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ELECTROCHEMICAL REDUCTION BEHAVIOUR OF 1,4-NAPHTHOQUINONES

K. Manvizhi* & Dr. K. R. Sankaran**
* Lecturer, Department of Chemistry, Anand Institute of Higher Technology, Chennai, Tamilnadu
** Professor, Department of Chemistry, Annamalai University, Annamalai Nagar, Chidambaram, Tamilnadu

Abstract:

Quinone is well known functional moiety in various biological systems. Compounds 2-methoxy-1,4-naphthoquinone and 2-hydroxy-1,4-naphthoquinone were prepared by adding sulphuric acid and methonal with ammonium1,2-naphthoquinone-4-sulfonate. The cyclic voltammetric behaviour of the compounds was studied in different non-aqueous solvents. 1,4-naphthoquinone, 2-hydroxy-1,4-naphthoquinone, 2-bromo-1,4-naphthoquinone undergo one electron reduction giving semiquinone radical whereas 2-hydroxy-1,4-naphthoquinone undergoes two one electron reduction giving semiquinone radical anion and dianion. The electron transfer is reversible in first step and in some cases second step is quasi-reversible. The reduction potential of 1,4-naphthoquinone were correlated in terms of linear solvation energy relationship according to Kamlet's triparametric equation. The reduction potential of naphthoquinones in six solvents was correlated in terms of Swain's equation.

Introduction:

Quinones are group of organic pigments characterized by structural similarities that give their bright colours, usually red, yellow or orange. Many biological redox reactions involving quinones take place in hydrophobic membrane bilayers and since most quinone based organic synthesis utilize non-aqueous solvents. Hence, in the present study, we investigated the electrochemical reduction behaviour of naphthoquinone and substituted naphthoquinones in non-aqueous solvents.

Experimental:

The following solvents was used in the cyclicvoltammetric experiments

- ✓ Dimethyl Formamide
- ✓ Acetonitrile
- ✓ Dichloromethane
- ✓ Chloroform
- ✓ Methanol
- ✓ Ethanol

Tetra-n-Butylammonium Perchlorate (TBAP):

Tetra-n-butylammonium perchlorate (TBAP) was used as the supporting electrolyte in all experiments. It was recrystallized from ethanol and dried in a vacuum desiccators. The recrystallized TBAP has the m.p. of $212^{o}C$ which agreed with literature value.

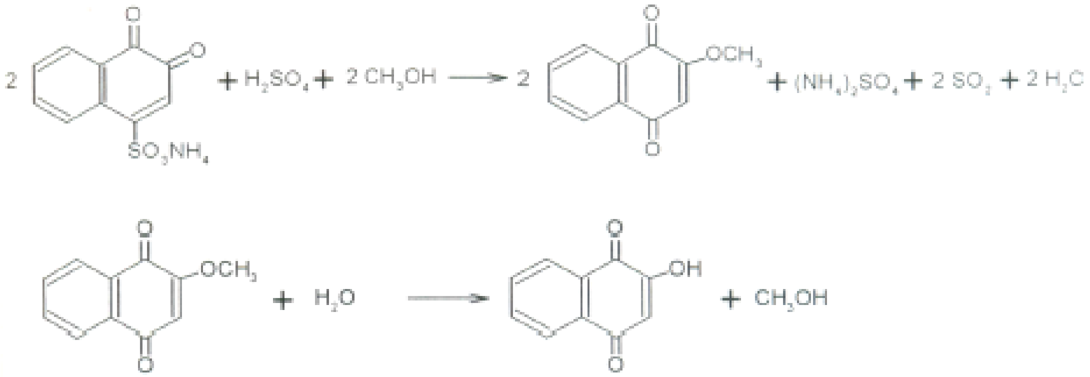
Perparation of Naphthoquinones:

Procedure:

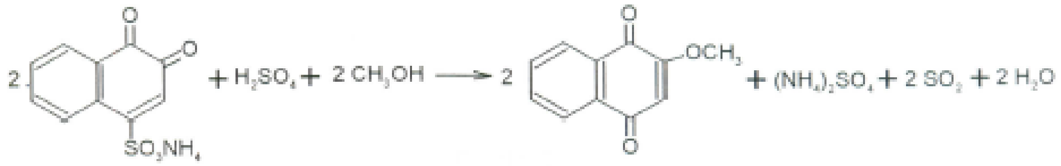
50 ml of absolute methylalcohol was cooled in an ice salt bath and 4 ml of concentrated H_2SO_4 was added. Then 13g of ammonium1,2-naphthoquinone-4-sulfonate was added with shaking and then heated, the sulphurdioxide was evolved. The 2-methoxy-1,4-naphthoquinone was separated.

The mixture was filtered and washed with 1.5g of NaOH in water and it was heated. All the ether was hydrolysed and then filtered. It was acidified with HCl and 2-hydroxy-1,4-naphthoquinone was obtained. It was washed with water and then dried. It was recrystallized from ethanol.

2-hydroxy-1,4-naphthoquinone:



2-methoxy-1,4-naphthoquinone:



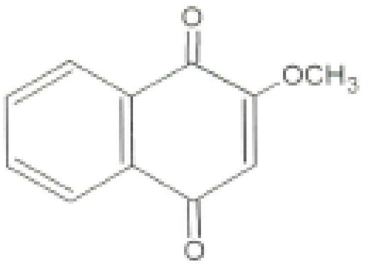
Procedure:

50 ml of absolute methylalcohol was cooled in an ice salt bath and 4 ml of concentrated H_2SO_4 was added. Then 13g of ammonium1,2-naphthoquinone-4-sulfonate was added with shaking and then heated, the sulphurdioxide was evolved. The 2-methoxy-1,4-naphthoquinone was separated.

Then 13 ml of methyl alcohol was added and heated. It was cooled, filtered and washed with cold water. The 2-methoxy-1,4-naphthoquinone was collected. It was recrystallized from ethanol.

The following 1,4-naphthoquinones were prepared for the present study.

- ✓ 2-methoxy-1,4-naphthoquinone
- ✓ 2-hydroxy-1,4-naphthoquinone



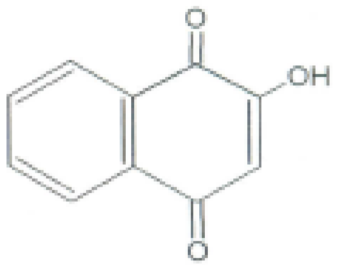


Table 1:

S.No	Compound	Observation m.p. (°C)	Literature m.p. (°C)
1	2-methoxy-1,4-naphthoquinone	183	183-184
2	2-hydroxy-1,4-naphthoquinone	190	191

Experimental Solutions:

The stock solutions of 1,4-naphthoquinone in different solvents were prepared as 1mM concentration of the sample with 0.1M concentration of pure TBAP. By using the silver nitrate with 0.1M TBAP reference electrode solution was prepared in respective solvents. In silver nitrate a polished silver rod was immersed through a septum. By using the ferrocenium/ferrocence couple the reference electrode was calibrated in each time. During calibration the 1mM of ferrocence along with 0.1M TBAP in respective solvents were employed.

Instruments:

Model ECDA-001 Basic Electrochemistry System

Working Electrode: Glassy carbon electrode (GCE)

Reference Electrode: Silver, Silver nitrate ($Ag/AgNo_3$)

Counter Electrode: Platinum wire fused in glass

In the present study scan rate (SR) was employed as 100 mV/s and the current sensitivity(s) was given as 0.1μA for all measurements. 1,4-naphthoquinone, 2-hydroxy-1,4-naphthoquinone, 2-methoxy-1,4-naphthoquinone and 2-bromo-1,4-naphthoquinone in various solvents were taken in the cell and fitted with the three electrodes then the peaks were recorded.

The experiments were done at 28 ± 0.2 °C. It was taken under dry and inert atmosphere accomplished by purging pure nitrogen gas. The gas passed for about 15 minutes before starting the experiments. And then, a blanket of nitrogen atmosphere was kept over the solution doing the measurements without disturbing the solution. To maintain the homogeneity, the solution was stirred after each measurement.

Results and Discussion:

The electrochemical behavior of 1,4-naphthoquinone, 2-hydroxy-1,4-naphthoquinone, 2-methoxy-1,4-naphthoquinone and 2-bromo-1,4-naphthoquinone were studied in different non-aqueous solvents. In order to avoid moisture contamination in the non-aqueous solvents, we employed $Ag/AgNO_3$ (1mM) tetra-n-butylammonium perchlorate (1 M) and the corresponding solvents are used as reference. The potential was calibrated with respect to ferrocenium/ferrocene couple in DMF, shown in figure 1.

The redox potentials of ferrocence in various solvents are given in table 2 The reference electrode was freshly prepared for each time and used with in 10 hrs of its preparation and every time the electrode was stored under dark.

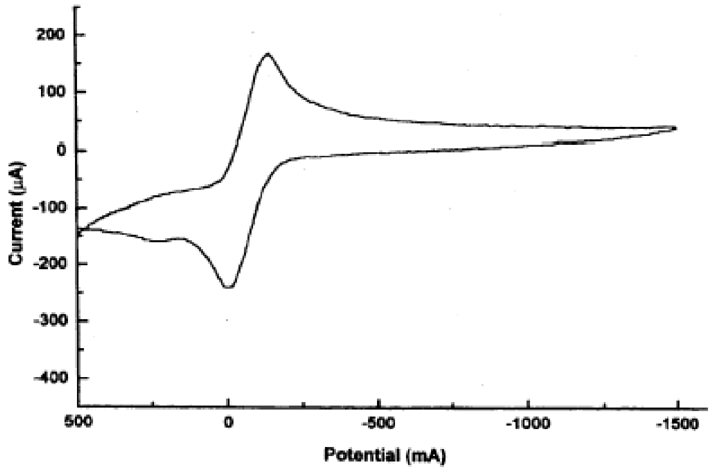


Figure 1: Ferrocene in DMF

Table 2: Redox potentials of ferrocene in various solvents

Solvent	**Epc Cathodic (V)**	**Epa Anodic (V)**
Dimethyl formamide	-0.137	0.004
Acetonitrile	-0.058	0.026
Dichloromethane	-0.207	-0.037
Chloroform	-0.282	0.296
Methanol	-0.156	-0.038
Ethanol	-0.207	-0.039

Redox potentials of 1,4-naphthoquinone in Various Solvents:

The cyclicvoltammetric behaviour of 0.01mM of 1,4-naphthoquinone was studied in different solvents.(Table3)

Table 3: Peak potentials of 1,4-naphthoquinones in various solvents

Solvent	**E_{pc}^1 (V)**	**E_{pa}^1 (V)**	**E_{pc}^2 (V)**	**E_{pa}^2 (V)**	**$E_{1/2} = (E_{pc} + E_{pa})/2$ (V)**
Dimethyl formamide	-1.269	-1.042	-0.646		-1.155
Acetonitrile	-1.293	-0.934			-1.113
Dichloromethane	-1.715	-1.013	-2.658	-2.054	-1.364
Chloroform	-1.684	-0.742			-1.213
Methanol	-1.283	-0.867			-1.075
Ethanol	-1.228	-0.852			-1.04

The voltammogorams were recorded at 100mV/s and represented in (fig 2 to 6). For all solvents the voltammograms were recorded in the potential range from 0 to -3000mv, produced reversible waves.The first wave is attributed to the addition of an electron to the 1 ,4-naphthoquinone(NQ) to produce a semiquinone radical anion($NQ^{\cdot -}$) and the second is due to the subsequent addition of an electron to the semiquinone radical anion,producing a dianion(NQ^{2-})

$$NQ + e^{-} \leftrightarrow NQ^{\cdot -}$$
$$NQ^{\cdot -} + e^{-} \leftrightarrow NQ^{2-}$$

From the voltammetric curves, we evaluated the Half-wave potential $E_{1/2} = \frac{E_{pc} + E_{pa}}{2}$ corresponding to the peaks I and II where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials. The electron transfer is reversible in first step. However the voltammograms in dichloromethane the electron transfer is reversible in both steps. Cyclicvoltammogram for the first step proved to the reversible and reproducible than more for the second step. Another factor that is known to limit the accuracy of second step determination is the tendency of the supporting electrolyte to form ion-pairs with the dianion product of the second step, thereby affecting measured E_{pc}^2 values.

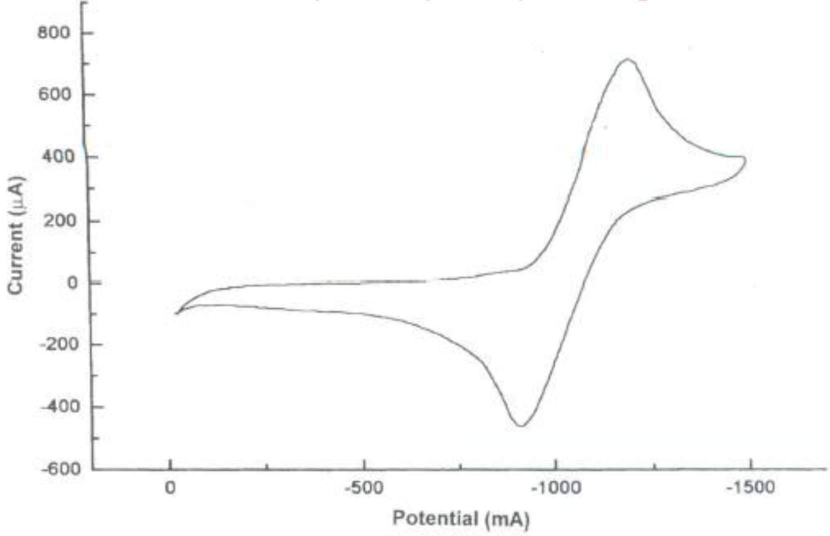


Figure 2: 1,4-Naphthoquinone in DMF

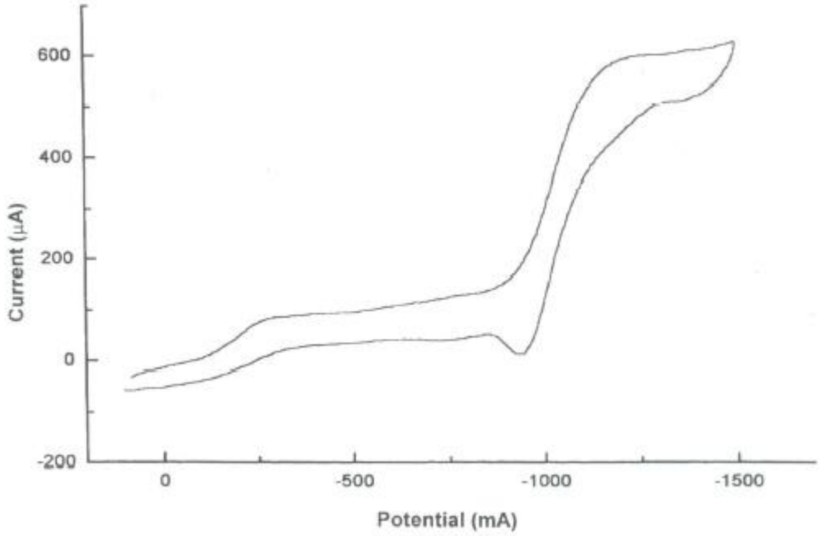


Figure 3: 1,4-Naphthoquinone in acetonitrile

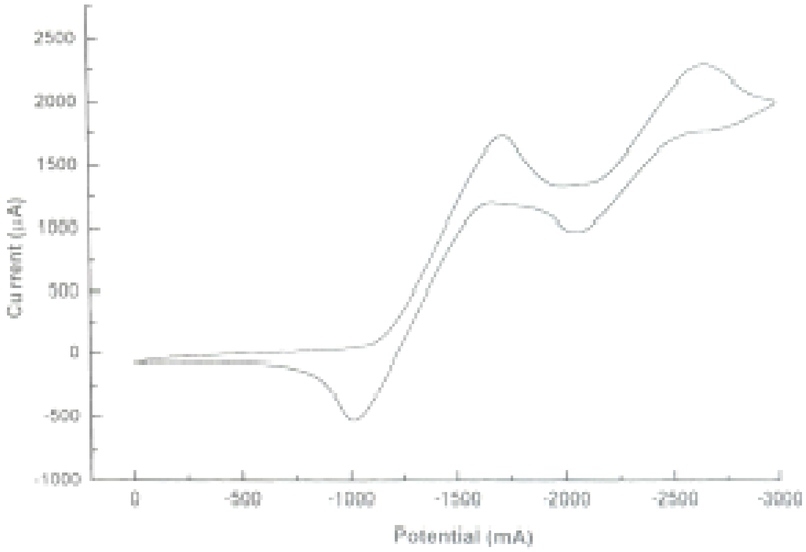


Figure 4: 1,4-Naphthoquinone in DCM

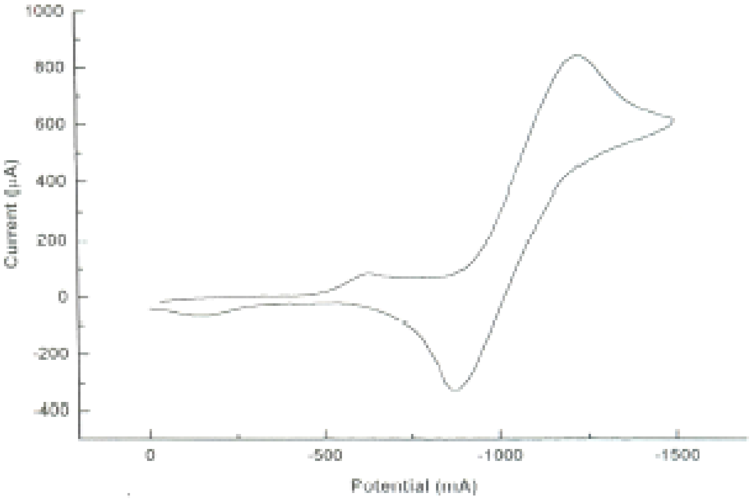


Figure 5: 1,4-Naphthoquinone in methanol

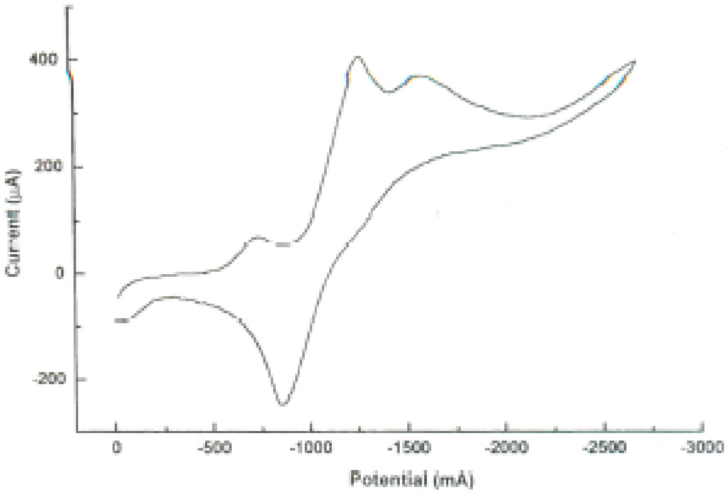


Figure 6:1,4-Naphthoquinone in ethanol

The peak potential of the compound investigation are shifted to more negative values on increases the sweep rates, thereby revealing the reversible nature of the electrode.(fig7)

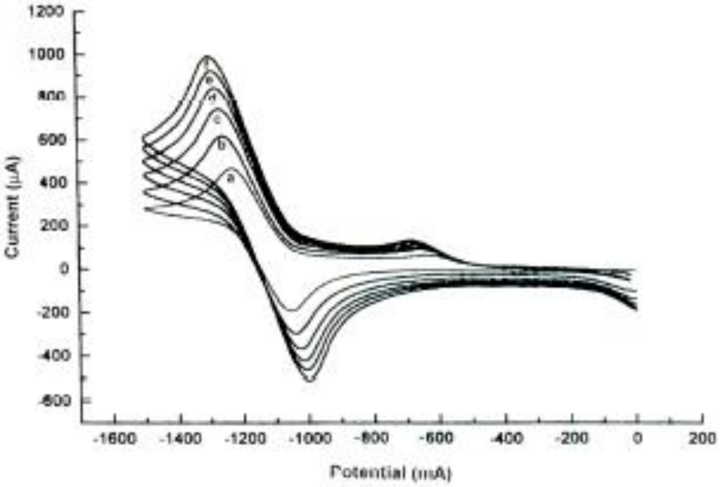


Figure 7: 1,4-Naphthoquinone in DMF at various scan rate
[a) 50 mV/s, b) 100 mV/s, c) 150 mV/s, d) 200 mV/s, e) 250 mV/s and f) 300 mV/s]

The reduction potentials of 1,4-naphtoquinone in six solvents were correlated in terms of linear solvation energy relationship. According to amlet's triparametric equation the correlation is good. The solvatochromic parameters values are listed in Table 4.

Table 4

Solvent	**Solvatochromic Parameters**			**E_{pc} (V) (Uncorrected Value)**	**E_{pc} (V) (Corrected Value)**	**E_{pc} (V) (ferrocene)**
	$X_1(\pi^*)$	**$X_2(\beta)$**	**$X_3(\alpha)$**			
Dimethyl formamide	0.88	0.69	0.00	-1.269	-1.406	-0.137
Acetonitrile	0.75	0.31	0.19	-1.293	-1.351	-0.058
Dichloromethane	0.82	0.00	0.30	-1.715	-1.922	-0.207
Chloroform	0.58	0.00	0.44	-1.584	-1.866	-0.282
Methanol	0.60	0.62	0.93	-1.283	-1.439	-0.156
Ethanol	0.54	0.77	0.83	-1.228	-1.435	-0.207

Reduction potential, $E_{pc} = A_o + p\pi^* + b\beta + a\alpha$

In the above equation π^* represents the solvent polarity, β is the hydrogen bond acceptor basicities and α is the hydrogen bond acidity and A_o is the intercept term. Kamlet's triparametric equation with Epc (uncorrected values) explains 88% of the effect of solvent on the reduction of 1,4-napthoquinone. However similar correlation using corrected for ferrocene standard is poor. The poor correlation of the corrected value of 1,4-naphthoquinone using ferrocene as a standard is due to the poor correlation of the ferrocene reduction potential with the solvent parameters.

The data on the solvent effect were also analysed in terms of Swain's equation of cation and anion concept of solvents (Table 5)

Table 5

Solvent	**A**	**B**	**E_{pc} (V) (Uncorrected Value)**	**E_{pc} (V) (Corrected Value)**	**E_{pc} (V) (ferrocene)**
Dimethyl Formamide	0.30	0.93	-1.269	-1.406	-0.137
Acetonitrile	0.37	0.86	-1.293	-1.351	-0.058
Dichloromethane	0.33	0.80	-1.715	-1.922	-0.207
Chloroform	0.42	0.73	-1.684	-1.866	-0.282
Methanol	0.75	0.50	-1.283	-1.439	-0.156
Ethanol	0.66	0.45	-1.228	-1.435	-0.207

Reduction potential, $E_{pc} = aA + bB + C$

Where A represents the anion solvating power of the solvent, B represents the solvent, C is the intercept term. The reduction potential in different solvents were analysed in terms of Swain's equation. The correlation is poor in all cases.

Redox potentials of 2-hydroxy-1,4-naphthoquinone in Various Solvents:

The cyclicvoltammetic behaviour of 0.01mM 2-hydroxy-1,4-naphthoquinone was studied in non-aqueous solvents (Table 6). The experiments clearly show two peaks, suggesting that two step of electron transfer reaction are involved.

Table 6

Solvent	**E_{pc}^1 (V)**	**E_{pa}^1 (V)**	**E_{pc}^2 (V)**	**E_{pa}^2 (V)**	**$E_{1/2} = (E_{pc} + E_{pa})/2$ (V)**
Dimethyl formamide	-0.758	-0.229	-1.305	-1.202	-0.493
Acetonitrile	-1.306	-1.100			-1.203
Dichloromethane	-1.428	-1.204			-1.316
Chloroform	-1.638	-1.130			-1.384
Methanol	-0.744	-0.361	-1.259	-1.042	-0.552
Ethanol	-0.712	-0.309	-1.227	-1.028	-0.510

The reduction of 2-hydroxy-1,4-naphthoquinone occur by the consecutive addition of two electron to form a mono anion followed by the formation of dianions as follows.

$$NQ + e^- \leftrightarrow NQ^- + e^- \leftrightarrow NQ^{2-}$$

The 2-hydroxy-1,4-naphthoquinone in various solvents, the voltammogram show in interesting trend in position of the peaks (Figs. 8 to 10). In 2-hydroxy-1,4-naphthoquinone there is only one E_{pc} and E_{pa} peaks, where as in hydroxy compound there are two E_{pc} and two E_{pa} peaks. We compare the reduction potential of 2-hydroxy-1,4-naphthoquinone with 1,4-naphthoquinone in 2-hydroxy-1,4-naphthoquionone the reduction occurs at lower potential when compared to the 1,4-naphthoquinone. The reason for the reduction is due to the intramolecular hydrogen bonding reduces the electron density of the carbonyl oxgen significantly. This favouring the reduction at the electrode.

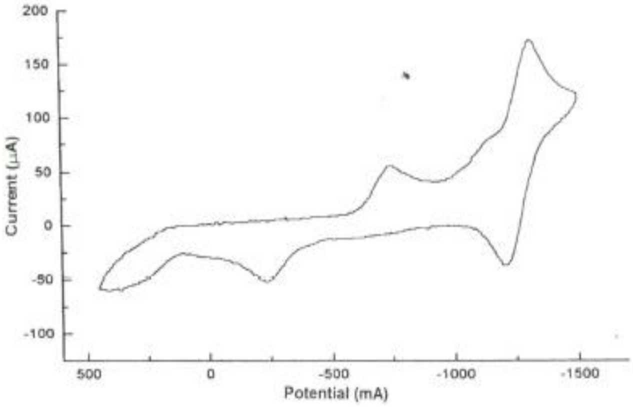


Figure 8: 2-Hydroxy-1,4-naphthoquinone in DMF

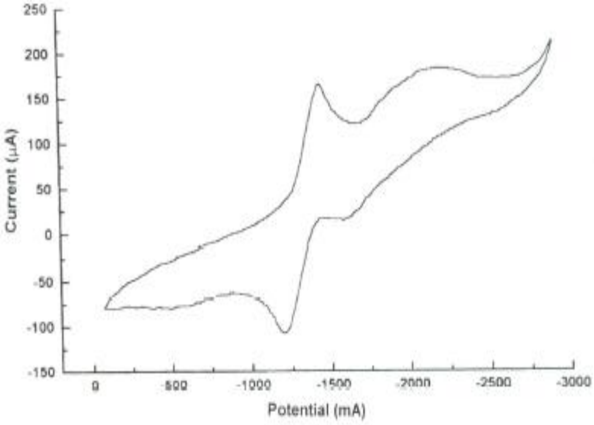


Figure 9: 2-Hydroxy-1,4-naphthoquinone in DCM

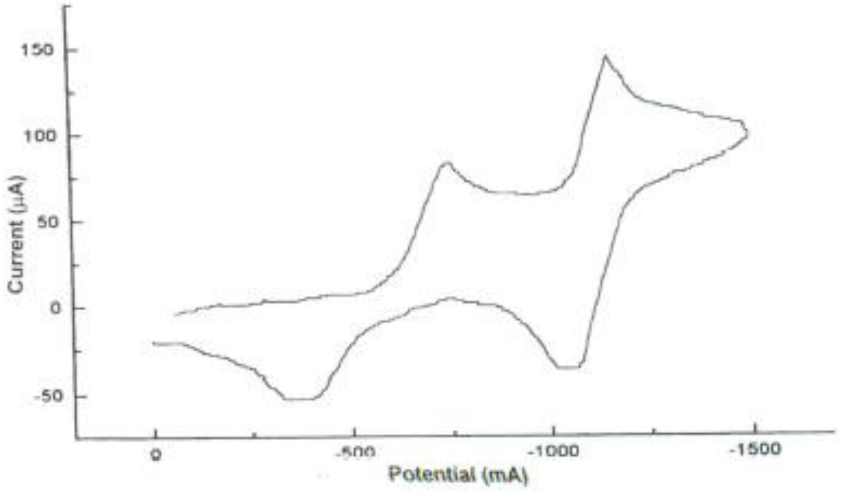


Figure 10: 2-Hydroxy-1,4-naphthoquinone in methanol

Redox potentials of 2-methoxy-1,4-naphthoquinone in Various Solvents:

The redox behaviour of 2-methoxy-1,4-naphthoquinone have been studied in six solvents (Table 7).

Table 7: Redox Potentials of 2-methoxy-1,4-naphthoquinone

Solvent	**E_{pc}^1 (V)**	**E_{pa}^1 (V)**	**E_{pc}^2 (V)**	**E_{pa}^2 (V)**	**$E_{1/2} = (E_{pc} + E_{pa})/2$ (V)**
Dimethyl formamide	-1.262	-1.042			-1.152
Acetonitrile	-1.891	-1.218			-1.554
Dichloromethane	-1.991				
Chloroform	-1.525	-1.190			-1.357
Methanol	-1.251	-0.339	-0.773	-1.034	-0.795
Ethanol	-1.238	-0.852	-0.611		-1.045

There is no much difference in the reduction of 1,4-naphthoquinone and 2-methoxy-1,4-naphthoquinone that shows the reduction is not sterically hindered by ortho substitutent (Fig. 11 and 12).

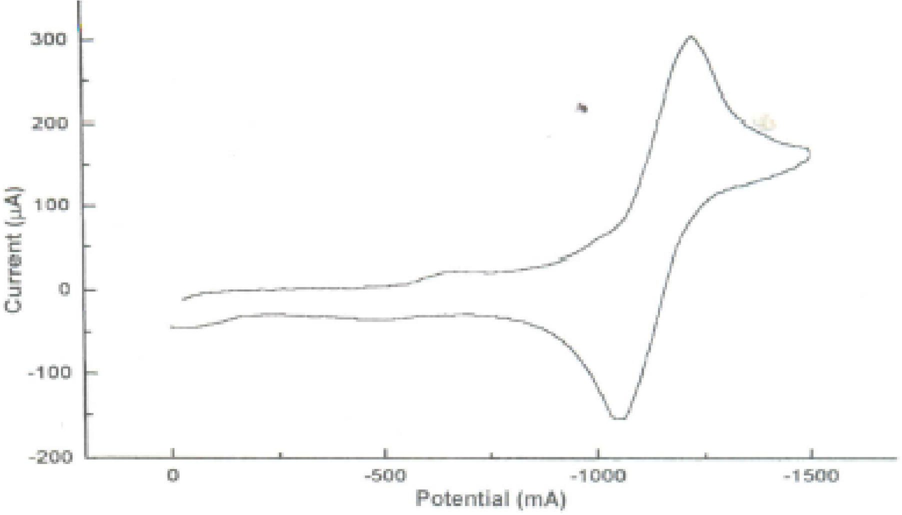


Figure 11: 2-Methoxy-1,4-naphthoquinone in DMF

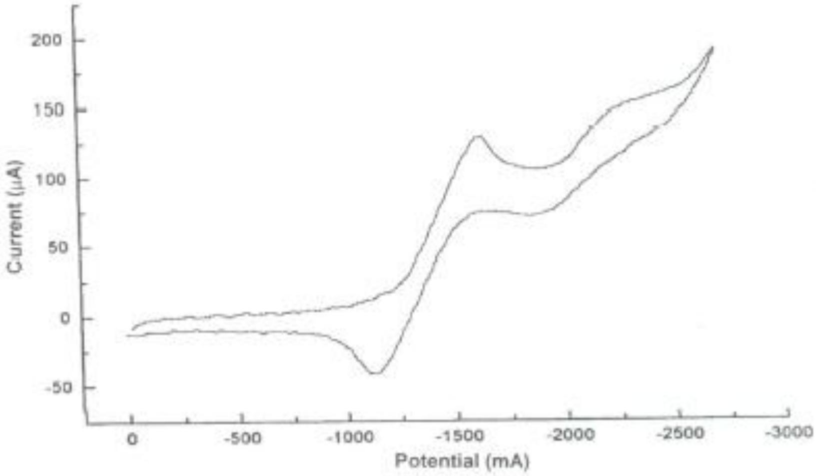


Figure 12: 2-Methoxy-1,4-naphthoquinone in Chloroform

Comparison of reduction potentials of 1,4-naphthoquinone, 2-hydroxy-1,4-naphthoquinone, 2-methoxy-1,4-naphthoquinone and 2-bromo-1,4-naphthoquinone:

The cyclicvoltammetry behaviour of 0.01mM of naphthoquione and substituted naphthoquinone was studied in DMF (Table 8).

Table 8: Comparison of Naphthoquinones in DMF

Compounds	**E_{pc}^1 (V)**	**E_{pa}^1 (V)**	**E_{pc}^2 (V)**	**E_{pa}^2 (V)**	**$E_{1/2} = (E_{pc} + E_{pa})/2$ (V)**
1,4-naphthoquinone	-1.269	-1.042			-1.155
2-hydroxy-1,4-naphthoquinone	-0.758	-0.229	-1.305	-1.202	-0.493
2-methoxy-1,4-naphthoquinone	-1.262	-1.042			-1.152
2-bromo-1,4-naphthoquinone	-1.128	-0.108			-0.618

There is no much difference in the reduction of 1,4-naphthoquinone, 2-methoxy-1,4-naphthoquinone and 2-bromo-1,4-naphthoquinone (Fig. 13) that shows the reduction is not sterically hindered by ortho substituents.

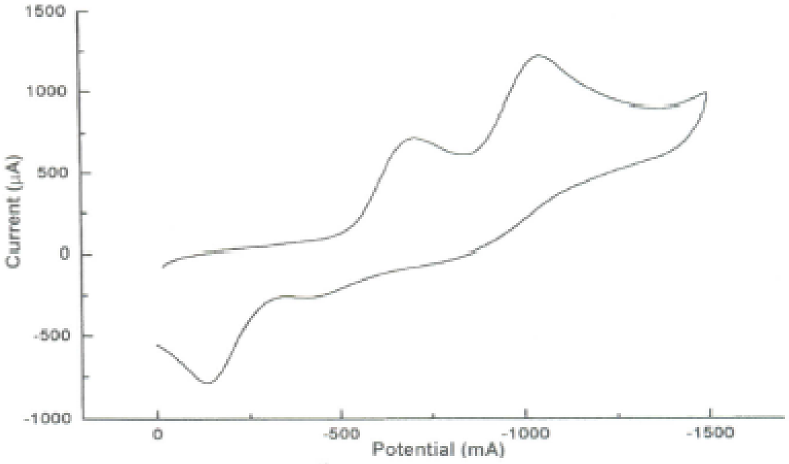


Figure 13: 2-Bromo-1,4-naphthoquinone in DMF

However, we compare the reduction potential with hydroxyl compound, the reduction occurs at lower potential. The cause of reduction is due to intramolecular hydrogen bonding. This hydrogen bonding reduces the electron density at the carbonyl oxygen significantly. This favours the reduction at the electrode.

Conclusion:

The present investigation was aimed to understand the solvent dependence of the reduction of substituted naphthoquinones in different non-aqueous solvents.

References:

1. 1,4-naphthoquinone, 2-methoxy-1,4-naphthoquinone and 2-bromo-1,4-naphthoquinone undergo one electron reduction giving semiquinone radical,whereas 2-hydroxy-1,4-naphthoquinone undergoes two one electron reduction giving semiquinone radical and dianion.
2. The electron transfer is reversible in first step and in some cases the second step is quasi-reversible.
3. The peak potential of the compounds under investigation are shifted to more negative values on increasing the sweep rates, thereby revealing the reversible nature of the electrode
4. In hydroxylic solvents such as methanol and ethanol the transition state is more stabilized as indicated by potential. Hence the reduction should be easier for such solvents. The electron density around the oxygen is lower because of the hydrogen bonding with solvents. The decreased electron density favours the reduction at the electrode, whereas in the dichloromethane such hydrogen bonding is not possible and electron rich carbonyl is reduced only at higher potential.
5. There is no much difference in the reduction of 1,4-naphthoquinone , 2-methoxy-1,4-naphthoquinone and 2-bromo-1,4-naphthoquinone that shows the reduction is not sterically hindered by ortho substituents. We compare the reduction potential of 2-hydroxy-1,4-naphthoquinone, the reduction occurs at lower potential. The cause of reduction is due to intramolecular hydrogen bonding.
6. The reduction potentials of 1,4-naphtoquinone in six solvents were correlated in terms of linear solvation energy relationship. According to Kamlet’s triparametric equation the correlation is good
7. The reduction potential of naphtoquinones in six sovents were correlated in terms of Swain’s equation the correlation is poor.