MECHANISM OF VOLTAMMETRIC REDUCTION OF 1,4-NAPHTHOQUINONE IN DMF

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Electrochemical reduction of 1,4-naphthoquinone has been investigated in TEAP/DMF solutions using convolution and deconvolution potential sweep voltammetry. In anhydrous media electrochemical reduction proceeds via two successive diffusion-controlled one electron steps, the first being reversible giving free radical anion, and the second as a reversible one-electron transfer coupled with a chemical reaction. In presence of proton donor, the addition of proton (the chemical step) becomes faster. The second step loses its reversible nature and at sufficiently high concentration, it merges with the first.

The voltammetric reduction behaviour of naphthoquinone derivatives in aqueous and in non-aqueous media has been investigated by several authors [1-7]. They have indicated that in aprotic media the electrochemical reduction proceeds in two successive one-electron steps, the first step to a stable anion radical and the second giving an unstable primary product.

This paper proposes to examine the mechanism of reduction in aprotic solvent (N, N-dimethyl formamide) by studying the influence of proton donor.

EXPERIMENTAL

Instrumentation

Cyclic voltammetry was performed using an E.G.& G. PAR model 363 scaning potentiostat. The current response and applied potentials were stored on magnetic disk via a fast data capture system, based upon twin channel 12 bit analogue to digital converter (50 μs conversion time) and a Gemini Galaxy 2 microcomputer. Data capture was written in Macro 80 assembler language which allowed a minimum aquisation time of 100 μs per point. In all experiments 500 data points were routinely captured, equally spaced in time and with a time interval appropriate to the time scale of the particular experiment. Background data were also stored, and were subtracted from the experimental data set, minimizing effects such as double layer charging currents.

The electrochemical measurements were made using a conventional three electrode cell configuration. An E.G.& G. PAR model SMDE 303 mercury-drop system in small hanging-drop mode (working electrode of area 1.05×10^{-2} cm^2). $Ag/AgNO_3$ (0.01M) in 0.1 mole dm^{-3} tetraethylammonium perchlorate (TEAP) in DMF (reference electrode) and a 1 cm^2 platinum sheet (auxilliary electrode). All experiments were made at 21°C in dimethylformamide containing 0.1 M TEAP as supporting electrolyte. Solutions were purged with nitrogen before each experiment and an atmosphere of nitrogen was maintained above the working solution. Internal resistance ohmic drop distortions were minimized by applying positive feedback compansation.

Reagents

Tetraethylammonium perchlorate (Fluka) was recrystallised from methanol and dried in a vacuum oven at 60°C. Dimethylformamide, (A.R. BDH) was passed through a column of active neutral alumina (activated at 300°C for 24 hrs) before use.

A stock solution (0.1 mole dm^{-3}) of TEAP was prepared in DMF. Solutions of 1,4-naphthoquinone (10 mM) and phenol (1.5 M) were prepared just before use in freshly prepared supporting electrolyte.

Treatment of the Electrochemical Data

It is common to find the analysis of cyclic voltammetric data based on the current and

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potential values at a few specific points like peak or half peak current, although these have in fact no special significance compared with the rest of the data throughout a linear sweep wave. It is much more preferable to use as many data as possible for an effective analysis to be performed and a convolution transform method has been proposed which can give simple mathematical forms to the transformed data [8-12]. This required convolution with a $(\pi t)^{-1/2}$ function.

$$I_1(t) = (\pi)^{-1/2} \int_0^t \frac{i(u)}{(t-u)^{1/2}}\, du \qquad (1)$$

where $I_1(t)$ is the convoluted current at time t. Recently, a general convolution transform method has been developed for electron transfer followed by chemical reaction (the so-called EC reaction) case [13] which encompasses the results of Saveant [9-12] and Oldham, [14].

In case of EC reaction, the reaction scheme[13] is

$$O + ne \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R$$

$$R \xrightarrow{k_c} P$$

where n is the respective charge numbers and k_f° is the standard heterogeneous electron transfer rate constant at $E = E^\circ$. Other parameters have their usual meaning. Thus, reduction currents are taken as negative and oxidation currents as positive. The corresponding convolution current is

$$I_2 = I_2(k_c', t) = (\pi)^{-1/2} \int_0^t \frac{i(u)\ \exp(-k_c'(t-u))}{(t-u)^{1/2}}\, du \qquad (2)$$

Absence of chemical reaction was in general indicated in cyclic voltammetric experiments by the I_1 -E curve retracing the curve in the reverse scan. Tests for reversibility always included an assessement of the overlay of the forward and backward convoluted currents. Logarithmic checks on the data could be applied and in principle the appropriate values of the various parameters could be extracted from this treatment. In the presence of chemical reaction, simple logarithmic forms can be written directly as follows [13]:

$$-\xi = \ln\left[\frac{(I_{lim} - I_1)}{I_2\left(\frac{D_A}{D_B}\right)^{1/2} + \frac{I_{lim}\ i \exp(1-\alpha)\xi}{i_o}}\right] \qquad (3)$$

and

$$-\alpha\xi = \ln\left[\frac{I_{lim} - I_1 - I_2\left(\frac{D_A}{DB}\right)^{1/2} \exp(-\xi)}{I_{lim}\ \frac{i}{i_o}}\right] \qquad (4)$$

where $\xi = (E - E^\theta)/(nF/RT)$, n = the number of electrons transferred, α is the symmetry factor, I_1 and I_2 are the convolutions given in equn. 1&2 respectively, $I_{lim} = (nFAC^{init.} D^{1/2})$ is the limit of I as E approaches infinity and i_o is the exchange current for the electron transfer process at $E = E^\theta$.

In the absence of chemical reaction I_2, = I_1 and these functions become indentical with appropriate elimination of terms to those derived by Saveant and others [9] for reversible ($i_o \to \infty$), quasi-reversible and irreversible ($i_o \to 0$) regimes. When chemical reactions are present, k_c is required for the computation of I_2. Tests on simulated data [13] showed that inappropriate k_c values gave quite large deviations of the log plot from linearity, particularly on the reverse sweep.

RESULTS AND DISCUSSION

1,4-naphthoquinone is seen to be electro reduced in two one-electron steps in the present medium. The two steps are diffusion-controlled (the peak current i_p correlates with square root of scan rate), $v^{1/2}$ with correlation coefficient amounts to 0.998). Cyclic voltammetric data (Table 1 and Fig.1) allows to regard the two reduction waves as reversible through the scan rate range used.

Convolution analysis of the cyclic voltammetric data offers a better examination of the system. The convolution processes of a series of cyclic voltammetric scans using scan rates between 0.05 and 0.50 V/s are made covering the complete reduction waves (from -0.8 to -1.8 volts). Figure 2 shows the cyclic voltammogram, (i-E) and the convoluted current-potential curve (I_1 - E) for 0.98 mM dm^{-3} 1,4-naphthoquinone in 0.1 M TEAP/DMF solution. It is observed from the data for the first wave that the convoluted current (I_1) reaches the same plateau value, regardless of the scan

TABLE 1

CYCLIC VOLTAMMETRIC DATA FOR 0.98 mM 1,4-NAPHTHOQUINONE IN 0.1 M TETRAETHYLAMMONIUM PERCHLORATE/DIMETHYLFORMAMIDE SOLUTION AT 21° C

Sweep rate mV/s	First Wave				Second Wave			
	$-E_p$ V	ΔE mV	$E_p - E_{p/2}$ mV	i_{pa}/i_{pc}	$-E_p$ V	ΔE mV	$E_p - E_{p/2}$ mV	i_{pa}/i_{pc}
50	1.0122	62.4	61.0	0.987	1.5592	61.0	63.2	0.926
100	1.0098	56.3	60.2	0.965	1.5621	63.8	61.8	1.029
200	1.0097	61.5	56.3	0.947	1.5670	65.7	63.8	0.838
500	1.0146	62.6	58.6	0.943	1.5641	68.0	62.2	0.883

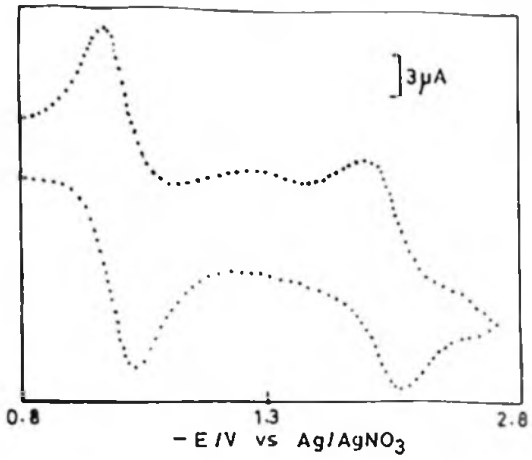


Fig. 1 Cyclic voltammogram of 0.98 mM 1,4-naphthoquinone in 0.1M TEAP/DMF at Scan Rate of 0.5 V/s

rate, and consistently returns, during the reverse half of the sweep to its initial (zero) value. This behaviour is consistent with the pure diffusion-controlled reversible electron transfer process and vertual absence of other processes on the electrochemical time scale. Deconvolution [15] (semiderivative or semidifferentiation) voltammetric analysis gives verification for the above behaviour. The ratio of the anodic to cathodic deconvoluted peak currents, dI_{ipa}/dI_{ipc}, for the first wave is close to unity (0.929 ± 0.009) through the scan rate range used (Table 2) with practically no potential separation between the anodic and cathodic deconvoluted peak current potentials (∽ -2 mV) (Fig. 2). Furthermore, it is found that the deconvoluted peak current potential receives no change on varying the scan rate. This is consistent with the diffusion-controlled charge transfer with neglegible influence of chemical reaction.

Logarithmic analysis of the convoluted data is tested for the different reaction schemes

TABLE 2

DECONVOLUTION VOLTAMMETRIC DATA OF THE FIRST WAVE FOR 0.98 mM 1,4-NAPHTHOQUINONE IN 0.1 M TEAP/DMF SOLUTIONS AT 21° C

Sweep rate mV/s	$-E_{pc}$ V	$-E_{pa}$ V	dI_{ipc}	dI_{ipa}	dI_{ipa}/dI_{ipc}
50	0.9829	0.9005	69.8	64.0	0.917
100	0.9805	0.9805	67.3	62.5	0.928
200	0.9805	0.9781	63.0	58.5	0.929
500	0.9853	0.9825	64.5	60.9	0.944

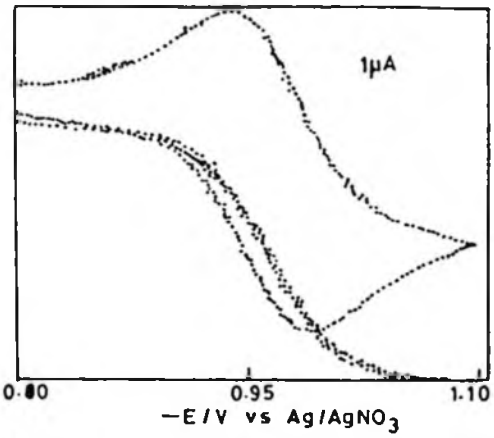


Fig. 2 Cyclic Voltammogram, (i-E), and Cyclic deconvoluted Voltammogram, (I -E), for the first wave of 0.98 mM 1,4-Naphthoquinone in 0.1M TEAP/DMF at Scan Rate of 0.5 V/s.

(E_{rev}, CE, EC, E_{irr}, ECE,...) making use of equations 3 and 4. In the sweep rates range used, the corresponding logarithmic analysis fits equation 5.

$$-(E - E^{\theta})\,(nF/RT) = \ln\,[(I_{lim} - I_l)/I_l] \quad (5)$$

with a slope close to the theoritical value (39.47/V at 21° C) indicating pure diffusion-controlled charge transfer nature of the first wave under these conditions. The standard potential E^{θ} of the reaction

$$Q \rightleftharpoons Q^{\bar{}},$$

can be estimated from the slope and intercept of equation 5. It is found to be equal to 981.4 ± 0.8 mV through the scan rate range used.

On the other hand, a second one-electron reduction wave is observed with a reduction peak potential 0.553 V negative to that of the peak of the first wave (Fig.1). Curves of I_l - E for the forward and backward scans superimpose, but convoluted current I_l does not reach the initial value during the reverse half of the sweep. This indicates that the second wave is due to diffusion-controlled reversible electron transfer coupled with a chemical reaction. This behaviour is established from the examination of the deconvoluted current data. It is observed that deconvoluted peak current potential is more or less constant with varying scan rate and potential separation between the anodic and cathodic deconvoluted peak current potentials are very small (~ 4 mV) (Table 3). However anodic to cathodic deconvoluted peak currents ratio, dI_{lpa}/dI_{lpc}, deviates from unity and varies with scan rate variations.

The convolution logarithmic analysis is carried out for the various schemes. It is found that the corresponding analysis follows equation 6 satisfactorily with sample standard deviation of 0.036 and theoretical slope.

$$-(E - E^{\theta'})\,(F/RT) = \ln\,[(i_{lim} - i)/I_l] \qquad (6)$$

This is indicative that the second wave is diffusion-controlled charge transfer with preceding first order chemical reaction (CE_r).

TABLE 3

DECONVOLUTION VOLTAMMETRIC DATA OF THE SECOND WAVE FOR 0.98 mM 1,4-NAPHTHOQUINONE IN 0.1 M TEAP/DMF SOLUTIONS AT 21° C

Sweep rate mV/s	$-E_{pc}$ V	$-E_{pa}$ V	dI_{lpa}/dI_{lpc}	dI_{2pa}/dI_{2pc}	k_1 sec^{-1}
50	1.5296	1.5330	0.450	0.757	0.15
100	1.5323	1.5325	0.614	0.880	0.25
200	1.5352	1.5316	0.705	0.927	0.42
500	1.5352	1.5340	0.766	0.977	1.00

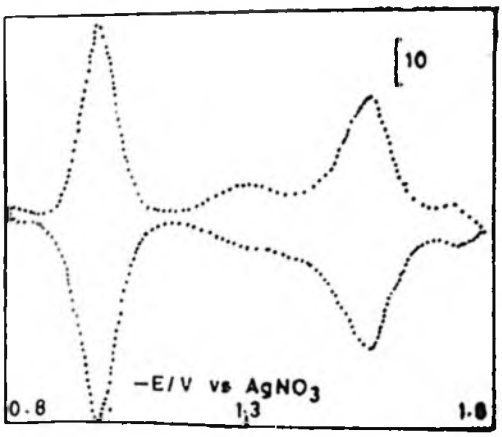


Fig. 3 Cyclic Deconvoluted Voltammogram of 0.98 mM 1,4-Naphthoquinone in 0.1M TEAP/DMF at Sweep Rate of 0.5 V/s

TABLE 4

CYCLIC VOLTAMMETRIC DATA FOR 0.98 mM 1,4-NAPHTHOQUINONE IN 0.1 M TEAP/DMF SOLUTIONS CONTAINING DIFFERENT AMOUNTS OF PHENOL AT SCAN RATE OF 500 mV/s AT 21°C

PhOH mM	First Wave $-E_{pc}$ V	ΔE mV	$E_p - E_{p/2}$ mV	i_{pa}/i_{pc}	Second Wave $-E_p$ V	ΔE mV	i_{pa}/i_{pc}
0	1.0146	62.6	58.6	0.943	1.5641	68.0	0.883
0.50	1.0113	61.9	55.8	0.945	1.5519	63.3	1.510
1.00	1.0098	61.1	56.2	1.130	1.4275	213.5	1.092
2.80	1.0113	66.6	64.3	0.915	1.2654	-	-
7.17	1.0049	75.7	61.0	0.968	1.2149	-	-
14.34	1.0110	102.5	73.2	1.005	1.1709	-	-
21.51	1.0120	119.6	87.9	1.109	-	-	-
35.85	1.0072	127.0	90.0	1.162	-	-	-
50.19	0.9927	131.8	87.9	1.115	-	-	-

The first order rate constant of the chemical reaction is measured according to the method described previously [13] and the values obtained are collected in Table 3. The $E^{\theta'}$ for this wave under such conditions is estimated making use of equation 6 and found to be 1.4854 ± 0.006 volts through the scan rate used (assuming that the D_A / D_B ratio is one).

Thus, on the basis of the above facts, the whole electrochemical reduction of 1,4-naphthoquinone in anhydrous dimethylformamide can be formulated by the following scheme

$$Q + e \rightleftharpoons Q^{\cdot-} \quad , E_r \qquad \text{first wave}$$

$$Q^{\cdot-} + \text{Hsolv} \xrightarrow{k_f} Q^{\circ} - H + \text{solv}^{-} \quad , C$$

$$Q^{\circ} - H + e \rightleftharpoons Q^{-} - H \quad , E_r \qquad \text{second wave} \qquad \ldots\ldots (7)$$

$$Q^{-} - H + \text{Hsolv} \rightleftharpoons QH_2 + \text{solv}^{-} \qquad \text{very fast}$$

where Q stands for the substrate and Hsolv represents any proton donor in the solution.

Addition of proton donor such as phenol to anhydrous dimethylformamide solutions affects essentially the general electroreduction pattern of 1,4-naphthoquinone. The effect of phenol on the voltammetry of the depolarizer is demonstrated by cyclic voltammograms (at ν = 500 mV/s ·) shown in Fig.4. In absence of phenol $E_{p1} - E_{p2}$ for the two cathodic waves is found to be of the order of 549 mV (Fig 4a) and decreases to 417 mV at phenol concentration is 1.0 mM (Fig.4b). Further increase in phenol results in merging of the two distinct peaks into a single quasi-reversible voltammetric peak (Fig.4c). The diagnostic characteristics for one-electron transfer reversibility of the first wave, E_p , i_p , i_{pa} / i_{pc} , convolution and deconvolution data,...., are all unchanged up to a concentration of phenol of 14.34 mM. On increasing it further, the peak current does not · increase while other characteristics of the wave change (Table 4). The convolution logarithmic analysis follows equation 5 through the [PhOH] ≤ 14.34 mM. This is indicative that the protonation of radical anion $Q^{\cdot-}$ is slow during the time scale of the voltammetric measurements in [PhOH] of 0 - 14.34 mM range and the mechanism proposed in (7) hold good.

The second wave decreases in height (both the cathodic and the reverse anodic steps) at higher phenol content. At a phenol content of 2.8 mM, the step becomes irreversible and the

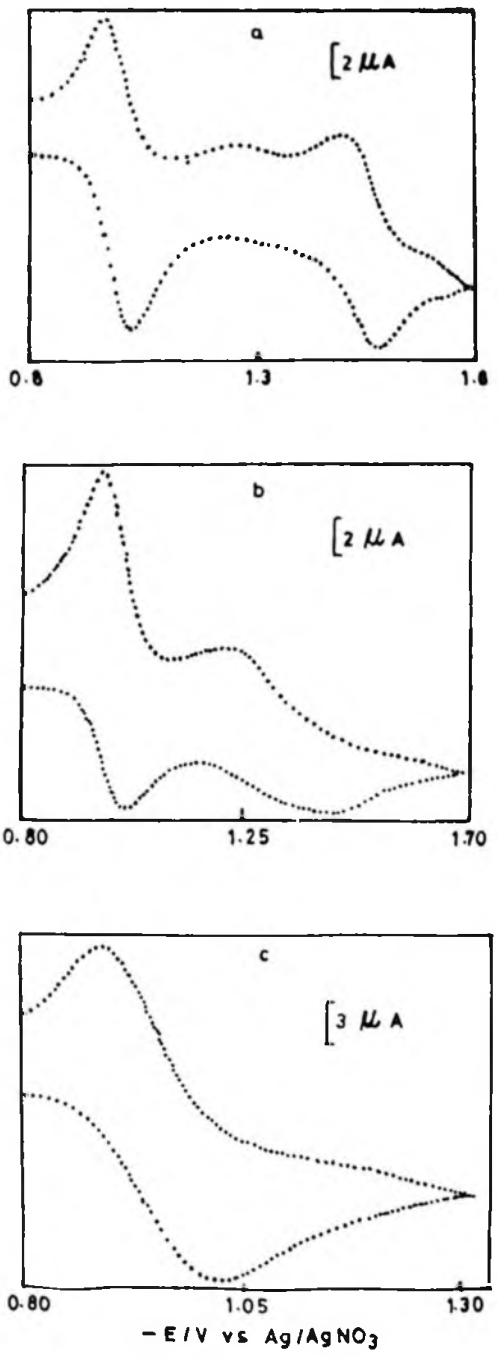


Fig. 4 Cyclic voltammogram at 0.5 V/s Sweep Rate of 0.98 mM 1,4-Naphthoquinone in 0.1 M TEAP/DMF solutions containing (a) 0, (b) 1.00 and (c) 35.85 mM phenol

corresponding anodic step in the reverse scan disappears. The peak potential shifts in the positive direction, finally merging with the first step at a phenol concentration of 21.51 mM and above. At higher concentration of phenol, the protonation step is faster. From the data in Table 4, it is clear that the

observed single wave has all of the characteristics of a one-electron transfer even though it is actually the result of a combined two one-electron steps. This case occurs where ΔE° (= $E^\circ_2 - E^\circ_1$) amounts to - (2RT/F) ln 2 = -35.1 mV (at 21°C)[16]. Thus, it is concluded that at [PhOH] $\leq$ 2.8 mM, the second wave could be ascribed to CE process. At higher phenol concentrations (2.8 $<$ c $<$ 21.5 mM) the wave is consistent with EC mechanism. The merged wave at high concentrations of phenol ($>$ 21.51 mM) follows the ECE mechanism.

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