

RATE CONSTANTS FOR THE ELECTRODE REACTIONS OF QUINONES IN CHLOROFORM: THE DEPENDENCE ON ELECTRODE MATERIALS AND APPARENT STANDARD POTENTIALS

M.H. Pournaghi-Azar* and S. Pourtork

*Electroanalytical Chemistry Laboratory, Faculty of Chemistry,
University of Tabriz, Tabriz, Islamic Republic of Iran*

Abstract

The reduction process for some quinones has been studied by cyclic voltammetry, rotating disk electrode voltammetry and chronopotentiometry in chloroform at platinum, gold and glassy carbon electrodes using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The results obtained from this study reveal that the reduction of the quinones is two one-electron processes, the first reduction to the semiquinone anion radical is nearly reversible and the second to the dianion is quasi-reversible. The kinetic parameters for the reduction of the quinones to the semiquinone were evaluated and the dependence on the electrode materials and apparent standard potential is discussed. The diffusion coefficients of the quinones were determined from both chronopotentiometric and chronoamperometric measurements in 0.5 M chloroform solution of TBAP.

Introduction

The electrochemistry of quinones under nonaqueous conditions is well documented [1-16]. In dry nonaqueous electrolytes, quinones are characterized by two one-electron reductions to the semiquinone anion radical and to the dianion respectively [1,3-13]. The first reduction step is reversible under a variety of conditions and the second is nearly reversible or irreversible depending on the specific conditions employed. In the presence of proton donors or some supporting electrolyte, a single two-electron reduction step is observed [2,5,14].

In our earlier papers [1-3], we have reported the electrochemical behaviour of some quinones and anthraquino-

nes in chloroform at mercury electrode. In the absence of proton donors, the reduction of the quinones was two one-electron reduction steps, while in the presence of proton donors they reduced in a single two-electron step by a CE, EC, ECE or CECE mechanism depending on the quinone and proton donor [2].

It is known that the electrochemical electron transfer rate of quinones depends on the solvent, supporting electrolyte, quinone [11-13] and electrode materials [17,18]. To make the influence of some of these parameters clear in an aliphatic hydrocarbon solvent with very low dielectric constant such as chloroform, the present work deals with the electrochemical behaviour of p-benzoquinone, 1,4 naphthoquinone and tetrachloroquinone (having the apparent standard potentials with a suitable interval range) at platinum, gold and glassy carbon electrodes in the absence

Keywords: Chloroform; Kinetic parameters; Quinones; Solid electrodes

of proton donor.

The electrode reaction mechanism was studied by rotating disk electrode voltammetry, cyclic voltammetry and chronopotentiometry.

The heterogeneous standard rate constant k^o of the first reduction step of quinones was measured and the related diffusion coefficients were also determined in 0.5 M TBAP solution.

Experimental Section

Reagents and Chemicals

The solvent used was chloroform G.R. from E. Merck or Fluka. Tetrabutylammonium perchlorate (TBAP) and iodide (TBAI) purum from Fluka were used. TBAP was purified by recrystallization from a mixture of water-acetone. After drying in 60°C in vacuum for 24 h, it was used as supporting electrolyte. Other chemicals were P.A. grade from E. Merck or Fluka.

The reference electrode, Ag/AgI(sat.), TBAI 0.05 M, TBAP 0.5 M in chloroform in a separate compartment with a dense ceramic in the bottom was directly immersed in the reaction cell. The working electrode was glassy carbon (GC), gold (Au) or platinum (Pt) disks (area of each 0.126 cm²) obtained from EG and G. The counter electrode was a platinum wire. The working electrode was polished with alumina powder (0.05 μm) for 10 minutes, then washed with water and acetone in turn before each voltammetry.

Apparatus

All voltammograms were recorded with a three electrode-system. A multipurpose instrument from EG and G "Princeton on Applied Research" potentiostat/galvanostat model 273 with an IBM personal computer and an Epson FX 850 printer were used. A rotating electrode system model 616 was from EG and G. A Beckman Electroscan model 30 was used for chronopotentiometric measurements. In all experiments, the test solutions were deaerated by a stream of N₂ passing through chloroform for 30 min.

Results and Discussion

Rotating Disk Electrode Voltammetry

Current-potential curves for the reduction of 5 x 10⁻⁴ M p-benzoquinone (BQ), tetrachloroquinone (TCQ) and 1,4-naphthoquinone (NQ) in chloroform in the presence of TBAP 0.5 M were recorded at polished Pt, Au and GC electrodes. Under these conditions with various rotation speeds, two one-electron cathodic waves were obtained. Plots of diffusion limiting current i_l vs rotation speed ω for first reduction waves are straight lines with a correlation coefficient very close to unity and the height of the waves are linear dependent on the concentration of the quinones. On the other hand, the plot of $\log[(i_l - i)/i]$ against E for

reduction curves is also a straight line with a slope close to that expected for electrochemically reversible behaviour (0.059 V). The characteristic data of the curves are given in Table 1 and a typical RDE voltammogram is shown for BQ in Figure 1. As can be seen from Table 1, an effect of the electrode materials on the half-wave potential was not detected and the first reduction of the quinones at the solid electrodes is a one-electron quasi-reversible process.

Cyclic Voltammetry

Cyclic voltammetry of BQ, TCQ and NQ with all scan rates v (dE/dt) (0.02-5 Vs⁻¹) at Pt, Au and GC electrodes showed two successive cathodic peaks (A, B), for reversal sweep (oxidation) two anodic peaks (A*, B*) appeared for TCQ, but only one peak was discernible for BQ and NQ. This behaviour suggests that the dianions Q²⁻ (BQ²⁻ NQ²⁻) electrogenerated at second reduction step of BQ and NQ participate in a fast homogeneous electron transfer reaction, in which the related Q²⁻ is consumed and the resulting anion radical Q^{•-} is oxidized during the more positive of the two peaks A*. The homogeneous reaction was other than syn. proportionation within the diffusion layer according

to $Q^{2-} + Q \rightarrow 2Q^{\bullet-}$, because i_p^a/i_p^c ratio for A-A* was almost 1 and remained unchanged when the potential scan was limited to 1.000 V. We have previously revealed the liable homogeneous reaction consuming BQ²⁻ and NQ²⁻ in this medium [1].

Typical cyclic voltammograms for TCQ and NQ at

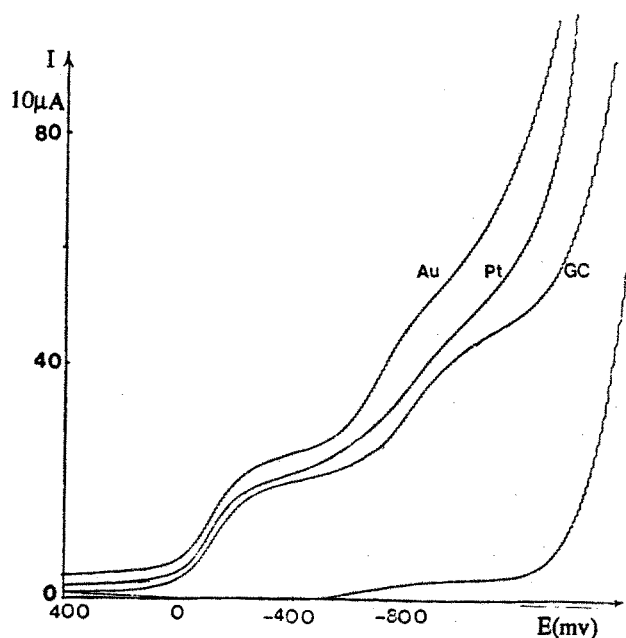


Figure 1. Dc voltammogram of 0.5 mM benzoquinone at rotating disk gold, platinum and glassy carbon electrodes, rotation speed $\omega = 500$ rpm

Table 1. Voltammetric data for the quinones at Pt, Au and GC electrodes in 0.5 M chloroform solution of TBAP

Quinone	Electrode	$E_{1/2}$ (V)	S^* (V)	E_{p1}^c (V)	E_{p1}^a (V)	$E_{p1}^a - E_{p1}^c$ (mV)	E_{p2}^c (V)	E_{p2}^a (V)
BQ	Pt	-0.124	0.067	-0.090	-0.014	76	-0.600	-
	Au	-0.127	0.061	-0.086	-0.016	70	-0.605	-
	GC	-0.128	0.066	-0.093	-0.011	82	-0.603	-
TCQ	Pt	0.334	0.062	0.380	0.458	78	-0.366	-0.270
	Au	0.329	0.061	0.382	0.457	75	-0.351	-0.258
	GC	0.324	0.070	0.377	0.461	84	-0.360	-0.268
NQ	Pt	-0.348	0.68	-0.309	-0.236	73	-0.895	-
	Au	-0.345	0.60	-0.313	-0.246	67	-0.890	-
	GC	-0.350	0.070	-0.300	-0.220	80	-0.885	-

$$*slope = dE/d\log [(i_d - i)/i]$$

scan rates of 20-100 mV s^{-1} on the Pt electrode are shown in Figure 2. The characteristic data of cyclic voltammograms for the quinones at the scan rate of 20 mV s^{-1} with IR compensation are given in Table 1. Over the range of scan rate lower than 1000 mV s^{-1} , the i_p^a/i_p^c ratio for A-A* peaks is 1 and current function values $i_p^c/v^{1/2}$ are independent of

scan rate. These confirm that the $Q/Q^{\cdot -}$ system is nearly electrochemically reversible without any complicating process from adsorption or chemical reaction in this medium.

Chronopotentiometry

In this work, chronopotentiometry has been used both as a diagnostic tool for confirming the diffusional nature of the current raised on the reduction of the quinones and as an indication of their electrochemical reduction mechanism in chloroform.

Chronopotentiograms for BQ, TCQ and NQ solutions of 3×10^{-3} M at various constant currents (10-30 μA) depending on the quinones were recorded at Pt, Au and GC disk electrodes. Two transition times were observed with the ratio of 3.1 very close to the theoretical value for two one-electron reversible reduction steps. The chronopotentiogram with current reversal for TCQ also shows two transition times, while for BQ and NQ only one transition time was discernible. The reverse transition time for first reduction step of the quinones is 1/3 that of the forward. On the other hand, a graphic plot of E vs $\log [\tau^{1/2} - t^{1/2} / t^{1/2}]$ for recorded chronopotentiograms at each electrode gives a straight line with a slope of about 0.07 V. This confirms that the first reduction step of the quinones is nearly reversible and is followed by oxidation

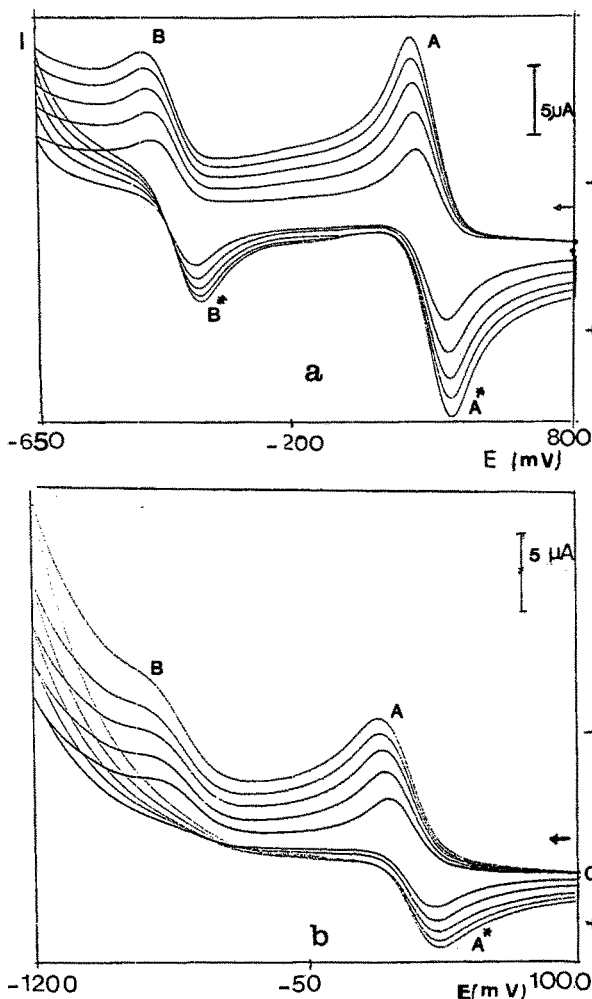


Figure 2. Cyclic voltammograms for reduction of 1 mM (a) tetrachloroquinone (b) naphthoquinone at Pt electrode, scan rate: 20-100 mV s^{-1} in 20 mV increments

of stable semiquinones $Q^{\cdot-}$. The examination of Sand's equation and plotting of $it^{1/2}$ vs i showed that the $it^{1/2}$ is independent of i confirming the diffusional nature of the electrolysis current. Figure 3 shows a typical example of chronopotentiograms obtained at Pt electrode for NQ and TCQ solutions of 3×10^{-3} M.

Determination of Diffusion Coefficient of the Quinones

The diffusion coefficient D of studied quinones was determined in 0.5M TBAP in chloroform from

chronoamperometric and chronopotentiometric data using the equations of Cottrel and Sand respectively.

The chronoamperogram was recorded for a fixed and polished Pt, Au and GC disk electrode in unstirred 10^{-3} M solutions of the quinones in 0.5 M TBAP. The applied potential was the potential related to the top of the first cathodic wave of the quinones. An illustrative chronoamperogram is shown in Figure 4 for BQ at Pt electrodes. The intercept of plot of $\log(i)$ vs $\log(t)$ for the chronoamperograms is $\log [nFAC(D_0/\pi)^{1/2}]$ and diffusion coefficients of the quinones can be obtained. In this manner the intercept with the axis of plot $it^{1/2}$ vs i for the chronopotentiograms is $nFACD_0^{1/2} \pi^{1/2} / 2$ and diffusion coefficients of the quinones may be calculated (Table 2). The values determined for D_0 are shown in Table 2 and agree well with those obtained from the chronoamperometric measurement. As seen in Table 2, the value of D_0 with the order $D_{TCQ} > D_{NQ} > D_{BQ}$ increases with a decrease in the solvation ability of the quinones in chloroform. In fact, TCQ with four polar groups (Cl) and BQ without any substituted group, show the lowest and the highest ability to be solvated in less polar solvents (i.e. chloroform) respectively.

Determination of Kinetic Parameters

The standard rate constant k^0 of the electron transfer

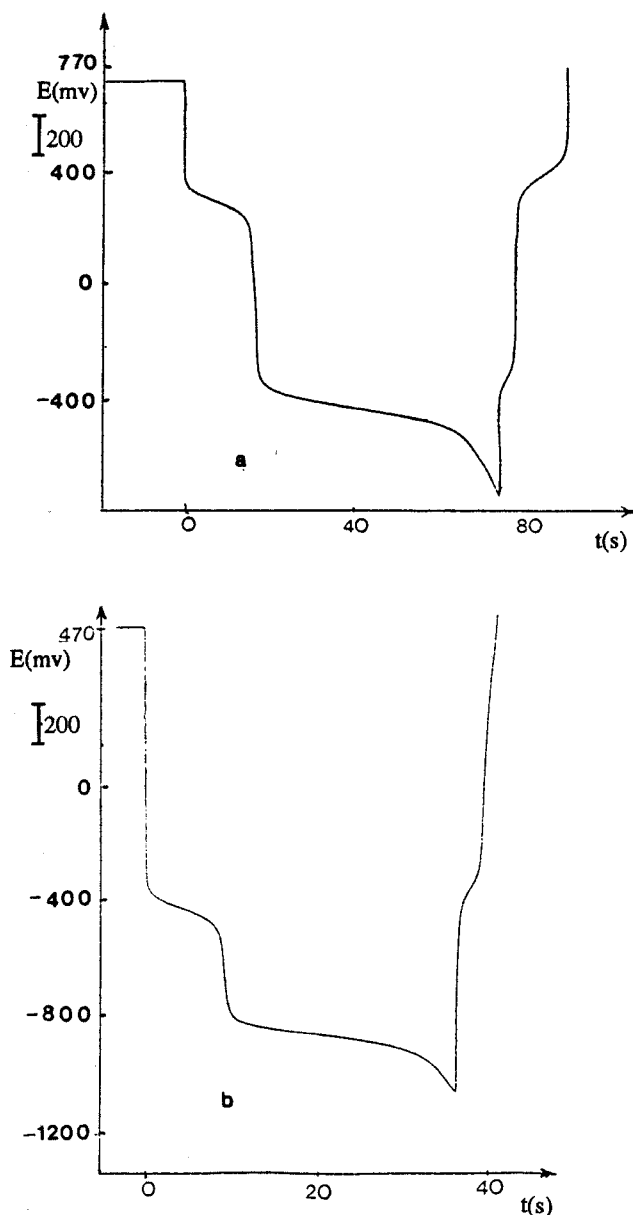


Figure 3. Chronopotentiograms of (a) 3.3 mM tetrachloroquinone and (b) 2.5 mM naphthoquinone at GC electrode with constant current of 24 and 12 μ A respectively

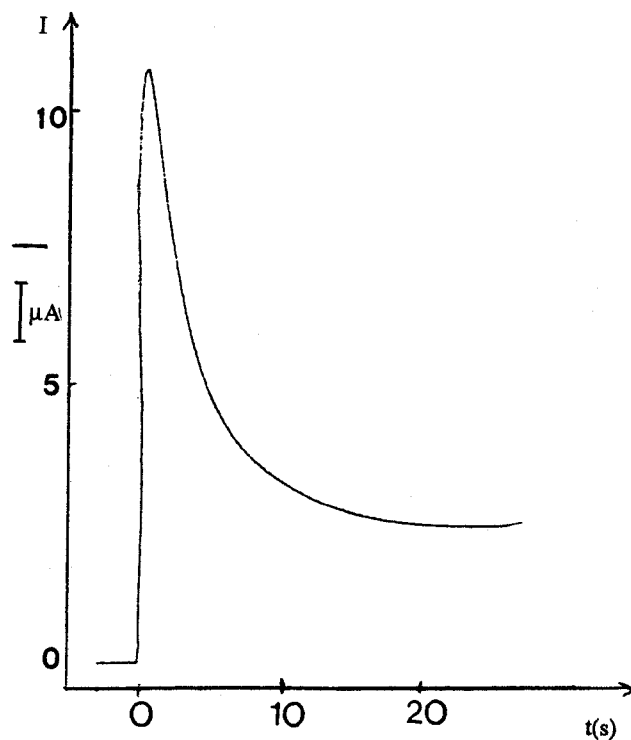


Figure 4. Chronoamperogram of 0.65 mM of benzoquinone at Pt electrode at -250 mV vs used reference electrode

between the quinones and their anion radicals can be evaluated from cyclic voltammetry or rotating disk voltammetry if the IR compensation is exact. It is difficult to obtain exact values for charge transfer coefficient from the cyclic voltammograms especially at solid electrodes [11]. Therefore, in this work, the values of k° and α were determined by the mass transport extrapolation method using the IR compensated RDE voltammograms according to the following relationship [19].

$$\frac{1}{i} = \frac{1}{I} + \frac{K}{\omega} \quad (1)$$

with: $K = (0.620 nFA C_0^{2/3} \nu^{-1/6})^{-1}$

where i = measured current at any potential, I = current corrected for diffusion, ω = electrode rotation speed, (rad s^{-1}), A = electrode area (cm^2) and C = concentration of analyte (mol/cm^3). The intercept of the plot of $1/i$ vs $1/\omega$ gives $1/I$. An example of such a series of the extrapolated plots is shown in Figure 5a for TCQ at Au electrode. The measured I as a function of potentials gives a plot $\log(I)$ vs $(E - E^0)$ according to the relationship between current and potential [20].

$$\log I = \log(nFA C_0 k^\circ) + \frac{\alpha nF}{2.3 RT} (E - E^0) \quad (2)$$

k° and α can be obtained from the slope and intercept respectively (Fig. 5b), where $E^0 = (E_p^a + E_p^c)/2$; and can be obtained from the CV gramms of each quinone at each electrode. The values of k° and α obtained for TCQ and NQ are shown in Table 3.

Since the cathodic reduction current-potential curve of BQ in RDE voltammetry exhibited some anomalous behaviour when rotation speed was varied, k° was derived from the observed values of ΔE_p in cyclic voltammograms according to the relationship established by Nicholson [21].

$$k^\circ = n^{1/2} D_0^{1/2} (nF/RT)^{1/2} (D_0/D_R)^\alpha \nu^{1/2} \Psi(\Delta E_p) \quad (3)$$

where D_0 and D_R are diffusion coefficients for the oxidized and reduced participants in the redox reaction and ν ($V s^{-1}$) is the potential scan rate. The parameter $\Psi(\Delta E_p)$ is determined from a reference curve of $\Psi(\Delta E_p)$ vs ΔE_p , which is readily constructed from data supplied by Nicholson [21]. Since, for the system which has been studied here there is little difference in molecular structure between oxidized and reduced form, thus $D_0 = D_R$ and $(D_0/D_R)^\alpha = 1$. The values calculated for BQ are shown in Table 2. As seen in

Table 2. Diffusion coefficients for the quinones in 0.5 M chloroform solution of TBAP

Quinone	Electrode	$D^* \times 10^5$ $cm^2 s^{-1}$	$D^{**} \times 10^5$ $cm^2 s^{-1}$
BQ	Pt	1.25	1.10
	Au	1.08	1.22
	GC	1.29	1.32
TCQ	Pt	1.77	1.72
	Au	2.18	1.86
	GC	1.76	2.19
NQ	Pt	1.80	1.40
	Au	1.40	1.41
	GC	1.20	1.50

* Chronoamperometric measurement.

** Chronopotentiometric measurement

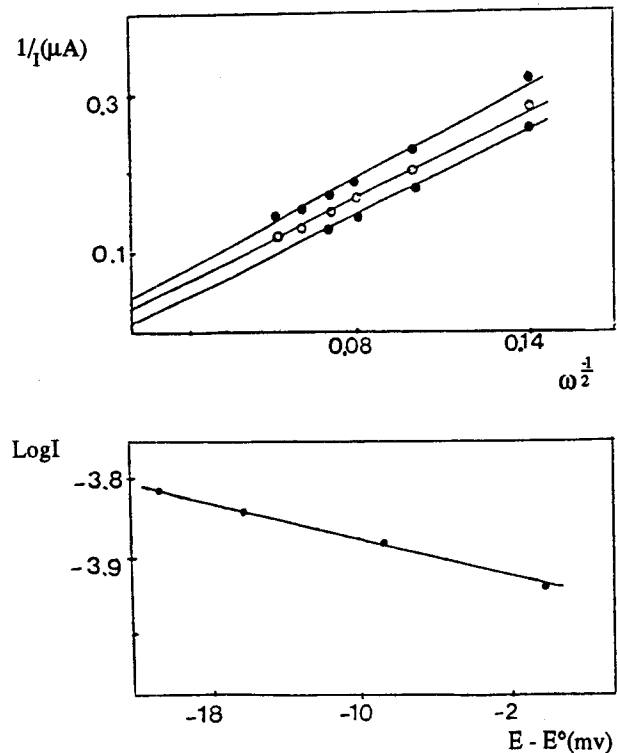


Figure 5. (a) Mass extrapolation graphs following equation 1 for reduction of TCQ at Au electrode, each line corresponds to a different electrode potential. (b) Graph used to evaluate k° and α at Au electrode by the diffusion extrapolation method

Table 3. Kinetic parameters for the quinones in chloroform, dimethylformamid DMF and propionitrile PN

Quinone	Electrode	Chloroform k°x 100 cm s ⁻¹	α	DMF* k°x 100 cm s ⁻¹	PN* k°x 100 cm s ⁻¹
BQ	Pt	0.87	-	5.1	-
	Au	1.11	-	6.4	6.2
	GC	0.72	-	14	18
TCQ	Pt	0.79	0.41	-	-
	Au	1.01	0.39	-	-
	GC	0.68	0.40	-	-
NQ	Pt	0.93	0.40	6.3	-
	Au	1.22	0.37	13	11
	GC	0.94	0.41	10	17

*From Ref. 22

this table the values obtained for k° in chloroform with a polarity parameter of γ = 0.26 [11] are unexpectedly low compared with those obtained in aprotic solvents with high polarity parameters such as dimethylformamid DMF (γ = 0.46) and propionitrile PN (γ = 0.51) [22]. This behaviour can be understood when with solvent of low dielectric constant the radical anion is assumed to be associated with TBA⁺ ion. In this case, an additional reorganization term is necessary and can be expressed by means of the coulomb energy:

$$E_a = -Z_1 Z_2 e^2 N / 4\epsilon \epsilon_0 a \quad (4)$$

where a is the contact distance and is the sum of the radii of radical anion and TBA⁺ ion (r = 0.4 nm) i.e. a = 0.72 nm

(0.4 + 0.32) for TBA⁺...BQ^{•-}, 0.77(0.4+0.37) for NQ and 0.82(0.4+0.42) for TCQ.

The experimental values of k° with order k_{NQ}⁰ > k_{BQ}⁰ > k_{TCQ}⁰ decreases with an increase in the apparent standard potential E_{NQ}⁰ (E_{BQ}⁰ < E_{TCQ}⁰ < E_{NQ}⁰). Furthermore the lower experimental values obtained for k° in chloroform (ε = 4.8), in comparison with that in dichloromethane (ε = 9.2) and tetrahydrofuran (ε = 7.4) [11], show that E_a in chloroform is higher than the expected value because of higher association.

It is also found from Table 3 that the values of k° slightly depend on the electrode materials. The trend of the k° for the quinones in chloroform with order Au > Pt > GC is certainly that to be expected from double layer correction, because the potential of zero charge becomes positive commonly in the order Au < Pt < GC. Capon and Parsons [16] suggest that double layer correction in nonaqueous

systems is likely to be small because of a low dielectric constant and a high concentration of electrolyte especially for reactions involving single electron transfer to a noncharged reactant, which is the case for the present systems.

Vojnovic and Sepa [23] proposed a relationship between the exchange current, i₀ and density of electron states at the Fermi level, p_f, as ln i₀ = ln p_f + constant, on the basis of the Levich [24] and Dogonadze-Chizmadzhev theory [25]. This relation predicts the larger magnitude of k° (k° = i₀/F) at Pt electrode than the Au one by a factor of 10. Neither such a large difference nor even the order k°(Pt) > k°(Au) were observed in our experiment. Therefore, secondary effects of different metals resulting from structural changes in the double layer are judged to be the most probable causes of slight variations in reaction rate in this work.

Conclusion

Electrochemical techniques such as RDE and cyclic voltammetry reveal that the reduction of the quinones in chloroform at solid electrodes occurs in two one-electron nearly reversible processes. Cyclic voltammetry and chronopotentiometric measurements show that the first reduction product of the quinones is stable and does not participate in any chemical reaction or adsorption phenomena. RDE and cyclic voltammetry can be used for the determination of electrode kinetic parameters of the quinones reduction at solid electrodes depending upon the materials of the electrode. The values obtained for k° for first reduction step of BQ, TCQ and NQ are unexpectedly low compared with those obtained in aprotic solvents with high polarity parameter. It can be explained by ion-pair

formation between radical anion and TBA⁺ ion in this medium and consequently an additional reorganisation term expressed by means of coulomb energy E_a . In addition, the very low experimental values obtained for k^0 in chloroform in comparison with that in dichloromethane and tetrahydrofuran may be attributed to a higher value of E_a . It can be understood when association in chloroform is assumed to be very high. The slight dependence of the k^0 value on the electrode material can be explained with double layer correction.

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