIIb	$2\text{Q} + 4\text{e} + 3\text{H}^+ = \text{HQ}^- \cdot \text{H}_2\text{Q}$	0.500	0.741	0.663	
	IIIa/IIIc	$2\text{Q} + 4\text{e} + 2\text{H}^+ = \text{Q}^{2-} \cdot \text{H}_2\text{Q}$	0.422	0.663		
or	IIIa/IIId	$2\text{Q} + 4\text{e} + 2\text{H}^+ = \text{HQ}^- \cdot \text{HQ}^-$			0.606	
	IIIa/IIIe	$2\text{Q} + 4\text{e} + \text{H}^+ = \text{Q}^{2-} \cdot \text{HQ}^-$	0.365	0.606		
IV	IVa/IVb	$\text{Q} + 2\text{e} + 2\text{H}^+ = \text{H}_2\text{Q}$	0.578	0.819	0.641	
	IVa/IVc	$\text{Q} + 2\text{e} + \text{H}^+ = \text{HQ}^-$	0.400	0.641		
V	Va/Vb	$\text{Q} + 2\text{e} + 2\text{H}^+ = \text{H}_2\text{Q}$	0.522	0.763	0.541	
	Va/Vc	$\text{Q} + 2\text{e} + \text{H}^+ = \text{HQ}^-$	0.300	0.541		
VI	VIa/VIb	$\text{Q} + 2\text{e} + 2\text{H}^+ = \text{H}_2\text{Q}$	0.526	0.767	0.546	
	VIa/VIc	$\text{Q} + 2\text{e} + \text{H}^+ = \text{HQ}^-$	0.305	0.546		
VII	VIIa/VIIb	$\text{Q} + 2\text{e} + 2\text{H}^+ = \text{H}_2\text{Q}$	0.529	0.770	0.535	
	VIIa/VIIc	$\text{Q} + 2\text{e} + \text{H}^+ = \text{HQ}^-$	0.294	0.535		
VIII	VIIIa/VIIIb	$\text{QH} + 2\text{e} + 2\text{H}^+ = \text{H}_2\text{QH}$	0.615	0.856	0.364	[30]
	VIIIc/VIIIb	$\text{Q}^- + 2\text{e} + 3\text{H}^+ = \text{H}_2\text{QH}$	0.630	0.871		
	VIIIc/VIIId	$\text{Q}^- + 2\text{e} + 2\text{H}^+ = \text{H}_2\text{Q}^-$	0.575	0.816		
	VIIIc/VIIIe	$2\text{Q}^- + 4\text{e} + 3\text{H}^+ = \text{HQ}^{2-} \cdot \text{H}_2\text{Q}^-$	0.465	0.706		
IX	IXa/IXb	$\text{Q} + 2\text{e} + 2\text{H}^+ = \text{H}_2\text{Q}$	0.148	0.389	0.364	[30]
	IXa/IXc	$\text{Q} + 2\text{e} + \text{H}^+ = \text{HQ}^-$	-0.058	0.183		
X	Xa'/Xb'	$\text{QNH}_3^+ + 2\text{e} + 2\text{H}^+ = \text{H}_2\text{QNH}_3^+$	0.134	0.375	0.404	
	Xa/Xb'	$\text{QNH}_2 + 2\text{e} + 3\text{H}^+ = \text{H}_2\text{QNH}_3^+$	0.163	0.404		
	Xa/Xb	$\text{QNH}_2 + 2\text{e} + 2\text{H}^+ = \text{H}_2\text{QNH}_2$	0.069	0.310		
XI	XIa/XIb	$\text{Q} + 2\text{e} + 2\text{H}^+ = \text{H}_2\text{Q}$	0.550	0.791	0.650	
	XIa/XIc	$\text{Q} + 2\text{e} + \text{H}^+ = \text{HQ}^-$	0.409	0.650		

a) The values obtained from the intercept of each linear segment with Y axis in $E_{1/2}$ -pH diagrams. b) Q denotes the oxidized form of the redox couple. c) Data obtained for 0.15 M solution of NaNO_3 in methanol at a glassy carbon electrode.

Table 2. Acid-base equilibria at the surface of some o-quinone spiked carbon paste electrode.

Spiking Compound	Acid-Base Couple	Acid-Base Equilibrium	pK' _a	pK' _a ^a
I	Ib/Ic	$\text{H}_2\text{Q} = \text{HQ}^- + \text{H}^+$	10.1	9.54
II	IIb/IIc	$\text{H}_2\text{Q} = \text{HQ}^- + \text{H}^+$	10.8	9.89
III	IIIb/IIIc	$\text{HQ}^- \cdot \text{H}_2\text{Q} = \text{Q}^{2-} \cdot \text{H}_2\text{Q} + \text{H}^+$	3.22	
	IIIc/IIIe	$\text{Q}^{2-} \cdot \text{H}_2\text{Q} = \text{Q}^{2-} \cdot \text{HQ}^- + \text{H}^+$	4.94	
IV	IVb/IVc	$\text{H}_2\text{Q} = \text{HQ}^- + \text{H}^+$	11.0	
V	Vb/Vc	$\text{H}_2\text{Q} = \text{HQ}^- + \text{H}^+$	10.0	
VI	VIb/VIc	$\text{H}_2\text{Q} = \text{HQ}^- + \text{H}^+$	8.6	
VII	VIIb/VIIc	$\text{H}_2\text{Q} = \text{HQ}^- + \text{H}^+$	10.0	
VIII	VIIIb/VIIId	$\text{H}_2\text{QH} = \text{H}_2\text{Q}^- + \text{H}^+$	1.7	
	VIIIa/VIIIC	$\text{HQ} = \text{Q}^- + \text{H}^+$	0.55	
	VIIId/VIIIe	$2\text{H}_2\text{Q}^- = \text{HQ}^{2-} \cdot \text{H}_2\text{Q}^- + \text{H}^+$	8.7	9.7
IX	IXb/IXc	$\text{H}_2\text{Q} = \text{HQ}^- + \text{H}^+$	10.0	9.3
X	Xa'/Xa	$\text{QNH}_3^+ = \text{QNH}_2 + \text{H}^+$	1.1	
	Xb'/Xb	$\text{H}_2\text{QNH}_3^+ = \text{H}_2\text{QNH}_2 + \text{H}^+$	3.7	4.8
XI	XIb/XIc	$\text{H}_2\text{Q} = \text{HQ}^- + \text{H}^+$	6.4	

a) Values calculated using Hammett equation[19].

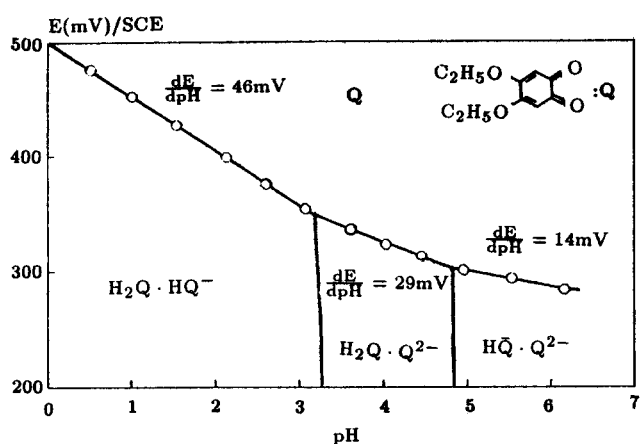


Figure 2. Potential-pH diagram of 4,5-diethoxy-o-benzoquinone obtained by plotting the calculated $E_{1/2}$ values as a function of pH.

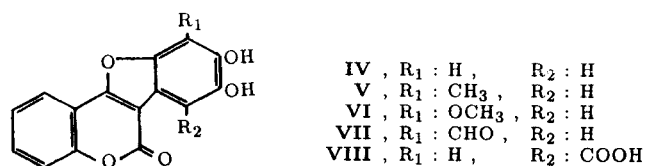
Finally, the process at pH higher than 4.94 is related to a one-proton, four-electron reaction (Equation 1e).

Although the formation of intermolecular hydrogen bond is reported for o-diphenols (catechol) [21], it seems that the high concentration of 4,5-diethoxy-o-benzoquinone molecules in a hydrophobe and non-polar medium of mineral oil favors the hydrogen bond formation between dissociated and undissociated states of formed o-diphenols [8]. The calculated values of $E^{\circ'}$ and pK'_a for all possible equilibria between the conjugated forms of III are quoted in Tables 1 and 2.

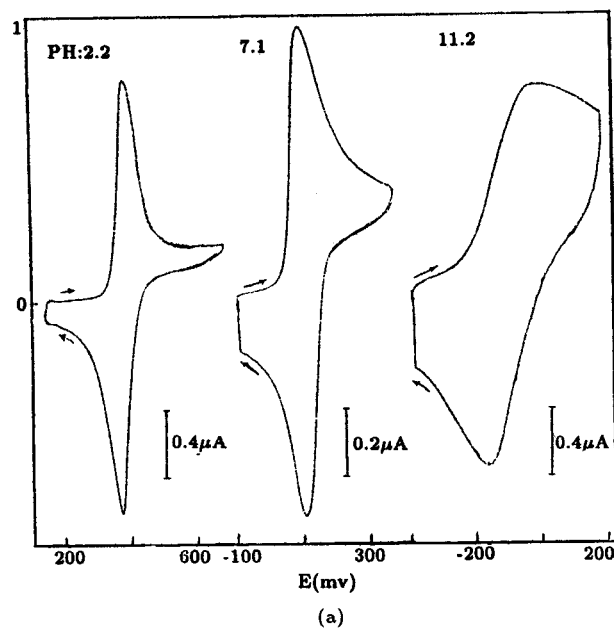
Coumestan Spiked Carbon Paste Electrodes

Coumestans or 6H-benzofuro[3,2-c][1]benzopyrane-6-one [23] are an important class of oxygenated aromatic organic compounds that constitute the basic structure of many natural products with physiological activities [24,25]. This is the reason for many works being directed in the last years around the isolation and identification of these compounds from various natural resources or towards their synthetic preparations [26–29]. Recently, the authors have reported the electro-organic synthesis of some new coumestans that are presented in Scheme 2 [14,15] and here the electro-chemical properties of the carbon paste electrodes spiked by these new and water-insoluble compounds are reported.

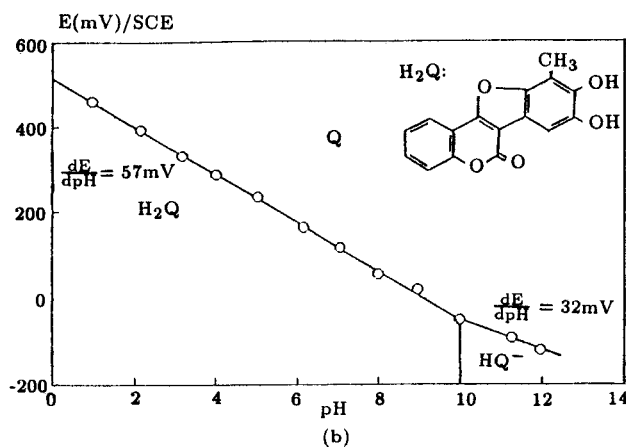
The behavior of these electrodes was studied as before by cyclic voltammetry in aqueous buffered solutions at different pH in the absence of dioxygen.



Scheme 2



(a)

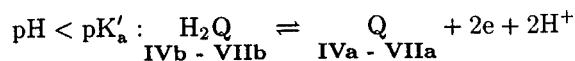


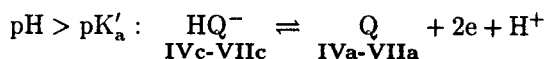
(b)

Figure 3. a) Cyclic voltammograms of 1-methylcoumestan spiked carbon paste electrode recorded at three different pH. Scan rate: 50 mV s^{-1} . b) Potential-pH diagram of 1-methylcoumestan constructed as described in text.

As an example, the cyclic voltammograms and $E_{1/2}$ -pH diagram of carbon paste electrode spiked by coumestan (V) are shown in Figure 3.

Based on $E_{1/2}$ -pH diagrams, all coumestans (IV) to (VII) exhibit three different forms at different electrode potentials and pH, one of which is in an oxidized form and two others are reduced. The slopes of two straight lines of these diagrams at various regions of pH are as follows: $-58 \pm 1 \text{ mV}$ for $\text{pH} < \text{p}K'_a$ and $-31 \pm 1 \text{ mV}$ for $\text{pH} > \text{p}K'_a$ per unit of pH. Assuming a Nernstian behavior for electrode reactions, these slopes refer to the following processes involving two-electron, two-proton and two-electron, one-proton respectively:





The apparent redox potentials, E^o and pK'_a values of different forms of coumestans studied are listed in Tables 1 and 2, respectively.

Cyclic voltammograms of 3-carboxycoumestan, (VIII), spiked carbon paste electrode show also an anodic peak and the corresponding cathodic counterpart in aqueous buffered solutions at pH ranging from 0.5 to 11 (Figure 4a) in the absence of dioxygen. A plot of $E_{1/2}$ versus pH produces the diagram illustrated in Figure 4b. This diagram shows four distinct linear regions with the slopes of -56 mV , -91 mV , -58 mV and -47 mV which correspond to the domains of $\text{pH} < 0.55$, $0.55 > \text{pH} > 1.7$, $1.7 > \text{pH} > 8.7$ and $\text{pH} > 8.7$, respectively. As in the other early cases, a Nernstian behavior for all interfacial processes are again assumed. Therefore, the segments having a slope of about -59 mV correspond to two-electron two-proton reactions, whereas the segments with the slopes higher (-91 mV) and lower (-47 mV) than

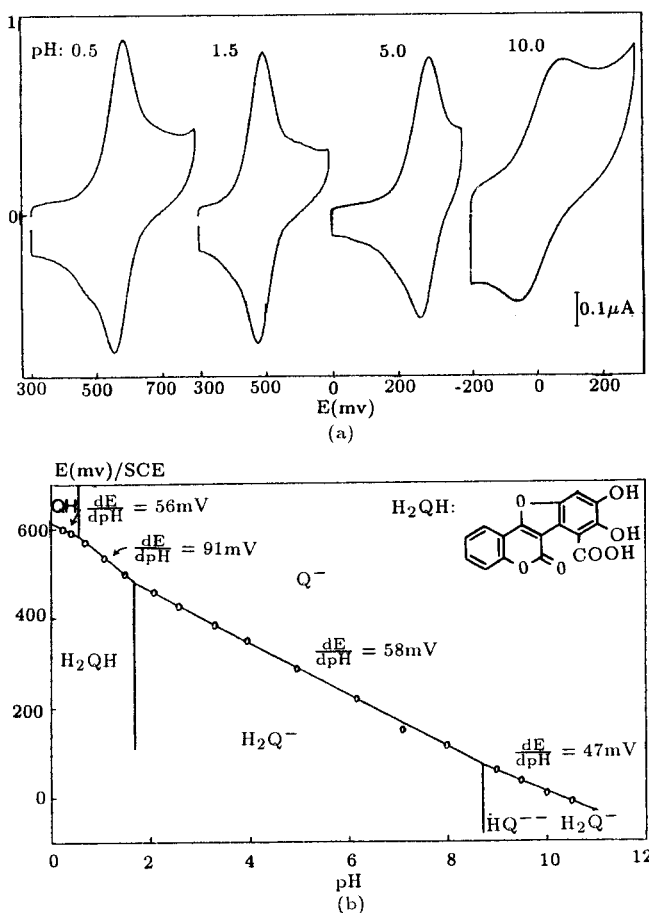
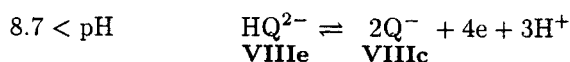
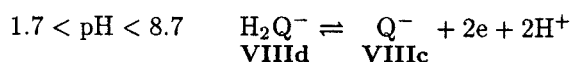
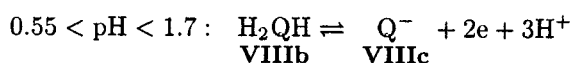
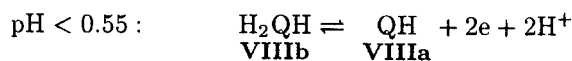


Figure 4. a) Cyclic voltammograms of 3-carboxycoumestan spiked carbon paste electrode recorded at various pH. Scan rate: 50 mV s^{-1} . b) $E_{1/2}$ -pH diagram of 3-carboxycoumestan plotted as described in text.

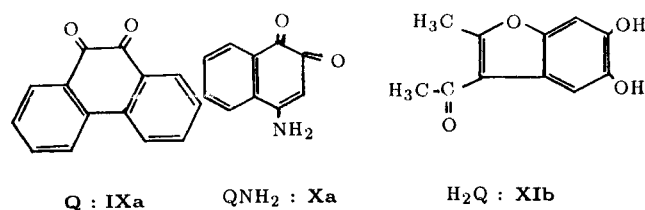
this value correspond to two-electron, three-proton and four-electron, three-proton reactions, respectively. Formation of a dimeric state at higher pH followed by a hydrogen bond formation is also expected [10]. All of these processes can be presented as follows:



The formal potentials of VIIIa/VIIIb, VI-Ic/VIIIb, VIIIc/VIIId and VIIIc/VIIIe redox couples and the pK'_a values of VIIIb/VIIIc, VI-IIa/VIIIc and VIIId/VIIIe acid-base couples are readily estimated from $E_{1/2}$ -pH diagram shown in Figure 4b. These values are quoted in Tables 1 and 2 respectively. A low pK'_a value of 0.55 for VIIIa/VIIIc couple can relate to the presence of two oxygen in o-quinone ring at ortho and meta positions with respect to carboxy group in VIIIa, strengthening the acidity of the later group by their mesomeric effects [19]. Low pK'_a value of VIIIb/VIIIc couple (i.e., 1.7) in comparison with that of benzoic acid (i.e., 4.21) can also be explained by the presence of hydroxy groups with electron withdrawing character on catechol ring. However, the great difference between these two pK'_a values seems to be questionable. Using Hammett equation [19] and neglecting the effect of coumarine moiety on the acidity of catechol ring, the pK'_a value for VIIIc/VIIIe couple can be predicted as 9.7. This value is reasonably in agreement with that obtained from $E_{1/2}$ -pH diagram (i.e., 8.7) especially if the dimer-formation is also considered.

9,10-Phenanthrenequinone, 4-Amino-O-Naphthoquinone and 3-Acetyl-5,6-Dihydroxy-2-Methylbenzofurane Spiked Carbon Paste Electrodes.

9,10-phenanthrenequinone (IX) (Scheme 3) is an insoluble o-quinone in water at the entire pH range



Scheme 3

and its formal potential or pK'_a cannot be determined using simple methods such as potentiometry or spectrophotometry, while cyclic voltammetric investigation of carbon paste electrode containing this compound results in the estimation of these parameters. Cyclic voltammogram of such electrode is shown in Figure 5a. It can be seen that the electrode processes are almost reversible at the entire pH range, but the peak currents diminish with decrease in the solution acidity and remain nearly constant for neutral and alkaline pH. Such a property can arise from the pH-dependent nature of the electrode process as it has already been reported [18]. Figure 5b also shows the $E_{1/2}$ -pH diagram constructed from cyclic voltammograms recorded at various pH. On the basis of this diagram, 9,10-phenanthrenequinone can exist in three different forms, appearing as two redox and one acid-base couple at different electrode potentials and pH. The values obtained for $E^{\circ'}$ and pK'_a were collected in Tables 1 and 2, respectively.

The data reported elsewhere for $E^{\circ'}$ of 9,10-phenanthrenequinone generally correspond to non-

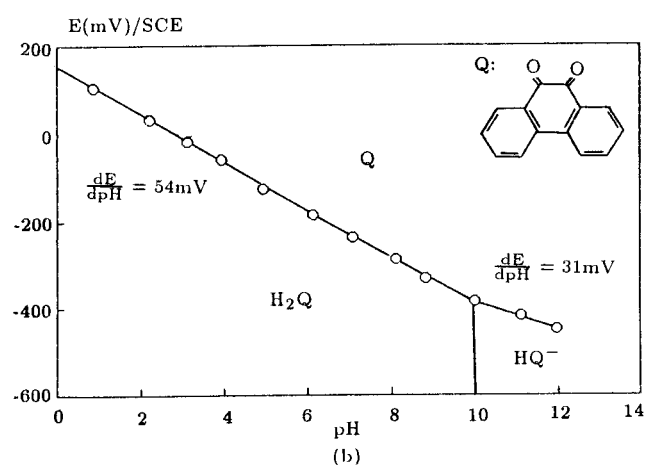
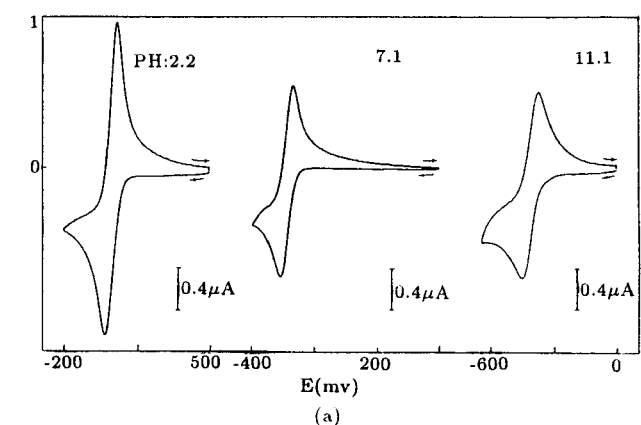


Figure 5. a) Cyclic voltammograms of 9,10-phenanthrenequinone spiked carbon paste electrode recorded at three different pH. Scan rate: 50 mV s^{-1} . b) $E_{1/2}$ -pH diagram of 9,10-phenanthrenequinone plotted as described in text.

aqueous media [30,31] and show some discrepancy with those obtained from this method. Indeed, such a difference can arise from the fact that the studied compound existed in two different states, one, in solvated form in a non-aqueous medium and the other, in fixed form on the electrode surface.

The electrochemical behavior of 4-amino-1,2-naphthoquinone (**X**) (Scheme 3) modified carbon paste electrode has also been studied in buffered solutions at pH between 0.8–8.0 in the absence of dioxygen. An $E_{1/2}$ -pH diagram of this electrode is shown in Figure 6. This diagram demonstrates that four different forms can exist at different pH, two of which are reduced forms and two of which are oxidized. The slopes of this diagram at various regions of pH are as follows: -61 mV (for $\text{pH} < 1.1$), -87 mV (for $3.7 > \text{pH} > 1.1$) and -61 mV (for $\text{pH} > 3.7$) per pH unit. The -61 mV/pH unit refers to the fact that the electrode reaction is a two-electron, two-proton process; whereas, the -87 mV/pH unit corresponds to a two-electron, three-proton reaction. The following equations show how these four forms constitute three redox and two acid-base couples at different electrode potentials and pH:

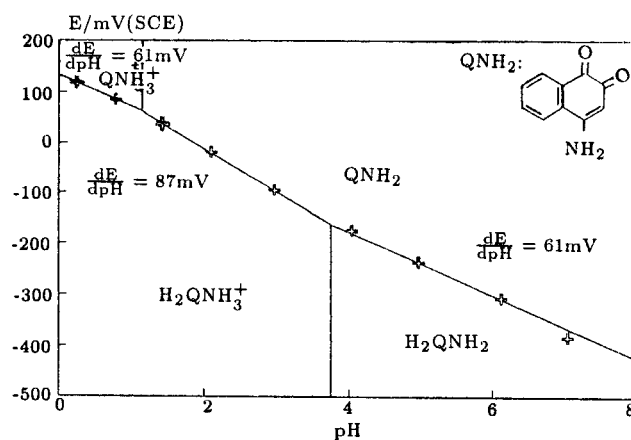
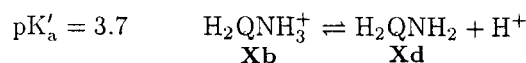
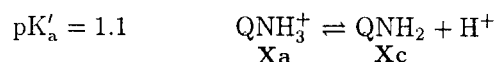
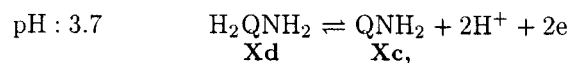
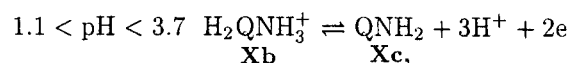
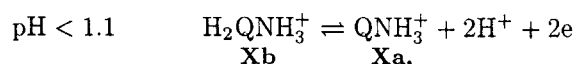


Figure 6. Potential-pH diagram of 4-amino-1,2-naphthoquinone obtained by plotting the calculated $E_{1/2}$ values against pH.

However, the estimation of half-way potentials was only possible up to $\text{pH} = 7$, since at higher pH , the peaks of parent compound surprisingly coalesce the reduction wall of the solvent. Considering that for a plain carbon paste electrode at $\text{pH} = 7$, the reduction of solvent appears around -1.4 V/SCE ; it seems that at this pH , the reduction of solvent is significantly catalyzed at the surface of a 4-amino-1,2-naphthoquinone spiked electrode. The formal potential and pK'_a values resulting from the $E_{1/2}$ - pH diagram were summarized in Tables 1 and 2, respectively.

Finally, the cyclic voltammetric study of 5,6-dihydroxy-2-methyl-3-acetoxybenzofurane (XI) spiked carbon paste electrode has been accomplished in aqueous solution with various buffered pH between 0.5 to 10. This compound was synthesized electrochemically [16] and was used as a modifier in the construction of spiked carbon paste electrode. Cyclic voltammograms obtained exhibit one anodic and corresponding cathodic peak with a peak separation very close to the expected Nernstian value. The potential- pH diagram shows two linear segments having slopes of -61 mV (at $\text{pH} < 6.44$) and -32 mV (at $\text{pH} > 6.44$) per pH unit, respectively. These slopes refer to the contribution of two-electron, two-proton and two-electron, one-proton, respectively, in the electrode surface reactions. The effect of pH variation on peak current and peak separation is similar to that of 9,10-phenanthrenequinone. The formal potentials and pK'_a values were also collected in Tables 1 and 2.

CONCLUSION

The present work demonstrates that from the investigation of electrochemical behavior of carbon paste electrodes spiked with some water-insoluble orthoquinones, the formation of different redox and acid-base couples at the surface of electrode can easily be detected at different electrode potentials and pH . Furthermore, the values of the formal potential and pK'_a of the involving redox and acid-base couples are estimated using the $E_{1/2}$ - pH diagrams. The method also contributes to a better understanding of the redox processes occurring at the electrode-electrolyte interface as well as the effect of some substituents on the electrochemical responses of water-insoluble spiking compounds.

REFERENCES

1. Berdy, J., Aszalos, M. and McNitt, K.L. *Handbook of Antibiotic Compounds, Quinone and Similar Antibiotics, III*, CRC Press Inc., Boca Raton, Florida (1980).
2. Fieldler, H.P., Kulik, A. and Schuez, T.C. "Biosynthetic capacities of actinomycetes. 2. Juglomycin Z, a new naphthoquinone antibiotic from *Streptomyces lendae*", *J. Antibiot.*, **47**, pp 1116-22 (1994).
3. Driebergen, R.J., Den Hartigh, J., Holthuis, J.J.M., Hulshoff, A., Van Oort, W.J., Postma Kelder, S.J., Verboom, W., Reinhoudt, D.N., Bos, M. and Van Der Linden, W.E. "Electrochemistry of potentially bioreductive alkylating quinones, Part 1. Electrochemical properties of relatively simple quinones as model compounds of mitomycin and aziridinyl quinone-type antitumour agents", *Anal. Chim. Acta*, **233**, pp 251-268 (1990).
4. Lown, J.W. "Discovery and development of anthracycline antitumour antibiotics", *Chem. Soc. Rev.*, pp 165-176 (1993).
5. Arcamone, F. "Doxorubicin anticancer antibiotics. Medicinal chemistry", *A Series of Monographs*, Academic press, New York, **17** (1981).
6. Dyrust, G., Kadish, K.M., Scheller, F. and Renneberg, R., *Biological Electrochemistry*, Academic Press, New York, **1** (1982).
7. Golabi, S.M. and Pournaghi, M.H. "Electrochemical behavior of p-benzo-quinone, 2,3,5,6-tetrachloroquinone and 1,4-naphthoquinone in chloroform - I. in the absence of proton donors", *Electrochim. Acta*, **33**, pp 425-431 (1987).
8. Albert, A. and Serjeant, E.P. *The Determination of Ionization Constants*, 3rd Edn., Chapman and Hall, London (1984).
9. Mann, C.K. and Barnes, K.K., *Electrochemical Reactions in Nonaqueous Systems*, Marcel Dekker, New York, pp 190-197 (1970).
10. Petrova, S.A., Kolodyazhny, M.V. and Ksenzhek, O.S. "Electrochemical properties of some naturally occurring quinones", *J. Electroanal. Chem.*, **277**, pp 189-196 (1990).
11. Raoof, D.B. and Golabi, S.M. "Electrochemical properties of carbon-paste electrodes spiked with some 1,4-Naphthoquinone derivatives", *Bull. Chem. Soc. Jpn.*, **68**, pp 2253-2261 (1995).
12. Nematollahi, D. and Golabi, S.M. "Electrochemical study of catechol and 4-methylcatechol in methanol. Application to the electro-organic synthesis of 4,5-dimethoxy- and 4-methoxy-5-methyl-o-benzoquinone", *J. Electroanal. Chem.*, **405**, pp 133-140 (1996).
13. Golabi, S.M. and Nematollahi, D. "Electrochemical study of catechol in ethanol. Application to the electro-organic synthesis of 4,5-diehoxy-o-benzoquinone", *Bull. Electrochem.*, **13**, pp 156-160 (1997).
14. Golabi, S.M. and Nematollahi, D. "Electrochemical study of catechol and some 3-substituted catechols in the presence of 4-hydroxy coumarin. Application to the electro-organic synthesis of new coumestan derivatives", *J. Electroanal. Chem.*, **420**, pp 127-134 (1997).
15. Golabi, S.M. and Nematollahi, D. "Electrochemical study of 3,4-dihydroxybenzoic acid and 4-tert-butylcatechol in the presence of 4-hydroxycoumarin.

- Application to the electro-organic synthesis of coumestans derivatives", *J. Electroanal Chem.*, **430**, pp 141-146 (1997).
16. Nematollahi, D. and Golabi, S.M. "Electrochemical synthesis of benzofuran derivatives. 1. Electrochemical investigations", *Iranian. J. Sc. & Techol.*, **21**, pp 121-133 (1997).
 17. Katz, E.Y. and Solovev, A.A. "Chemically modification of platinum and gold electrodes by naphthoquinone using amines containing sulfhydryl or disulfide groups", *J. Electroanal. Chem.*, **291**, pp 171-186 (1990).
 18. Degrand, C. "Electron transfer in quinonoid modified electrodes-Mediation and catalytic applications", *Ann. Chim.*, **75**, pp 1-18 (1985).
 19. Perrin, D.D., Dempsey, B. and Serjeant, E.P., *pK_a Prediction for Organic Acids and Bases*, Chapman and Hall, London, pp 44-52 (1981).
 20. Slabbert, N.P. "Ionization of some flavanols and dihydroflavonols", *Tetrahedron*, **33**, pp 821-824 (1977).
 21. Corse, J. and Ingraham, L.L. "Dissociation constants of substituted catechols", *J. Am. Chem. Soc.*, **73**, pp 5706-5707 (1951).
 22. Bailey, S.I., Ritche, I.M. and Zhang, H.G. "The electrochemistry of aqueous solutions of 4-methoxy-1,2-benzoquinone", *Bioelectrochem. Bioenerg.*, **19**, pp 521-531 (1988).
 23. Vallet, C.D. and Mentzer, C. "A new method of access to the coumestan series", *C.R. Acad. Sci., Paris*, **251**, pp 736-738 (1960).
 24. Darbarwar, M., Sundaramurthy, V. and Subba Rao, N.V. "Synthesis of amino-, methyl- and benzo-11, 12-oxygenated coumestans", *Indian J. Chem.*, **11**, pp 115-117 (1973).
 25. Ibid, "New route to the synthesis of coumestans", *Proc. Indian Acad. Sci., Sect. A*, **80**, pp 93-96 (1974).
 26. Bhalerao, U.T., Muralikrishna, C. and Pandey, G. "An efficient synthesis of coumestans. A probable biogenetic approach", *Synth. Commun.*, **19**, pp 1303-1307 (1989).
 27. Shah, R.R. and Trivedi, K.N. "Synthesis of 2,2-dimethylpyranocoumestan derivatives", *J. Indian Chem., Soc.*, **56**, pp 995-998 (1979).
 28. Raju, K.V., Subba, Raju, P.V.N. and Raju, G.J.V.J. "Electrochemical synthesis of 8,9-dihydroxy-1-thiocoumestans", *Bull. Electrochem.*, **6**, pp 877-878 (1990).
 29. Tabakovic, I., Gujic, Z. and Bejtovic, Z. "Electrochemical synthesis of heterocyclic compounds. XII. Anodic oxidation of catechol in the presence of nucleophiles", *J. Heterocycl. Chem.*, **20**, pp 635-638 (1983).
 30. Kano, K. and Uno, B., "Surface redox reaction mechanism of quinones adsorbed on basal-plane pyrolytic graphite electrodes", *Anal. Chem.*, **65**, pp 1088-1093 (1993).
 31. Jaworski, J.S., Lesniewska, E. and Kalinowski, M.K. "Solvent effect on the redox potential of quinone-semiquinone systems", *J. Electroanal Chem.*, **105**, pp 329-334 (1979).